

LIQUID CRYSTAL SEALANT AND LIQUID CRYSTAL DISPLAY CELL USING SAME

TECHNICAL FIELD

The present invention relates to a liquid crystal sealant for a liquid crystal dropping process, which is curable by heat. More specifically, the present invention relates to a liquid crystal sealant for a liquid crystal dropping process, having good thermosetting property, and also excellent cured product properties, such as handling properties, storage stability, and adhesive strength, and a manufacture method thereof and 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 in that the liquid crystal sealant in the uncured state is in contact with the liquid crystal, and thus at this time

components of the liquid crystal sealant 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, the use of a thermal radical generator is proposed, whereby to raise the curing speed by heat, and reduce the elution of the components, and also the application of this technique is proposed in which the liquid crystal dropping process is realized by heat only (Patent documents 5 and 6). However, an organic peroxide or azo compound is currently used as a thermal radical generator, but these have problems in that nitrogen, oxygen and the like are generated when radicals are generated by heat, and bubbles are caused in the cured product, and the properties of the cured product, such as adhesive strength, decrease.

In addition, the technique has the problem of poor handling properties due to the quickness of the reaction. Handling properties mean easiness of use of the liquid crystal sealant. For example, a liquid crystal sealant has a phenomenon of curing or gelation in a process under vacuum or under heat, such as degassing process of the liquid crystal sealant and mixing process of a spacer agent, and in the

present application, easy generation of this phenomenon is defined as the handling properties. Accordingly, those hardly generating gelation are viewed as liquid crystal sealants having good handling properties, and those easily generating gelation are viewed as liquid crystal sealants with poor handling properties.

Furthermore, separately from handling properties, storage stability is also an important property of a liquid crystal sealant. This is the property with which the sealing application becomes difficult with the increase of viscosity under room temperature, and a liquid crystal sealant using a thermal radical generator also has poor storage stability. A method to resolve this problem is proposed in Patent document 7, but not sufficient to resolve all of the problems.

As described above, development of a liquid crystal sealant for a liquid crystal dropping process has been very intensively performed, but a liquid crystal sealant having excellent thermal reactivity and light-shielded part curability, and having a balance of handling properties, storage stability and the like, and, furthermore, having excellent cured product properties has not been yet 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: Japanese Unexamined Patent Application,
Publication No. 2009-42409

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

The present invention relates to a liquid crystal sealant used in the liquid crystal dropping process 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 laminating the other substrate, and curing the portion of the liquid crystal sealant by heat only, or light-heat combination, and proposes a liquid crystal sealant that has fast reaction by heat, and thus has extremely low contamination with respect to the liquid crystal through the processes, and has excellent handling properties such as degassing, and in addition, is excellent in terms of application, lamination, adhesive strength and the like to a substrate, and thus can be adapted to any design of a liquid crystal panel.

Means for Solving the Problems

The present inventors intensively investigated, and as a result thereof, found that a liquid crystal sealant that is combined with a specific thermal radical polymerization initiator and a radical polymerization inhibitor, has a balance of the thermal reactivity and handling properties, and, as a result thereof, can suppress the liquid crystal contamination as well, and furthermore, is also excellent in terms of the properties of the cured product, such as adhesive strength, and completed the present invention.

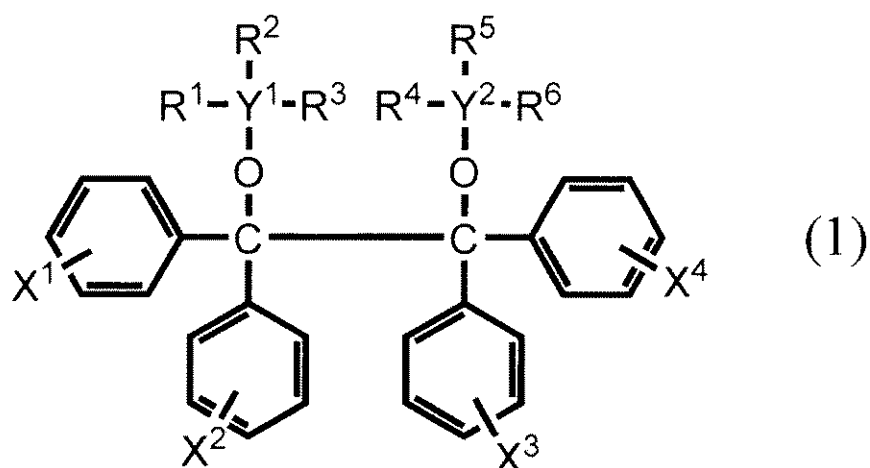
Specifically, the present invention relates to the following (1) to (12). In addition, in the specification, the "(meth)acrylic" means either one or both of "acrylic" and "methacrylic". Likewise, in the specification, the "(meth)acryloyl" means either one or both of "acryloyl" and "methacryloyl".

(1)

A liquid crystal sealant for a liquid crystal dropping process, which is characterized by containing (a) a thermal radical polymerization initiator not having an oxygen-oxygen bond (-O-O-) or a nitrogen-nitrogen bond (-N=N-) in the molecule thereof, (b) a radical polymerization inhibitor, and (c) a curable resin having a (meth)acryloyl group.

(2)

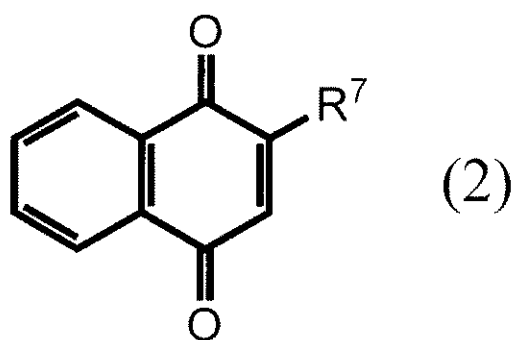
The liquid crystal sealant for the liquid crystal dropping process according to (1), in which the component (a) is a compound represented by formula (1) below:



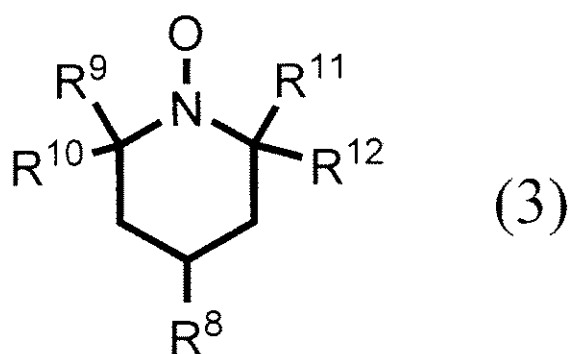
in the formula, Y^1 and Y^2 each independently represent a hydrogen atom, a phenyl group, or a silicon atom, R^1 to R^6 each independently represent a hydrogen atom or a C1-C4 straight or branched alkyl group, and X^1 to X^4 each independently represent a hydrogen atom, a methyl group, an ethyl group, a methoxy group, an ethoxy group, a phenoxy group, or a halogen atom, with the proviso that R^1 to R^3 or R^4 to R^6 that are bonded respectively to Y^1 or Y^2 are not present when Y^1 or Y^2 is a hydrogen atom.

(3)

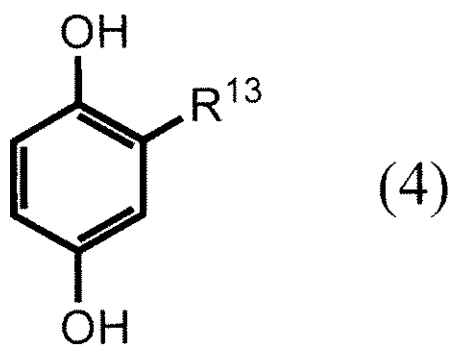
The liquid crystal sealant for the dropping process according to (1) or (2), in which the component (b) is one, or two or more of radical polymerization inhibitors selected from formulae (2) to (4) below:



in the formula, R^7 represents a hydrogen atom, a hydroxy group, a C1-C4 straight or branched alkoxy group, or a C1-C4 straight or branched alkyl group,



in the formula, R^8 represents a hydrogen atom, a hydroxy group, a C1-C4 straight or branched alkoxy group, a phenoxy group, an acetoamide group ($-\text{NHCOCH}_3$), an amino group ($-\text{NH}_2$), a carboxy group ($-\text{COOH}$), a cyano group ($-\text{CN}$), a benzoyloxy group ($-\text{OCOC}_6\text{H}_5$), an isothiocyanate group ($-\text{NCS}$), or an oxo group ($=\text{O}$), and R^9 to R^{12} each independently represent a C1-C4 straight or branched alkyl group,



in the formula, R^{13} represents a hydrogen atom, or a C1-C4 straight or branched alkyl group.

(4)

The liquid crystal sealant for the liquid crystal dropping process according to any one of (1) to (3), further containing (d) a curable resin that has an epoxy group and (e) a heat-curing agent.

(5)

The liquid crystal sealant for a liquid crystal dropping process according to (4), in which the component (e) is an organic acid hydrazide.

(6)

The liquid crystal sealant for the liquid crystal dropping process according to any one of (1) to (5), further containing (f) a silane coupling agent.

(7)

The liquid crystal sealant for the liquid crystal dropping process according to any one of (1) to (6), further containing (g) an inorganic filler.

(8)

The liquid crystal sealant for the liquid crystal

dropping process according to any one of (1) to (7), further containing (h) a photopolymerization initiator.

(9)

The liquid crystal sealant for the liquid crystal dropping process according to (4) or (5), in which the content of the component (b) is from 0.0001 to 1 parts by mass with respect to 100 parts by mass of the total amount of the component (c) and the component (d).

(10)

A method of manufacturing the liquid crystal sealant for the liquid crystal dropping process according to any one of (1) to (9), including a step of dissolving the component (b) in the component (c).

(11)

A method of manufacturing the liquid crystal sealant for the liquid crystal dropping process according to (4) or (5), including a step of dissolving the component (b) in the component (d).

(12)

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), or the liquid crystal sealant for the liquid crystal dropping process obtained by the manufacturing method according to (10) or (11).

Effects of the Invention

The liquid crystal sealant of the present invention has a fast curing speed at the time of heat-curing, and thus can be applied to a liquid crystal dropping process in which a liquid crystal sealant is cured with heat only. In addition, the liquid crystal sealant of the present invention has sufficient curability even under a wiring to 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 a panel wiring, and easily manufacture a liquid crystal display panel having high reliability.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

The (a) thermal radical polymerization initiator that does not have an oxygen-oxygen bond (-O-O-) or a nitrogen-nitrogen bond (-N=N-) in the molecule used in the present invention is not particularly limited as long as it is a compound that generates radicals by heat, and initiates a chain polymerization reaction, and examples thereof include benzoin, benzoin ethers, acetophenones and benzopinacols. Among them, the compound represented by formula (1) is particularly suitably used from the viewpoint of reactivity and solubility into liquid crystal.

In formula (1), Y^1 and Y^2 each independently represent a hydrogen atom, a phenyl group, or a silicon atom, and at least one of them is preferably a silicon atom. In formula (1), examples of the C1-C4 straight or branched alkyl group

(hereinafter, simply also referred to as the C1-C4 alkyl group) in R^1 to R^6 may include, for example, methyl, ethyl, n-propyl, i-propyl, t-butyl and the like. In addition, examples of the halogen in X^1 to X^4 may include a fluorine atom, a chlorine atom, a bromine atom and the like.

When Y^1 or Y^2 of formula (1) is not a hydrogen atom, $R^1R^2R^3Y^1-$ or $R^4R^5R^6Y^2-$ is preferably a phenyl group, a phenyl group substituted with one to three C1-C4 alkyl groups, a di(C1-C4 alkyl)silyl group, or a tri(C1-C4 alkyl)silyl group, more preferably a di(C1-C4 alkyl)silyl group or a tri(C1-C4 alkyl)silyl group, and further preferably a tri(C1-C4 alkyl)silyl group.

The two or three C1-C4 alkyl groups in the di- or tri-(C1-C4 straight or branched alkyl)silyl group in $R^1R^2R^3Y^1-$ or $R^4R^5R^6Y^2-$ of formula (1), may be the same or different. Examples of the silyl group include, for example, di(C1-C4 alkyl)silyl groups such as dimethylsilyl, diethylsilyl and methylethylsilyl; and tri(C1-C4 alkyl)silyl groups such as trimethylsilyl, triethylsilyl, dimethylethylsilyl and t-butyl dimethylsilyl. Among them, the silyl group is most preferably a tri(C1-C4 alkyl)silyl group, and more preferably a trimethylsilyl group.

X^1 to X^4 of formula (1) each independently represent a hydrogen atom, a methyl group, an ethyl group, a methoxy group, an ethoxy group, a phenoxy group, or a halogen atom, and preferably all of X^1 to X^4 represent a hydrogen atom.

Examples of the compound represented by formula (1)

include, specifically, benzopinacol, 1,2-dimethoxy-1,1,2,2-tetraphenylethane, 1,2-diethoxy-1,1,2,2-tetraphenylethane, 1,2-diphenoxy-1,1,2,2-tetraphenylethane, 1,2-dimethoxy-1,1,2,2-tetra(4-methyl phenyl)ethane, 1,2-diphenoxy-1,1,2,2-tetra(4-methoxyphenyl)ethane, 1,2-bis(trimethylsiloxy)-1,1,2,2-tetraphenylethane, 1,2-bis(triethylsiloxy)-1,1,2,2-tetraphenylethane, 1,2-bis(t-butylldimethylsiloxy)-1,1,2,2-tetraphenylethane, 1-hydroxy-2-trimethylsiloxy-1,1,2,2-tetraphenylethane, 1-hydroxy-2-triethylsiloxy-1,1,2,2-tetraphenylethane, 1-hydroxy-2-t-butylldimethylsiloxy-1,1,2,2-tetraphenylethane and the like, preferably 1-hydroxy-2-trimethylsiloxy-1,1,2,2-tetraphenylethane, 1-hydroxy-2-triethylsiloxy-1,1,2,2-tetraphenylethane, 1-hydroxy-2-t-butylldimethylsiloxy-1,1,2,2-tetraphenylethane and 1,2-bis(trimethylsiloxy)-1,1,2,2-tetraphenylethane, and further preferably 1-hydroxy-2-trimethylsiloxy-1,1,2,2-tetraphenylethane and 1,2-bis(trimethylsiloxy)-1,1,2,2-tetraphenylethane. However, the compound is not limited to these compounds as long as the compound has the structure of formula (1). In addition, two or more kinds may be used in combination.

Among the thermal radical polymerization initiators, benzopinacol is marketed by Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd. and the like. In addition, a compound obtained by etherification of the hydroxy group of benzopinacol can be easily synthesized by a well-known method. In addition, a compound obtained by silyl etherification of

the hydroxy group of benzopinacol can be synthesized by a method of heating a corresponding benzopinacol and various silylating agents under the presence of a basic catalyst, such as pyridine.

Examples of the silylating agent include generally known trimethylsilylating agents such as trimethyl chlorosilane (TMCS), hexamethyl disilazane (HMDS) and N,O-bis(trimethylsilyl)trifluoroacetoamide (BSTFA), triethylsilylating agents such as triethyl chlorosilane (TECS), t-butyldimethylsilylating agents such as t-butylmethyl silane (TBMS) and the like. These reagents are easily available from the market, such as makers of silicon derivatives. The reaction amount of the silylating agent is preferably 1.0 to 5.0-fold moles with respect to 1 mole of the hydroxy group of the subject compound. The reaction amount is further preferably 1.5 to 3.0-fold moles. If the reaction amount is less than 1.0-fold mole, the reaction efficiency is poor, and the reaction time becomes long, and thus heat decomposition is promoted. If the reaction amount is 5.0-fold moles or more, isolation becomes worse in the recovery, and purification becomes difficult.

Examples of the basic catalyst include pyridine, triethyl amine and the like. The basic catalyst has effects of trapping hydrogen chloride generated at the time of the reaction, and keeping the reaction system to be basic, and effects of pulling out hydrogen from a hydroxy group, and promoting the reaction further. The content of the basic catalyst may be

0.5-fold moles or more with respect to a hydroxy group of the subject, and the basic catalyst may be used as a solvent.

As the solvent, a non-polar organic solvent such as hexane, ether and toluene is excellent since it does not participate in the reaction. In addition, the solvent is also preferably a polar solvent such as pyridine, dimethyl formaldehyde (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) or acetonitrile. The content of the solvent is preferably such an amount that the mass concentration of the solute is from 5% by mass to 40% by mass. The content of the solvent is further preferably from 10% by mass to 30% by mass. If the content of the solvent is too small, the reaction is slow, decomposition by heat is promoted and the yield decreases. In the reverse case, if the content of the solvent is too great, byproducts increase, and the yield decreases.

The (a) thermal radical polymerization initiator used in the present invention is preferably those making the particle diameter fine, and being uniformly dispersed. If the average particle diameter is too great, it becomes a defect factor in such that a gap cannot be formed well when the upper and the lower glass substrates are laminated at the time of manufacture of the liquid crystal display cell having a narrow gap, and thus is preferably 5 μm or less and more preferably 3 μm or less. In addition, the average particle diameter may be fine without limit, but ordinarily the lower limit is about 0.1 μm . The particle diameter can be measured by a laser diffraction and scattering type particle size distribution

measurement apparatus (dry type) (manufactured by SEISHIN ENTERPRISE Co., Ltd.; LMS-30).

The content of the thermal radical polymerization initiator is preferably from 0.0001 to 10 parts by mass, further preferably from 0.0005 to 5 parts by mass, and particularly preferably from 0.001 to 3 parts by mass with respect to 100 parts by mass of the total of the curable resin of the liquid crystal sealant of the present invention. Meanwhile, the curable resin represents the component (c), and the component (d) that is contained as necessary. The same applies hereafter in the present application.

In addition, the component (b), a radical polymerization inhibitor used in the present invention is not particularly limited as long as it is a compound that reacts with a radical generated from a radical polymerization initiator or a curable resin monomer whereby to prevent the polymerization, and quinone-based, piperidine-based, hindered phenol-based, nitroso-based compounds or the like may be used. Specifically, examples of the component (b) include naphthoquinone, 2-hydroxy naphthoquinone, 2-methyl naphthoquinone, 2-methoxynaphthoquinone, 2,2,6,6,-tetramethyl piperidin-1-oxyl, 2,2,6,6,-tetramethyl-4-hydroxy piperidin-1-oxyl, 2,2,6,6,-tetramethyl-4-methoxypiperidin-1-oxyl, 2,2,6,6,-tetramethyl-4-phenoxy piperidin-1-oxyl, hydroquinone, 2-methyl hydroquinone, 2-methoxyhydroquinone, parabenzoquinone, butylated hydroxy anisole, 2,6-di-t-butyl-4-ethyl phenol, 2,6-di-t-butylcresol, stearyl β -(3,5-dit-butyl-4-hydroxy phenyl)propionate, 2,2' -

methylene bis(4-ethyl-6-t-butylphenol), 4,4'-thiobis-3-methyl-6-t-butylphenol), 4,4'-butylidene bis(3-methyl-6-t-butylphenol), 3,9-bis[1,1-dimethyl-2-[β -(3-t-butyl-4-hydroxy-5-methyl phenyl)propionyloxy]ethyl], 2,4,8,10-tetraoxaspiro[5,5]undecane, tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenylpropionate)methane, 1,3,5-tris(3',5'-di-t-butyl-4'-hydroxy benzyl)-sec-triazin-2,4,6-(1H,3H,5H)trione, paramethoxyphenol, 4-methoxy-1-naphthol, thiodiphenylamine, aluminum salts of N-nitroso phenyl hydroxyamine, trademark ADECA STAB LA-81, trademark ADECA STAB LA-82 (manufactured by ADECA CORPORATION) and the like, but are not limited thereto.

Among them, those exerting remarkable effects in combination with the thermal radical polymerization initiator are the radical polymerization inhibitors described in formulae (2) to (4). These radical polymerization inhibitors may be used alone, or may be used in a combination of two or more kinds.

Meanwhile, R⁸ in formula (3) represents a hydrogen atom, a hydroxy group, a C1-C4 straight or branched alkoxy group, a phenoxy group, an acetoamide group (-NHCOCH₃), an amino group (-NH₂), a carboxy group (-COOH), a cyano group (-CN), a benzoyloxy group (-OCOC₆H₅), an isothiocyanate group (-NCS), or an oxo group (=O), preferably a hydrogen atom, a hydroxy group, a C1-C4 straight or branched alkoxy group, a phenoxy group, an amino group, or a carboxy group, further preferably a hydrogen atom, a hydroxy group, an amino group, or a carboxy group, and particularly preferably a hydrogen atom, or a hydroxy group.

The component (b), a radical polymerization inhibitor may be added when the component (c), a curable resin that has a (meth)acryloyl group is synthesized, or may be added to either one or both of the component (c), a curable resin that has a (meth)acryloyl group and the component (d), a curable resin that has an epoxy group, and is dissolved. However, the component (b) radical polymerization inhibitor is preferably added to either one or both of the component (c), a curable resin that has a (meth)acryloyl group and the component (d), a curable resin that has an epoxy group, and is dissolved in order to obtain effective effects.

The content of the (b) radical polymerization inhibitor is preferably from 0.0001 to 1 parts by mass, further preferably from 0.001 to 0.5 parts by mass, and particularly preferably from 0.01 to 0.2 parts by mass with respect to 100 parts by mass of the total of the curable resin in the liquid crystal sealant of the present invention. If the amount of the radical polymerization inhibitor is too small, sufficient handling properties cannot be obtained. If the amount of the radical polymerization inhibitor is too great, the liquid crystal contamination may be troublesome due to the delay of the thermal reaction.

The liquid crystal sealant of the present invention contains the component (c), a curable resin that has a (meth)acryloyl group. Examples of such curable resin include, for example, (meth)acrylic ester, epoxy (meth)acrylate and the like. Examples of the (meth)acrylic ester include benzyl

methacrylate, cyclohexyl methacrylate, glycerol dimethacrylate, glycerol triacrylate, EO-modified glycerol triacrylate, pentaerythritol acrylate, trimethylol propane triacrylate, tris(acryloxyethyl) isocyanurate, dipentaerythritol hexaacrylate, phloroglucinol triacrylate and the like. The epoxy (meth)acrylate may be obtained with a known method by a reaction of an epoxy resin and a (meth)acrylic acid. The epoxy resin that is a raw material is not particularly limited, but is preferably a bi-functional or higher-functional epoxy resin, and examples thereof include, for example, 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, catechol, a diglycidyl ether of bifunctional phenols, such as resorcinol, 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 resorcin diglycidyl ether from the viewpoint of the liquid crystal contamination. In addition, the ratio of the epoxy group and the (meth)acryloyl group is not limited, and is suitably selected from the viewpoint of process suitability and liquid crystal contamination.

In addition, the content of the (c) curable resin that has a (meth)acryloyl group in the liquid crystal sealant for the liquid crystal dropping process, is preferably in a range of 30 to 90 parts by mass, and further preferably about 50 to 90 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealant.

The liquid crystal sealant for the liquid crystal dropping process of the present invention may also use the component (d), a curable resin that has an epoxy group, whereby to seek improvement of adhesive strength. The curable resin that has an epoxy group used is not particularly limited, but is preferably a bi-functional or higher-functional epoxy resin, and examples thereof include, for example, 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 curable resin that has an epoxy group is preferably a bisphenol type epoxy resin, or a novolak type epoxy resin from

the viewpoint of liquid crystal contamination. The content of the component (d), the curable resin that has an epoxy group in the liquid crystal sealant is from about 1 to 30 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealant.

The component (e) heat-curing agent used together with the component (d) in the liquid crystal sealant for the liquid crystal dropping process of the present invention is not particularly limited, and examples thereof may include polyvalent amines, polyhydric phenols, hydrazide compounds and the like, and particularly suitably solid organic acid hydrazides. Examples of the component (e) heat-curing agent may include, for example, aromatic hydrazides such as salicylic acid hydrazide, benzoic acid hydrazide, 1-naphthoic acid hydrazide, 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 and the like. In addition, examples of the component (e) heat-curing agent may include aliphatic hydrazide compounds such as formhydrazide, acetohydrazide, propionic acid hydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, pimelic acid dihydrazide, sebacic acid dihydrazide, 1,4-cyclohexane dihydrazide, tartaric acid dihydrazide, malic acid dihydrazide, iminodiacetic acid dihydrazide, N,N'-hexamethylene bissemicarbazide, citric acid

trihydrazide, nitriloacetic acid trihydrazide, cyclohexane tricarboxylic acid trihydrazide; dihydrazide compounds that have a hydantoin skeleton, preferably a valine hydantoin skeleton (skeleton in which the carbon atom of the hydantoin ring is substituted with an isopropyl group) such as 1,3-bis(hydrazinocarbonoethyl)-5-isopropyl hydantoin; tris(1-hydrazinocarbonylmethyl) isocyanurate, tris(2-hydrazinocarbonylethyl) isocyanurate, tris(2-hydrazinocarbonylethyl) isocyanurate, tris(3-hydrazinocarbonylpropyl) isocyanurate, bis(2-hydrazinocarbonylethyl) isocyanurate and the like. This heat-curing agent may be used alone, or may be used as a mixture of two or more kinds. The component (e) heat-curing agent is preferably isophthalic acid dihydrazide, malonic acid dihydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, tris(1-hydrazinocarbonylmethyl) isocyanurate, tris(2-hydrazinocarbonylethyl) isocyanurate, tris(2-hydrazinocarbonylethyl) isocyanurate, or tris(3-hydrazinocarbonylpropyl) isocyanurate, and particularly preferably malonic acid dihydrazide or sebacic acid dihydrazide for the balance of curing reactivity and potentiality. The amount used of the component (e) heat-curing agent when such (e) heat-curing agent is used is from 0.5 to 2.0 eq., preferably from 0.8 to 1.2 eq. with respect to 1 eq. of epoxy of the epoxy group of the component (d) curable resin that has an epoxy group.

In the liquid crystal sealant for the liquid crystal

dropping process of the present invention, the component (f) silane coupling agent may be used to seek improvement of adhesive strength and improvement of moisture proof reliability. 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 (f) silane coupling agent 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 of the liquid crystal sealant of the present invention.

In the liquid crystal sealant for the liquid crystal dropping process of the present invention, the component (g) inorganic filler may be used to seek improvement of adhesive strength and improvement of moisture proof reliability. Examples of this (g) 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 (g) in the liquid crystal sealant, which may be used in the liquid crystal sealant of the present invention, is typically from 1 to 60 parts by mass, and preferably from 1 to 40 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, strength of adhesion to a

glass substrate decreases, and the moisture proof reliability is also poor, and thus a decrease of the adhesive strength may occur after moisture absorption increases. 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 for the liquid crystal dropping process of the present invention may contain the component (h), a photopolymerization initiator in order to render the liquid crystal sealant for the liquid crystal dropping process 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-2methyl-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 photopolymerization initiator in the liquid crystal sealant is preferably from about 1 to 10 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealant.

The liquid crystal sealant of the present invention may be also blended with a curing accelerator, such as an organic acid and an imidazole, an organic filler, and an additive, such as a pigment, a leveling agent, an antifoam agent and a solvent as necessary.

A method described below as one example of a method for obtaining the liquid crystal sealant of the present invention. First, the component (d) is dissolved and mixed in the component (c) as necessary. Then, in this mixture, the component (b) is dissolved, and also the component (h) is dissolved as necessary. Then, the solution is combined with the component (a), the component (f), the component (e), the component (g), 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

moisture proof reliability. 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 for the liquid crystal dropping process 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 is also excellent in terms of the handling property and the storage stability, and thus is suitable for manufacture of the 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 1-hydroxy-2-trimethylsiloxy-1,1,2,2-tetraphenylethane)

100 Parts (0.28 mol) of marketed benzopinacol (manufactured by Tokyo Chemical Industry Co., Ltd.) were dissolved in 350 parts of dimethyl formaldehyde, and 32 parts (0.4 mol) of pyridine as a basic catalyst, and 150 parts (0.58 mol) of BSTFA (manufactured by Shin-Etsu Chemical Co., Ltd.) as a silylating agent were added thereto and the mixture was heated to 70°C, and stirred for 2 hours. The obtained reaction liquid was cooled and combined with 200 parts of water while being stirred, and the product was precipitated, and the unreacted silylating agent was deactivated and isolated. After filtration, the filtrate was washed sufficiently, and recrystallized with acetone and purified, whereby to give 105.6 parts of 1-hydroxy-2-trimethylsiloxy-1,1,2,2-tetraphenylethane (88.3% yield). Analysis by HPLC gave 99.0% (area percentage). In addition, HPLC-MASS gave 438 of the

molecular ion peak. Furthermore, the product was dissolved in DMSO-d₆, and the target compound was identified from the NMR (proton) spectrum. As chemical shift values for the NMR spectrum, 5.8 ppm (1H) for hydroxy group proton, 0.0 ppm (9H) for siloxymethyl proton, and 7.1 ppm (16H) and 7.4 ppm (4H) for phenyl proton were obtained.

Reference 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. This reaction liquid was washed, and toluene was distilled, whereby to give 395 g of the intended bisphenol A type epoxy acrylate (KAYARAD^{RTM} R-93100).

Examples 1-5 and Comparative Examples 1-3

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

Each of the resin components (component (c), component (d)) was mixed in the ratio shown in Table 1 described below,

and stirred, and then a radical polymerization inhibitor (component (b)), and a photopolymerization initiator (component (h)) were heat-dissolved. The solution was cooled to room temperature, and then suitably combined with the silane coupling agent (component (f)), the inorganic filler (component (g)), the thermal radical initiator (component (a)), the heat-curing agent (component (e)) and the like, and stirred, and then dispersed with a three-roller milling machine, and then filtered with a metal mesh (635 mesh), to prepare the liquid crystal sealants for the liquid crystal dropping process of Examples 1 to 5. In addition, the liquid crystal sealants for the liquid crystal dropping process of Comparative Examples 1 to 3 were prepared likewise using each of the components shown in Table 1.

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

(Test for heat curability)

Each of the prepared liquid crystal sealants for the liquid crystal dropping process was molded to 3 cm × 3 cm × 1 mm, and cured at 120°C for 1 hour. Shore A hardness of the cured material was measured, whereby to evaluate the curability. The results are shown in Table 1.

(Test for handling property)

15 g of each of the prepared liquid crystal sealants for the liquid crystal dropping process was mixed with 0.15 g of 5 μm spacer (PF-50S: manufactured by Nippon Electric Glass Co., Ltd.), and then stirred and degassed in vacuum for 5 minutes at 500 rpm rotation and 1500 rpm revolution. A vacuum stirring-degassing mixer, VMXC-360K (manufactured by ENVIRONMENT & MATERIALS & ELECTRONICS GROUP) was used as the vacuum stirring-degassing apparatus. The prepared liquid crystal sealant for the liquid crystal dropping process was placed under a 23°C atmosphere, and measured for the gelation time, and evaluated by the criteria below. The results are shown in Table 1.

A: No gelation at 168 hours or more

B: Gelation at 96 hours or more and less than 168 hours

C: Gelation at less than 96 hours immediately after degassing

(Test for contamination of liquid crystal)

Each of the liquid crystal sealants for the liquid crystal dropping process was irradiated with 3000 mJ/cm^2 ultraviolet light, and then about 100 mg of the liquid crystal sealant was applied onto the bottom of a 10 ml vial, and then liquid crystal (MLC-6866-100: manufactured by Merck KGaA, Darmstadt, Germany) was added in an amount of 10 times thereof. The vial was heated for 1 hour at 120 °C, 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 not containing a sealing agent. Evaluation was performed by the criteria below.

A: $1.0E + 11$ or more of the value of specific resistance

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

C: Less than $1.0E + 10$ of the value of specific resistance

Meanwhile, " $1.0E + 11$ " of the value of specific resistance represents " 1.0×10^{11} ". The same applies to the other descriptions.

[Table 1]

			Example 1	Example 2	Example 3
Component (a)	#1	1-Hydroxy-2-trimethylsiloxy-1,1,2,2-tetra phenylethane	0.005 parts	0.005 parts	0.005 parts
Component (b)	#2	t-Butylperoxy2-ethyl hexanoate			
	#3	Nitroso-based piperidine derivative	0.005 parts		
	#4	Naphthoquinone		0.005 parts	
	#5	2-Hydroxy naphthoquinone			0.005 parts
	#6	Hydroquinone			
	#7	2,6-di-tert-butyl-2-cresol			
Component (c)	#8	Bisphenol A type epoxy acrylate	16 parts	16 parts	16 parts
Component (d)	#9	Resorcin diglycidyl ether	1.5 parts	1.5 parts	1.5 parts
Component (e)	#10	Sebacic acid dihydrazide	0.85 parts	0.85 parts	0.85 parts
Component (f)	#11	3-Glycidoxypropyl trimethoxysilane	0.05 parts	0.05 parts	0.05 parts
Component (g)	#12	Talc	1.5 parts	1.5 parts	1.5 parts
Component (h)	#13	Reaction product of 2-methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2methyl-1-propa n-1-one	1 part	1 part	1 part
Heat curability			99	99	99
Handling property			A	A	A
Contamination of liquid crystal			A	A	A

			Example 4	Example 5
Component (a)	#1	1-Hydroxy-2-trimethylsiloxy-1,1,2,2-tetra phenylethane	0.005 parts	0.005 parts
	#2	t-Butylperoxy2-ethyl hexanoate		
Component (b)	#3	Nitroso-based piperidine derivative		
	#4	Naphthoquinone		
	#5	2-Hydroxy naphthoquinone		
	#6	Hydroquinone	0.005 parts	
	#7	2,6-di-tert-butyl-P-cresol		0.005 parts
Component (c)	#8	Bisphenol A type epoxy acrylate	16 parts	16 parts
Component (d)	#9	Resorcin diglycidyl ether	1.5 parts	1.5 parts
Component (e)	#10	Sebacic acid dihydrazide	0.05 parts	0.05 parts
Component (f)	#11	3-Glycidioxypropyl trimethoxysilane	0.05 parts	0.05 parts
Component (g)	#12	Talc	1.5 parts	1.5 parts
Component (h)	#13	Reaction product of 2-methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-3methyl-1-propa n-1-one	1 part	1 part
Heat curability			99	98
Handling property			A	B
Contamination of liquid crystal			A	A

			Compara tive Example 1	Compara tive Example 2	Compara tive Example 3
Component (a)	#1	1-Hydroxy-2-trimethylsiloxy-1,1,2,2-tetra phenylethane			
	#2	t-Butylperoxy2-ethyl hexanoate	0.005 parts		
Component (b)	#3	Nitroso-based piperidine derivative	0.005 parts	0.005 parts	0.005 parts
	#4	Naphthoquinone			
	#5	2-Hydroxy naphthoquinone			
	#6	Hydroquinone			
Component (c)	#7	2,6-di-tert-butyl-P-cresol			
	#8	Bisphenol A type epoxy acrylate	16 parts	16 parts	16 parts
Component (d)	#9	Resorcin diglycidyl ether	1.5 parts	1.5 parts	1.5 parts
Component (e)	#10	Sebacic acid dihydrazide	0.85 parts	0.85 parts	0.85 parts
Component (f)	#11	3-Glycidoxypropyl trimethoxysilane	0.05 parts	0.05 parts	0.05 parts
Component (g)	#12	Talc	1.5 parts	1.5 parts	1.5 parts
Component (h)	#13	Reaction product of 2-methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2-methyl-1-propa n-1-one	1 part	1 part	1 part
Heat curability			-	-	-
Handling property			A	A	A
Contamination of liquid crystal			B	C	C

- Unable to measure because of no curing

#1 : Synthesized from Synthesis Example 1

#2 : Kayaester O (manufactured by Kayaku Akzo Corporation)

#3 : Polystop 7300P (manufactured by Hakuto Co., Ltd.)

#4 : NQI (manufactured by Kawasaki Kasei Chemicals Ltd.)

#5 : LSN (manufactured by Kawasaki Kasei Chemicals Ltd.)

#6 : HQ (manufactured by Kawaguchi Chemical Industry Co., Ltd.)

#7 : BHT (manufactured by Tokyo Chemical Industry Co., Ltd.)

#8 : Synthesized from Reference Synthesis Example 1

#9 : 1,3-bis(oxiranylmethoxy)benzene (marketed by Nagase ChemteX Corporation)

#10 : SDH (manufactured by Otsuka Chemical Co., Ltd.)

SDH used as pulverized by jet mill to 1.5 μm average particle diameter and 5 μm maximum particle diameter.

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

#12 : D-600 (manufactured by NIPPON TALC Co., Ltd.)

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

From the results of Table 1, it was confirmed that the liquid crystal sealants for the liquid crystal dropping process containing (a) a thermal radical polymerization initiator not having an oxygen-oxygen bond (-O-O-) or a nitrogen-nitrogen bond (-N=N-) in the molecule thereof, (b) a radical polymerization inhibitor, and (c) a curable resin having a (meth)acryloyl group (Examples 1 to 5) were very excellent in terms of heat curability, handling property, and liquid crystal contamination. It was confirmed that the liquid crystal sealants for the liquid crystal dropping process containing specific compounds, such as naphthoquinone as the (b) radical polymerization inhibitor (Examples 1 to 4) were particularly excellent among them.

INDUSTRIAL APPLICABILITY

The liquid crystal sealant for the liquid crystal dropping process of the present invention has good thermosetting properties, and is also excellent in terms of

handling property and storage stability, and the properties of a cured material such as adhesive strength. Accordingly, the liquid crystal sealant for the liquid crystal dropping process of the present invention allows flexibility of the design of the liquid crystal display cell to be secured, and contributes to the productivity, and long term reliability thereof.

CLAIMS

1. A liquid crystal sealant for a liquid crystal dropping process comprising:

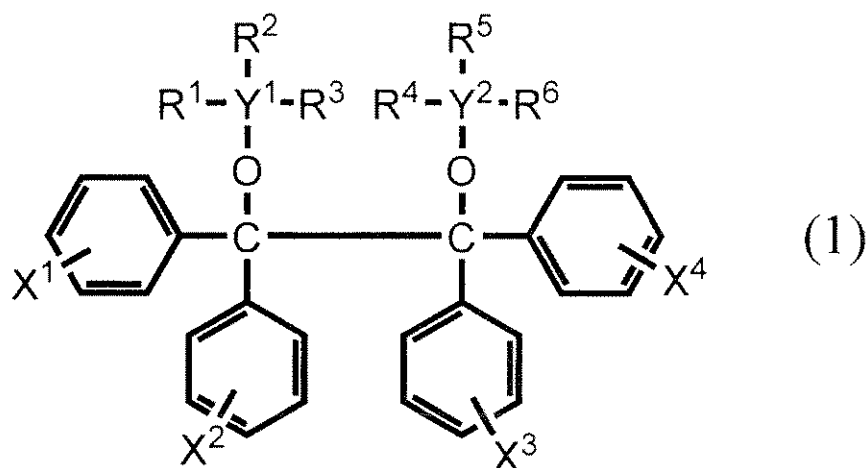
(a) a thermal radical polymerization initiator not having an oxygen-oxygen bond (-O-O-) or a nitrogen-nitrogen bond (-N=N-) in the molecule thereof,

(b) a radical polymerization inhibitor, and

(c) a curable resin having a (meth)acryloyl group.

2. The liquid crystal sealant for the liquid crystal dropping process according to claim 1, wherein the component

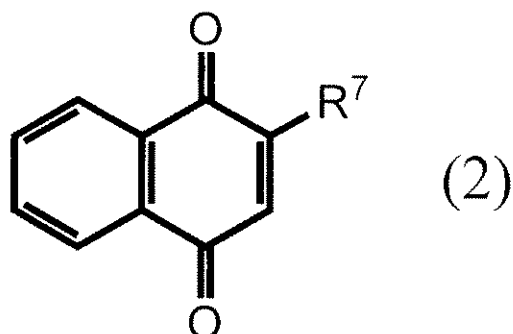
(a) is a compound represented by formula (1) below:



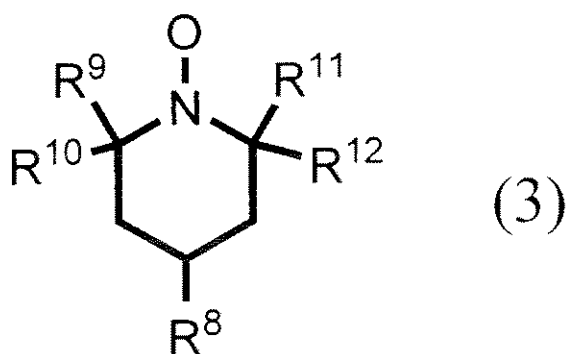
wherein, Y^1 and Y^2 each independently represent a hydrogen atom, a phenyl group, or a silicon atom, R^1 to R^6 each independently represent a hydrogen atom or a C1-C4 straight or branched alkyl group, and X^1 to X^4 each independently represent a hydrogen atom, a methyl group, an ethyl group, a methoxy group, an ethoxy group, a phenoxy group, or a halogen atom,

with the proviso that R^1 to R^3 or R^4 to R^6 that are bonded respectively to Y^1 or Y^2 are not present when Y^1 or Y^2 is a hydrogen atom.

3. The liquid crystal sealant for the dropping process according to claim 1 or 2, wherein the component (b) is one, or two or more of radical polymerization inhibitors selected from formulae (2) to (4) below:

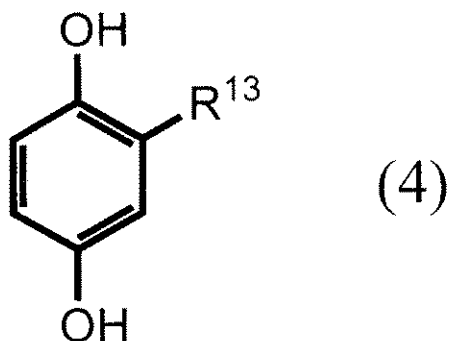


wherein, R^7 represents a hydrogen atom, a hydroxy group, a C1-C4 straight or branched alkoxy group, or a C1-C4 straight or branched alkyl group,



wherein, R^8 represents a hydrogen atom, a hydroxy group, a C1-C4 straight or branched alkoxy group, a phenoxy group, an acetoamide group, an amino group, a carboxy group, a cyano group, a benzoyloxy group, an isothiocyanate group, or an oxo

group, and R^9 to R^{12} each independently represent a C1-C4 straight or branched alkyl group,



wherein, R^{13} represents a hydrogen atom, or a C1-C4 straight or branched alkyl group.

4. The liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 3, further comprising (d) a curable resin that has an epoxy group and (e) a heat-curing agent.

5. The liquid crystal sealant for the liquid crystal dropping process according to claim 4, wherein the component (e) is an organic acid hydrazide.

6. The liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 5, further comprising (f) a silane coupling agent.

7. The liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 6, further comprising (g) an inorganic filler.

8. The liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 7, further comprising (h) a photopolymerization initiator.

9. The liquid crystal sealant for the liquid crystal dropping process according to claim 4 or 5, wherein the content of the component (b) is from 0.0001 to 1 parts by mass with respect to 100 parts by mass of the total amount of the component (c) and the component (d).

10. A method of manufacturing the liquid crystal sealant for the liquid crystal dropping process according to any one of claims 1 to 9, comprising a step of dissolving the component (b) in the component (c).

11. A method of manufacturing the liquid crystal sealant for the liquid crystal dropping process according to claim 4 or 5, comprising a step of dissolving the component (b) in the component (d).

12. 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, or the liquid crystal sealant for the liquid crystal dropping process obtained by the manufacturing method according to claim 10 or 11.