

LIQUID CRYSTAL SEALING MATERIAL AND LIQUID CRYSTAL DISPLAY
CELL USING SAME

TECHNICAL FIELD

The present invention relates to a liquid crystal sealing material that has good thermosetting properties. More specifically, the present invention relates to a liquid crystal sealing material that has good thermosetting properties and also has excellent storage stability, and, furthermore, also has excellent moisture resistance and the like for a cured product, and a liquid crystal display cell that is sealed with a cured product thereof.

BACKGROUND ART

The so-called liquid crystal drop fill method 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 drop fill method 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 sealing material formed on one substrate, and then bonding the other substrate whereby to seal the liquid crystal.

However, the liquid crystal drop fill method has problems that the liquid crystal sealing material in the uncured state is in contact with the liquid crystal, and thus components of

the liquid crystal sealing material 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 sealing material is currently used as a liquid crystal sealing material for the liquid crystal drop fill method, and practically applied (Patent documents 3 and 4). A liquid crystal drop fill method using this liquid crystal sealing material is characterized by irradiating the liquid crystal sealing material 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 sealing material with light and suppress dissolution (elution) of components of the liquid crystal sealing material 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 sealing material 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 sealing material. 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 sealing material 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, a thermal radical initiator generally has problems such that radicals are generated little by little even at normal temperature, and thus the storage stability and working stability of the liquid crystal sealing material are poor. In addition, a curing accelerator such as a polyvalent carboxylic acid acts as a catalyst, and it is not captured via chemical bond into a cured product by reacting itself, and thus has the problem that the curing accelerator dissolves in the liquid crystal and causes display defects.

As described above, development of liquid crystal sealing materials has been carried out with great intensity, but a liquid crystal sealing material having excellent thermal reactivity and also having good storage stability, and involving low contamination of the liquid crystal 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

eIFSE0283PCT-SG (KAYF-054SG)

The present invention relates to a liquid crystal sealing material that is cured by heating only, or light-heat combination, and proposes a liquid crystal sealing material for liquid crystal drop fill method which reacts fast by heat, and thus has extremely little contamination with respect to the liquid crystal throughout the steps, and excellent storage stability, and is also excellent in cured product properties such as moisture proof reliability.

Means for Solving the Problems

The present inventors earnestly investigated, and, as a result thereof, found that a liquid crystal sealing material that contains a curable resin that comprises one kind, or two or more kinds selected from among epoxy resins, (meth)acrylated epoxy resins, and partially (meth)acrylated epoxy resins, each resin bearing active hydrogen in the molecule (with the proviso that the active hydrogen is not hydrogen contained in a hydroxy 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, also has excellent storage stability, and completed the present invention.

Specifically, the present invention relates to 1) to 13) below. Meanwhile, in the specification, with respect to the component (a), it may be described as the "component (a) curable resin" in order to avoid the complicated description of "(a) a curable resin that comprises one kind, or two or

more kinds selected from among epoxy resins, (meth)acrylated epoxy resins, and partially (meth)acrylated epoxy resins, each resin bearing active hydrogen in the molecule".

1)

A liquid crystal sealing material containing: (a) a curable resin that comprises one kind, or two or more kinds selected from among epoxy resins, (meth)acrylated epoxy resins, and partially (meth)acrylated epoxy resins, each resin bearing active hydrogen in the molecule, with the proviso that the active hydrogen is not hydrogen contained in a hydroxy group, and (b) a heat-curing agent.

2)

The liquid crystal sealing material according to 1), in which the component (a) is a (meth)acrylated epoxy resin that has active hydrogen in the molecule.

3)

The liquid crystal sealing material according to 1) or 2), wherein the component (a) is a (meth)acrylated epoxy resin that has a carboxy group, a sulfanyl group, or an amino group in the molecule

4)

The liquid crystal sealing material according to any one of 1) to 3), in which the component (a) is a (meth)acrylated epoxy resin that has a carboxy group in the molecule.

5)

The liquid crystal sealing material according to any one of 1) to 4), in which the component (a) is an acrylated

resorcinol diglycidyl ether that has a carboxy group in the molecule.

6)

The liquid crystal sealing material according to any one of 1) to 5), further containing (c) a curable resin that comprises one kind, or two or more kinds selected from an epoxy resin, a (meth)acrylated epoxy resin, and a partially (meth)acrylated epoxy resin not having active hydrogen in the molecules, with the proviso that the active hydrogen is not hydrogen contained in a hydroxy group.

7)

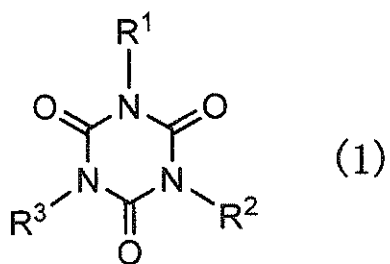
The liquid crystal sealing material according to any one of 1) to 6), in which the content of the component (a) is from 5 to 50 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealing material.

8)

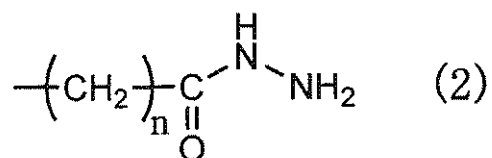
The liquid crystal sealing material according to any one of 1) to 7), in which the component (b) heat-curing agent is a polyvalent hydrazide compound.

9)

The liquid crystal sealing material according to 8), wherein 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.

10)

The liquid crystal sealing material according to any one of 1) to 9), further containing (d) a silane coupling agent.

11)

The liquid crystal sealing material according to any one of 1) to 10), further containing (e) an inorganic filler.

12)

The liquid crystal sealing material according to any one of 1) to 11), further containing (f) a photopolymerization initiator.

13)

A liquid crystal display cell sealed with a cured product obtained by curing the liquid crystal sealing material according to any one of 1) to 12).

Effects of the Invention

The liquid crystal sealing material 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 drop fill method, 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 drop fill method in which a liquid crystal sealing material is cured with heat only.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

The liquid crystal sealing material of the present invention contains a curable resin component (a) that comprises one kind, or two or more kinds selected from an epoxy resin, a (meth)acrylated epoxy resin, and a partially (meth)acrylated epoxy resin having active hydrogen in the molecules. However, with respect to the active hydrogen, hydrogen contained in a hydroxy group is excluded. The hydroxy group generally has a great acid dissociation constant (pKa) and the hydroxy group itself has weak nucleophilicity, and thus hardly functions as a catalyst. As a matter of fact, ordinary epoxy acrylate has a secondary hydroxy group, but does not function as a reaction catalyst at the time of heat curing. In the present invention, good thermal reactivity can be realized by it containing the curable resin. Furthermore,

the curable resin has a functional group that reacts to light or heat such as a (meth)acryloyl group or an epoxy group, and thus can be captured into a cured material, and dramatically suppress the amount that dissolves into the liquid crystal, and the display property of a liquid crystal display device is not harmed.

Meanwhile, in the specification, "(meth)acrylic" means either one or both of "acrylic" and "methacrylic". In addition, in the specification, "(meth)acryloyl" means either one or both of "acryloyl" and "methacryloyl".

Examples of the active hydrogen include active hydrogen contained in a carboxy group, a sulfanyl group, an amino group, a sulfo group, a phospho group and the like. Specifically, examples of the component (a) include, for example, curable resins containing one kind, or two or more kinds selected from a (meth)acrylated epoxy resin and a partially (meth)acrylated epoxy resin that has a carboxy group, a sulfanyl group, an amino group, a sulfo group, a phospho group and the like in the molecule, and an epoxy resin that has a carboxy group, a thiol group, an amino group, a sulfo group, a phospho group and the like in the molecule. Among the functional groups containing active hydrogen, a carboxy group, a thiol group or an amino group is preferred, and, furthermore, a carboxy group is particularly preferred in terms of function as a catalyst and easiness of synthesis. For example, amine-modified bisphenol A type epoxy acrylate EBECRYL 3703 (manufactured by DAICEL-ALLNEX LTD.) and the like are easily available as

commercial products to be used as the epoxy resin that has an amino group.

The (meth)acrylated epoxy resin is preferred as the curable resin of the component (a), rather than the epoxy resin and the partially (meth)acrylated epoxy resin. The (meth)acrylated epoxy resin reacts to light promptly, and thus dissolution into the liquid crystal can be further suppressed. This curable resin can be obtained by, for example, reacting a (meth)acrylated epoxy resin, which is obtained by a well-known reaction of an epoxy resin and a (meth)acrylic acid, with acid anhydride, a polyvalent carboxylic acid and the like.

Specifically, the (meth)acrylated epoxy resin is obtained by firstly adding (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) to an epoxy resin in a predetermined equivalent ratio, and by performing esterification reaction, for example, at 80°C to 110°C. The obtained (meth)acrylated epoxy resin is reacted with an acid anhydride with a method described in, for example, JP 49-2601 A, JP 3-143911 A, JP 5-32746 A or the like, whereby to obtain a (meth)acrylated epoxy resin that has active hydrogen in the molecule. Herein, the epoxy resin that is a raw material is not particularly limited, but is preferably a bi-functional or higher-functional epoxy resin, and the like. Examples thereof

include, for example, a resorcinol diglycidyl ether, 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, and a hydrogenated material thereof. Among them, the epoxy resin is preferably a resorcinol diglycidyl ether, a bisphenol A type epoxy resin or a bisphenol F type epoxy resin, and is particularly preferably a resorcinol diglycidyl ether.

The content of the component (a) is preferably from 5 to 50 parts by mass, and particularly preferably from 5 to 30 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealing material of the present invention. If the amount of component (a) is too small, sufficient heat curability is not obtained. On the other hand, if the amount of component (a) is too great, the liquid crystal sealing material has higher viscosity, and thus blending with other components may be restricted.

The heat-curing agent, which is the component (b) that is used in the liquid crystal sealing material 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(hydrazinocarbonyl)-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 1 to 20 parts by mass, and further preferably from 2 to 15 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealing material of the present invention, and two or more kinds may be used in a mixture.

The liquid crystal sealing material of the present invention may contain a curable resin as the component (c) that comprises one kind, or two or more kinds selected from an epoxy resin, a (meth)acrylated epoxy resin, and a partially (meth)acrylated epoxy resin not having active hydrogen in the molecules (with the proviso that the active hydrogen is not hydrogen contained in a hydroxy group). For example, examples of the component (c) 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. The component (c) used in the present

invention preferably has low contamination and solubility with respect to any liquid crystal. Examples of the 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 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, the (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) to an epoxy resin in a predetermined equivalent ratio, and by performing an esterification reaction, for example, at 80°C to 110°C. 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 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 and (meth)acryloyl group is not limited, and is suitably selected from the viewpoint of the process suitability and the contamination of the liquid crystal.

When the liquid crystal sealing material of the present invention contains the component (c), the amount used is suitably determined considering the workability and the physical properties of the obtained liquid crystal sealing material. The amount used is preferably from 20 to 80 parts by mass, and further preferably 30 to 70 parts by mass with

respect to 100 parts by mass of the total amount of the liquid crystal sealing material.

In the liquid crystal sealing material of the present invention, the component (d), silane coupling agent may be used to improve adhesive strength and 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 silane coupling agent (d) in the liquid crystal sealing material 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 sealing material of the present invention.

In the liquid crystal sealing material of the present invention, the component (e) inorganic filler may be used to improve adhesive strength and moisture proof reliability. 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 sealing material, which may be used in the liquid crystal sealing material of the present invention, is typically from 3 to 60 parts by mass, and preferably from 5 to 50 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealing material 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 sealing material of the present invention may contain the component (f), a photo-radical polymerization initiator in order to render the liquid crystal sealing material to be a light-heat combination curing type liquid crystal sealing material. The photo-radical polymerization 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 sealing material, which may be used in the liquid crystal sealing material of the present invention, is typically from 0.5 to 20 parts by mass, and preferably from 1 to 15 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealing material of the present invention.

In the liquid crystal sealing material 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.

The liquid crystal sealing material of the present invention may be further blended with curing accelerators such as an organic acid and an imidazole, organic fillers, and additives such as pigments, leveling agents, antifoam agents and solvents as necessary.

The method described below is one example of a method for obtaining the liquid crystal sealing material of the present invention. First, the component (c) and the component (f) are heat-dissolved in the component (a) as necessary. Then, the solution is cooled to room temperature, and then the component

(b), and the component (d), the component (e), and an organic filler, an antifoam agent, a leveling agent, a solvent and the like are added as necessary, and the solution is 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 sealing material 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 sealing material 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 sealing material of the present invention is combined with a spacer such as a glass fiber (space control material), and then the liquid crystal sealing material 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 sealing material, 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 sealing material 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 sealing material of the present invention.

The liquid crystal sealing material of the present invention has very good heat curability, and is promptly cured in the heating process in the liquid crystal drop fill method. 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 sealing material of the present invention is also excellent in terms of 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 sealing material 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 sealing material 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. This reaction liquid was washed with water, and toluene was distilled, whereby to give 395 g of the intended bisphenol A type epoxy acrylate (acrylated bisphenol A type epoxy resin) (KAYARAD^{RTM} R-93100).

Synthesis Example 2: Synthesis of acid anhydride adduct of bisphenol A type epoxy acrylate

4.84 g of the bisphenol A type epoxy acrylate obtained in Synthesis Example 1, 0.049 g of 4-dimethyl aminopyridine, 6.07 g of triethyl amine, and 1000 ml of methylene chloride were added together, and the mixture was stirred and dissolved at room temperature, and then 18.3 g of tetrahydrophthalic anhydride was added, and the mixture was stirred at room temperature for 3 hours. The obtained reaction liquid was washed with water 6 times, and then methylene chloride was distilled, whereby to give 7 g of a bisphenol A type epoxy acrylate having a carboxy group in the molecule. LC MS(m/z)=787(M-H), IR: 1709 cm⁻¹ (COOH).

Synthesis Example 3: Synthesis of acrylated resorcin diglycidyl ether

181.2 g of resorcin diglycidyl ether (Nagase Chemtex Corporation) 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, 0.6 g of trimethyl ammonium chloride was added as a reaction catalyst, and stirred at 98°C for about 30 hours to give the reaction liquid. This reaction liquid was washed with water, and toluene was distilled, whereby to give 253 g of epoxy acrylate of the intended resorcin diglycidyl ether (acrylated resorcin diglycidyl ether).

Synthesis Example 4: Synthesis of acid anhydride adduct of acrylated resorcin diglycidyl ether

3.66 g of epoxy acrylate of resorcin diglycidyl ether obtained in Synthesis Example 3, 0.049 g of 4-dimethyl aminopyridine, 6.07 g of triethyl amine and 1000 ml of methylene chloride were added, and the mixture was stirred and dissolved at room temperature, and then 11.8 g of maleic anhydride was added, and stirred at room temperature for 2 hours. The obtained reaction liquid was washed with water 6 times, and then methylene chloride was distilled, whereby to give 5 g of an acrylated resorcinol diglycidyl ether having a carboxy group in the molecule. LC MS(m/z)=561(M-H), IR: 1705 cm^{-1} (COOH).

Examples 1 to 3 and Comparative Examples 1 to 4

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

In addition, the curable resin component (component (c)) in the ratio shown in Table 1 described below was also heated at 90°C. Then, the photo-radical polymerization initiator (component (f)) was heat-dissolved, and then the solution was cooled to room temperature and the silane coupling agent (component (d)), the inorganic filler (component (e)), the heat-curing agent (component (b)) and a curing accelerator were added, and stirred, and then dispersed with a three-roller milling machine, and filtered with a metal mesh (635 mesh), to prepare the sealing materials for a liquid crystal drop fill method of Comparative Examples 1 to 4.

Evaluation tests were implemented with the method described below.

(Measurement for adhesive strength)

1 g of 5 μm glass fiber, as a spacer, was added to 100 g of the obtained liquid crystal sealing material, and mixed and stirred. This liquid crystal sealing material 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 sealing material, and irradiated with 3000 mJ/cm^2 ultraviolet light using a UV irradiation machine, and then placed into an oven and heat-cured at 120°C for 1 hour. The shear adhesive strength of the glass fragment was measured with a bond tester (SS-30WD: manufactured by SEISHIN TRADING CO., LTD). The results are shown in Table 1.

(Measurement for moisture-resistant adhesive strength)

A measurement sample identical to that of the adhesive strength test was prepared. The measurement sample was placed in a pressure cooker tester (TPC-411: manufactured by Tabai Espec Corp.) under the following conditions: 121°C, 2 atmospheres and 100% humidity for 12 hours, and then the shear adhesive strength of the glass fragment was measured with the bond tester. The results are shown in Table 1.

(Measurement for moisture absorptivity)

The obtained liquid crystal sealing material was sandwiched between polyethylene terephthalate (PET) films, and formed into a thin film with a thickness of 100 μm . This film was irradiated with 3000 mJ/cm^2 of ultraviolet light using a UV irradiation machine, and then placed into an oven and heat-cured at 120°C for 1 hour. After the curing the PET film was peeled off, which was taken as a sample. The weight of the

sample was measured, and then the sample was kept in an environment of 60°C and 90% RH for 12 hours, and the weight was measured again. The weight change rate (%) with respect to the initial weight is shown in Table 1.

(Measurement for pot life)

The viscosity change of the obtained liquid crystal sealing material at 25°C was measured. Viscosity measurement was performed after the obtained liquid crystal sealing material was kept under the conditions of 25°C and 50 RH% for 72 hours, and the viscosity increase rate (%) with respect to the initial viscosity was calculated. The results are shown in Table 1.

(Preparation of liquid crystal cell for evaluation)

An alignment film liquid (PIA-5540-05A; manufactured by CHISSO CORPORATION) was applied onto a transparent substrate having electrodes, and burned and subjected to rubbing treatment. The liquid crystal sealing material was applied to this substrate so that the line width after the lamination was 1 mm whereby to perform main sealing and dummy sealing, and then, microdroplets of liquid crystal (JC-5015LA; manufactured by CHISSO CORPORATION) were dropped in a frame of the sealing pattern. Furthermore, onto a substrate already finished with the rubbing treatment for one piece, in-plane spacers (Natoco spacer KSEB-525F; manufactured by Natoco Co., Ltd.; 5 μ m gap width after the lamination) were sprayed, heat-fixed, and laminated to the substrate previously finished with the liquid crystal dropping using a lamination apparatus in vacuo. The

atmosphere was opened and a gap was formed, and then the substrate was irradiated with 50 mJ/cm^2 ultraviolet light with a UV irradiation machine while only the inside of the sealing pattern frame was masked, and then placed into an oven and heat-cured at 120°C for 1 hour, whereby to prepare a liquid crystal test cell for evaluation.

The insertion resistance of the seal and the turbulence in alignment of the liquid crystal in the vicinity of the seal of the prepared liquid crystal cell for evaluation were observed with a polarizing microscope, the plug-in resistance and the alignment of the liquid crystal in the vicinity of the seal were evaluated in accordance with the criteria shown below. The results are shown in Table 1.

(Evaluation for insertion resistance)

S: The insertion of the liquid crystal into the seal is less than 0.2 mm, which is a level where the seal of the liquid crystal does not have any problem.

A: The insertion of the liquid crystal into the seal is 0.2 mm or more and less than 0.4 mm, which is a level where the seal of the liquid crystal does not have any problem.

B: The insettion of the liquid crystal into the seal is 0.4 mm or more and less than 0.6 mm, which is a level where the seal of the liquid crystal does not have any problem.

C: The insertion of the liquid crystal into the seal is 0.6 mm or more and less than 1.0 mm, which is a level where the seal of the liquid crystal does not have any problem.

F: The sealing is collapsed, and the cell cannot be

formed.

(Evaluation for alignment of the liquid crystal in the vicinity of the seal)

S: The alignment turbulence of the liquid crystal from the seal is less than 0.2 mm.

A: The alignment turbulence of the liquid crystal from the seal is 0.2 mm or more and less than 0.4 mm.

B: The alignment turbulence of the liquid crystal from the seal is 0.4 mm or more and less than 0.6 mm.

C: The alignment turbulence of the liquid crystal from the seal is 0.6 mm or more and less than 1.0 mm.

F: The sealing is collapsed, and the cell cannot be formed.

(Measurement for curing speed)

With respect to the obtained liquid crystal sealing material, the complex viscosity was measured with an apparatus for measuring dynamic viscoelasticity (Rheosol-G5000, manufactured by UBM). The settings of the apparatus for measuring dynamic viscoelasticity are as described below.

Cone: diameter 20 mm parallel cone, frequency: 1 Hz, deformation angle: 3 deg., the measurement temperature was elevated at a speed of 18°C/minute from 30°C to 120°C, and then maintained at 120°C. The time to 10000 Pa·s of the viscosity is shown in Table 1.

[Table 1]

			Example 1	Example 2	Example 3
Component (a)	#1	Acid anhydride adduct of epoxy acrylate of resorcin didiglycidyl ether		5 parts	
	#2	Acid anhydride adduct of bisphenol A type epoxy acrylate	5 parts		
	#3	Amine-modified bisphenol A type epoxy acrylate			5 parts
Component (b)	#4	Tris(2-hydrazinocarbonylethyl) isocyanurate	1.2 parts	1.2 parts	1.2 parts
Component (c)	#5	Bisphenol A type epoxy acrylate	5 parts	5 parts	5 parts
	#6	Resorcin didiglycidyl ether	3 parts	3 parts	3 parts
Component (d)	#7	3-Glycidoxypropyl trimethoxysilane	1 part	1 part	1 part
Component (e)	#8	Alumina	1.5 parts	1.5 parts	1.5 parts
	#9	Organic filler (rubber)	6 parts	6 parts	6 parts
Component (f)	#10	Reaction product of 2-methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2-methyl -1-propan-1-one	0.6 parts	0.6 parts	0.6 parts
	#11	1,3,5-tris(2-carboxylethyl) isocyanurate			
	#12	Dodecane diacid			
	#13	VPE-0201			
Adhesive strength (MPa)			67	71	75
Moisture-resistant adhesive strength (MPa)			45	42	39
Moisture absorptivity (%)			2.5	2.4	2.1
Viscosity (Pa·s)			270	320	330
Viscosity change rate (%)			12	8	18
Shape of seal			S	S	S
Alignment of liquid crystal in the vicinity of seal			A	S	A
Curing speed (seconds)			430	420	550

			Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Component (a)	#1	Acid anhydride adduct of epoxy acrylate of resorcin didiglycidyl ether				
	#2	Acid anhydride adduct of bisphenol A type epoxy acrylate				
	#3	Amine-modified bisphenol A type epoxy acrylate				
Component (b)	#4	Tris(2-hydrazinocarbonyl ethyl) isocyanurate	1.2 parts	1.2 parts	1.2 parts	1.2 parts
Component (c)	#5	Bisphenol A type epoxy acrylate	10 parts	10 parts	10 parts	10 parts
	#6	Resorcin didiglycidyl ether	3 parts	3 parts	3 parts	3 parts
Component (d)	#7	3-Glycidoxypopyl trimethoxysilane	1 part	1 part	1 part	1 part
Component (e)	#8	Alumina	1.5 parts	1.5 parts	1.5 parts	1.5 parts
	#9	Organic filler (rubber)	6 parts	6 parts	6 parts	6 parts
Component (f)	#10	Reaction product of 2-methacryloyloxyethyl isocyanate and 1-[4-(2-hydroxy ethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one	0.6 parts	0.6 parts	0.6 parts	0.6 parts
	#11	1,3,5-tris(2-carboxylethyl) isocyanurate		1 part		
	#12	Dodecane diacid			1 part	
	#13	VPE-0201				1 part
Adhesive strength (MPa)			71	65	67	34
Moisture-resistant adhesive strength (MPa)			42	6	12	7
Moisture absorptivity (%)			1.8	3.5	3.5	2.3
Viscosity (Pa.s)			230	240	240	270
Viscosity change rate (%)			5	42	46	78
Shape of seal			F	S	S	F
Alignment of liquid crystal in the vicinity of seal			F	C	C	F
Curing speed (seconds)			Not reached	390	400	260

#1 : Synthesized from Synthesis Example 2

#2 : Synthesized from Synthesis Example 4

#3 : EBECRYL 3703 (Manufactured by DAICEL-ALLNEX LTD.)

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

HCIC used pulverized to 1.5 μm average particle diameter and 5 μm maximum particle diameter using a jet mill.

#5 : Synthesized from Synthesis Example 1

#6 : 1,3-bis(oxiranylmethoxy)benzene (marketed by Nagase Chemtex Corporation)

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

#8 : SPC (Average particle diameter 50 nm: manufactured by C. I. KASEI CO., LTD.)

#9 : Paraloid EXL-2655 (butadiene/alkyl methacrylate/styrene copolymer, 0.2 μm average particle diameter: manufactured by Rohm and Haas Company)

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

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

CIC acid used pulverized to 1.5 μm average particle diameter and 5 μm maximum particle diameter using a jet mill.

#12 : Dodecane diacid (manufactured by UBE INDUSTRIES, LTD.)

Dodecane diacid used pulverized to 1.5 μm average particle diameter and 5 μm maximum particle diameter using a jet mill.

#13 : Azotized thermal radical initiator (manufactured by Wako Pure Chemical Industries, Ltd.)

From the results of Table 1, Comparative Example 1 not containing a curing accelerator component has poor curability, and as a result thereof, alignment defects in the panel display property occur. In addition, those using CIC acid or dodecane diacid or a thermal radical initiator as a curing accelerator, have shortcomings in the contamination of the liquid crystal and the moisture-resistant adhesiveness

although they achieve improvement in 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 sealing material of the present invention has excellent storage stability and curability, and thus is excellent in workability, and it can be said that the liquid crystal sealing material 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 sealing material of the present invention is excellent in terms of workability, the liquid crystal sealing material 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 sealing material comprising:
 - (a) a curable resin that comprises one kind, or two or more kinds selected from among epoxy resins, (meth)acrylated epoxy resins, and partially (meth)acrylated epoxy resins, each resin bearing active hydrogen in the molecule, with the proviso that the active hydrogen is not hydrogen contained in a hydroxy group, and
 - (b) a heat-curing agent.
2. The liquid crystal sealing material according to claim 1, wherein the component (a) is a (meth)acrylated epoxy resin that has active hydrogen in the molecule.
3. The liquid crystal sealing material according to claim 1 or 2, wherein the component (a) is a (meth)acrylated epoxy resin that has a carboxy group, a sulfanyl group, or an amino group in the molecule.
4. The liquid crystal sealing material according to any one of claims 1 to 3, wherein the component (a) is a (meth)acrylated epoxy resin that has a carboxy group in the molecule.
5. The liquid crystal sealing material according to any one of claims 1 to 4, wherein the component (a) is an acrylated

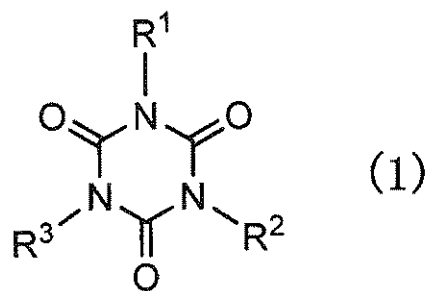
resorcinol diglycidyl ether that has a carboxy group in the molecule.

6. The liquid crystal sealing material according to any one of claims 1 to 5, further comprising (c) a curable resin that comprises one kind, or two or more kinds selected from the epoxy resin, the (meth)acrylated epoxy resin, and the partially (meth)acrylated epoxy resin not having the active hydrogen in the molecules, with the proviso that the active hydrogen is not hydrogen contained in the hydroxy group.

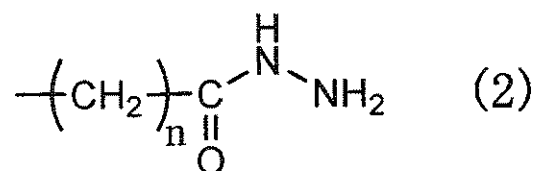
7. The liquid crystal sealing material according to any one of claims 1 to 6, wherein the content of the component (a) is from 5 to 50 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealing material.

8. The liquid crystal sealing material according to any one of claims 1 to 7, wherein the component (b) heat-curing agent is a polyvalent hydrazide compound.

9. The liquid crystal sealing material according to claim 8, wherein the component (b) heat-curing agent is one, or two or more of a hydrazide compound represented by formula (1) below:



wherein R¹ to R³ each independently represent, a hydrogen atom, or a molecular skeleton represented by formula (2) below:



wherein n represents an integer of 1 to 6.

10. The liquid crystal sealing material according to any one of claims 1 to 9, further comprising (d) a silane coupling agent.

11. The liquid crystal sealing material according to any one of claims 1 to 10, further comprising (e) an inorganic filler.

12. The liquid crystal sealing material according to any one of claims 1 to 11, further comprising (f) a photo-radical polymerization initiator.

13. A liquid crystal display cell sealed with a cured product obtained by curing the liquid crystal sealing material

according to any one of claims 1 to 12.