

LIQUID CRYSTAL SEALING AGENT, AND LIQUID CRYSTAL DISPLAY CELL USING SAME

TECHNICAL FIELD

The present invention relates to a liquid crystal sealant and a liquid crystal display cell using the liquid crystal sealant.

BACKGROUND ART

Nowadays liquid crystal display cells are used in various fields from small-sized displays such as mobile phones and liquid crystal monitors to large-sized television sets, and further expansion in the future is expected. The processes for producing liquid crystal display cells are mainly two processes: a liquid crystal injection process and a liquid crystal dropping process. The liquid crystal dropping process is a process for producing a liquid crystal display cell by applying a liquid crystal sealant onto a transparent glass substrate or plastic substrate on which a transparent electrode and an orientation film are suitably disposed, and dropping a liquid crystal into the inner side of a pool of the sealant, and there is an increased demand for shortening production takt time (the time required per step) and easiness of increasing size. However, there is a problem that the liquid crystal is contaminated by the step when the liquid crystal comes into contact with uncured liquid crystal sealant, and causes a problem in the quality of the liquid crystal

display cell. Compared to this, the liquid crystal injection process is a process including attaching upper and lower glass substrates and the like with a liquid crystal sealant in advance to thereby form an empty cell, injecting a liquid crystal from an injection port, and finally sealing the injection port. In this process, a high-quality liquid crystal display cell can be produced, and the liquid crystal sealant can be cured by only heat. Therefore, this is an effective production process specifically in the production of a small-sized liquid crystal display cell.

In the preparation of an empty cell that is used in the above-mentioned liquid crystal injection process, the liquid crystal sealant is applied onto the substrate by dispensing, screen printing or the like, the substrate is subjected to preliminary heating (precuring), an opposing substrate is then superposed thereon, and the liquid crystal sealant is cured.

Liquid crystal sealants are curable resin compositions having the roles of attaching glass substrates or plastic substrates and enclosing a liquid crystal inside of the substrates. Liquid crystal sealants used in the above-mentioned liquid crystal dropping process are mainly photocurable resin compositions, and liquid crystal sealants used in the liquid crystal injection process are mainly heat-curing resin compositions. Specifically, the property required for a liquid crystal sealant significantly differs depending on the format of use. Specifically, the objects that are inherent to a liquid crystal sealant used in the liquid

crystal injection process are as follows: the liquid crystal sealant is excellent in coating workability; the liquid crystal sealant has stable behavior of thickening by preliminary heating (precuring); the liquid crystal sealant is excellent in contact performance against an opposing substrate (the substrate onto which the liquid crystal sealant is not applied) since the liquid crystal sealant is transported in an uncured state after lamination; the liquid crystal sealant has shape retention property during heat curing; and the like. The contact performance against an opposing substrate is deemed to be good in the case when the liquid crystal sealant is sufficiently crushed when it is preheated and then attached to the opposing substrate to give a large contact surface area on the opposing substrate, ideally in the case when the liquid crystal sealant is brought into contact with the same surface area as that of the substrate on which the liquid crystal sealant is applied. The case when the contact property is poor is the case when the thickening by the preliminary heating is too high and thus the liquid crystal sealant is not sufficiently crushed and thus gives a small contact surface area on the opposing substrate.

Furthermore, in recent liquid crystal display cells, a multi-processing process, which includes forming many electrodes on a large glass substrate, then assembling by laminating upper and lower substrates, and cutting the substrates into individual liquid crystal display cells, is adopted. However, the number of substrates to be processed has

increased, and mother glasses (substrates before dividing) have grown in size, and thus the stress applied on the liquid crystal sealants after being cured has increased. In accordance with this, further improvement of the adhesiveness and flexibility of liquid crystal sealants is required.

For the above-mentioned reasons, liquid crystal sealants used in the liquid crystal injection process have been energetically developed.

For example, Patent Document 1 discloses a heat-curing liquid crystal sealant that is excellent in adhesiveness, reliability of humidity resistance and flexibility.

Patent Document 2 discloses a heat-curing liquid crystal sealant that is excellent in adhesiveness, reliability of humidity resistance, flexibility and heat curability.

Patent Document 3 discloses a heat-curing liquid crystal sealant that is excellent in screen printing property and moisture resistance.

Patent Document 1: Japanese Unexamined Patent Application, Publication No. H10-273644

Patent Document 2: Japanese Unexamined Patent Application, Publication No. H11-15005

Patent Document 3: PCT International Publication No. WO2005/038519

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

The present invention aims at providing a heat-curing

liquid crystal sealant that is excellent in coating workability, contact performance against an opposing substrate and viscosity stability after preliminary heating, and is extremely excellent in adhesiveness and flexibility after curing.

Means for Solving the Problems

The present inventors have carried out intensive studies in order to solve the above-mentioned problem, and consequently found that a liquid crystal sealant that contains a phenol novolac resin having a specific property and an acrylic polymer having a core-shell structure, and has a gel time at 150°C of 50 seconds or more and 200 seconds or less can solve the above-mentioned problem, and thus completed the present invention.

Specifically, the present invention relates to the following 1) to 12).

1)

A liquid crystal sealant containing (a) a solid phenol novolac resin having a softening point of 75°C or less, (b) an acrylic polymer having a core-shell structure, (c) an epoxy resin, and (d) an organic solvent, and having a gel time at 150°C of 50 seconds or more and 200 seconds or less.

2)

The liquid crystal sealant according to 1), in which the core layer of the component (b) is a polymer of n-butyl acrylate, and the shell layer is a polymer of methyl

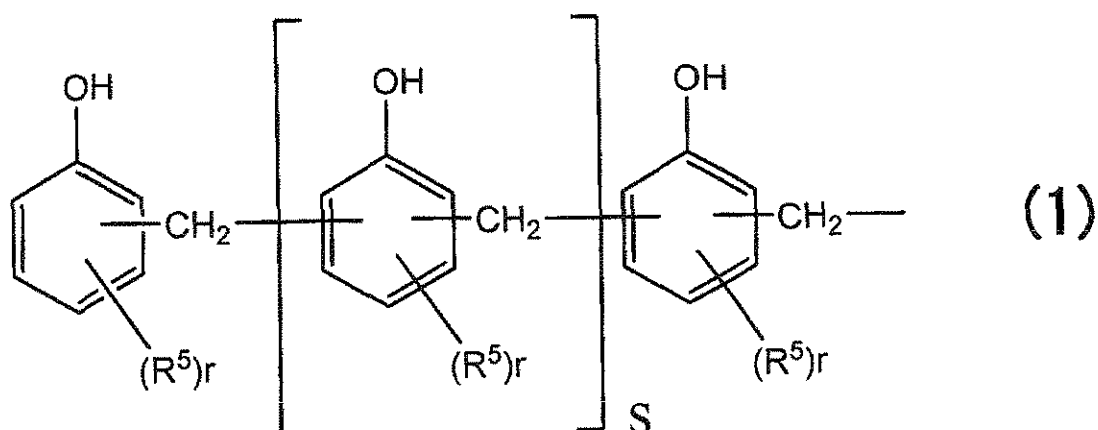
methacrylate.

3)

The liquid crystal sealant according to 1) or 2), in which the component (d) is one or more organic solvent(s) selected from the group consisting of propylene glycol diacetate, dimethyl esters of dibasic acids, propylene glycol monoethyl ether acetate and ethylene glycol dibutyl ether.

4)

The liquid crystal sealant according to any one of 1) to 3), in which the component (a) is a compound represented by the following formula (1):



in the formula, R^5 represents a hydrogen atom, a lower alkyl group, a lower alkoxy group or a halogen atom, and r represents an integer of 1 to 3,

In which when r is 2 or 3, the respective R^5 may be the same or different, and s represents 0 or a positive integer.

5)

The liquid crystal sealant according to any one of 1) to 4), in which the equivalent amount of the hydroxy group of the component (a) with respect to 1 equivalent amount of the epoxy

group of the component (c) is 0.2 to 1.4 chemical equivalent amount.

6)

The liquid crystal sealant according to any one of 1) to 5), in which the component (c) is a bisphenol A type epoxy resin.

7)

The liquid crystal sealant according to any one of 1) to 6), further containing (e) a cure accelerator.

8)

The liquid crystal sealant according to 7), wherein the component (e) is at least one selected from 2,4-diamino-6-[2'-methylimidazolyl-(1')] -ethyl-s-triazine isocyanuric acid adduct and epoxy resin amine adducts.

9)

The liquid crystal sealant according to any one of 1) to 8), further containing (f) a coupling agent.

10)

The liquid crystal sealant according to 9), in which component (f) is an epoxysilane coupling agent.

11)

The liquid crystal sealant according to any one of 1) to 10), further containing (g) an inorganic filler.

12)

A liquid crystal display cell, which has been sealed by the cured product obtained by curing the liquid crystal sealant according to any one of 1) to 11).

Effects of the Invention

The liquid crystal sealant of the present invention is excellent in contact performance against an opposing substrate after precuring, very excellent in adhesiveness after curing, and is also excellent in humidity resistance. Therefore, it becomes possible to produce a liquid crystal display cell having high reliability.

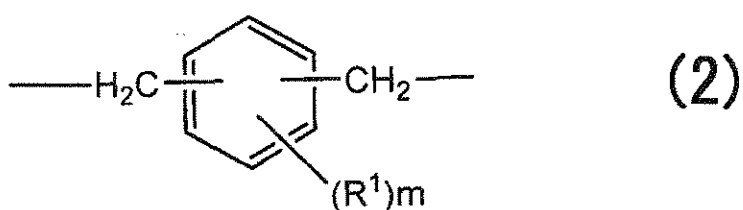
PREFERRED MODE FOR CARRYING OUT THE INVENTION

The liquid crystal sealant of the present invention contains, as essential components, a component (a) a phenol novolac resin having a softening point of 75°C or less, a component (b) an acrylic polymer having a core-shell structure, a component (c) an epoxy resin, and a component (d) an organic solvent.

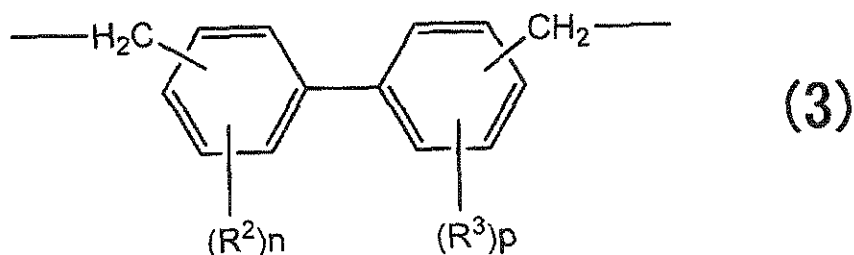
The component (a) used in the present invention is a phenol novolac resin having a softening point of 75°C or less, preferably 65°C or less, more preferably 50°C or less, and is not specifically limited as long as it has this property. Although the lower limit value of the softening point is not specifically limited, it is preferably 40°C or more. The softening point is measured by the ring and ball method defined in JIS K7234.

Examples of the phenol novolac resin may include novolac resins containing, as raw materials, various phenols such as bisphenol A, tetrabromobisphenol A, bisphenol F, bisphenol S,

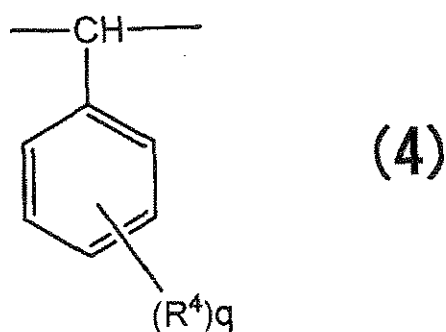
4,4-biphenylphenol, 2,2,6,6-tetramethyl-4,4-biphenylphenol, 2,2-methylene-bis(4-methyl-6-tert-butylphenol), trishydroxyphenylmethane, pyrogallol, phenols having diisopropylidene backbones, phenols having fluorene backbones such as 1,1-di-4-hydroxyphenylfluorene, polyphenol compounds such as phenolated polybutadiene, various phenols such as phenol, cresols, ethylphenols, butylphenols, octylphenols, bisphenol A, allylphenols, brominated bisphenol A, bisphenol F, bisphenol S and naphthols; phenol novolac resins such as phenol novolac resins having xylylene backbones, phenol novolac resins having dicyclopentadiene backbones and phenol novolac resins having fluorine backbones; phenol novolac resins obtained by bonding various phenols such as phenol, cresols, ethylphenols, butylphenols, octylphenols, bisphenol A, brominated bisphenol A, bisphenol F, bisphenol S and naphthols by using a crosslinking group (aralkylene group) of any of the following formulas (2) to (4); and the like.



In the formula, R¹ each represents a hydrogen atom, an alkyl group with a carbon number of 1 to 4, an allyl group or a halogen atom, and m represents an integer of 1 to 4. When m is 2 or more, the respective R¹ may be the same or different.



In the formula, R^2 and R^3 each independently represent a hydrogen atom, an alkyl group with a carbon number of 1 to 4, an allyl group or a halogen atom, and n and p each independently represent an integer of 1 to 4. When n or p is 2 or more, the respective R^2 and R^3 may be the same or different.



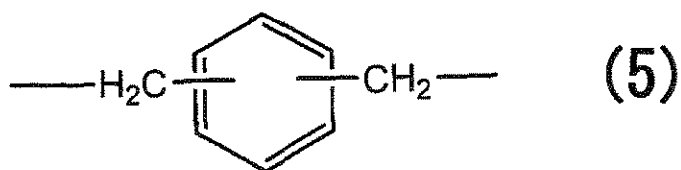
In the formula, R^4 represents a hydrogen atom, an alkyl group with a carbon number of 1 to 8, an allyl group, a halogen atom or a hydroxy group, and q represents an integer of 1 to 5. When q is 2 or more, the respective R^4 may be the same or different.

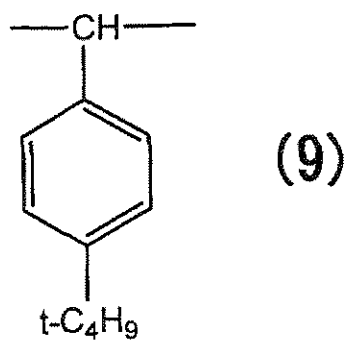
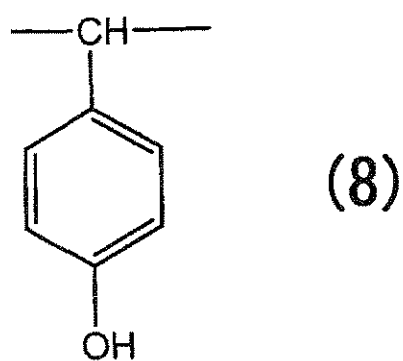
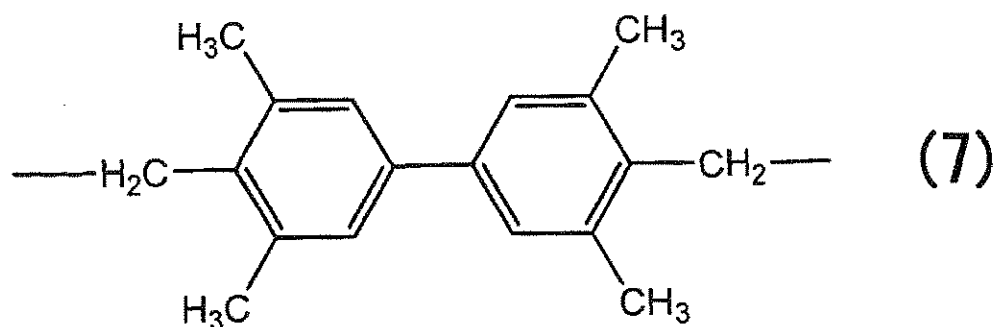
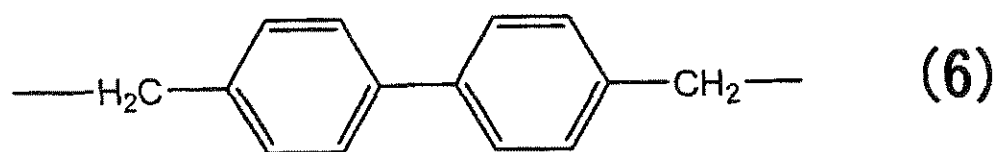
Examples of preferable phenol novolac resins may include novolac resins containing, as raw materials, various phenols such as phenols, cresols, ethylphenols, butylphenols, octylphenols, bisphenol A, allylphenols, bisphenol F, bisphenol S and naphthols; phenol novolac resins having xylylene backbones; phenol novolac resins having

dicyclopentadiene backbones; phenol novolac resins having fluorine backbones; and phenol novolac resins formed by bonding various phenols such as phenol, cresols, ethylphenols, butylphenols, octylphenols, bisphenol A, brominated bisphenol A, bisphenol F, bisphenol S and naphthols by using a crosslinking group (aralkylene group) of any of the above-mentioned formulas (2) to (4).

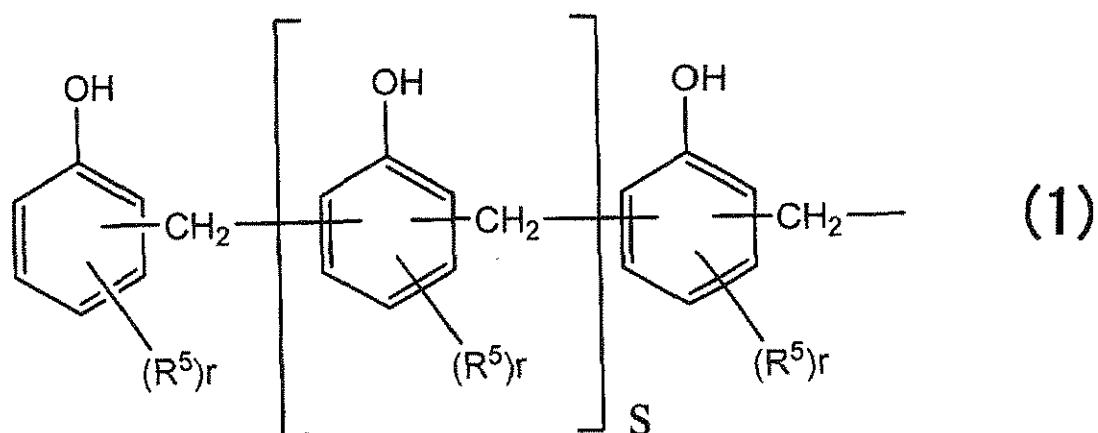
Examples of more preferable phenol novolac resins may include novolac resins containing, as raw materials, various phenols such as phenols, cresols, octylphenol, bisphenol A, bisphenol F, bisphenol S and naphthols; and phenol novolac resins obtained by bonding various phenols such as phenol, cresols, octylphenols, bisphenol A, bisphenol F, bisphenol S and naphthols by using a crosslinking group (aralkylene group) of any of the above-mentioned formulas (2) to (4).

Examples of further preferable phenol novolac resins may include novolac resins containing monophenols as raw materials, typically phenol novolac resins containing phenol as a raw material, cresol novolac resin containing cresols as raw materials, and the like; and phenol novolac resins obtained by bonding various phenols such as phenols, cresols and bisphenol A by using a crosslinking group of any of the following formulas (5) to (9).





The specifically preferable phenol novolac resins used in the present invention are phenol novolac resins containing monophenols as raw materials, and are represented by the following formula (1).



In the formula, R⁵ represents a hydrogen atom, a lower alkyl group, a lower alkoxy group or a halogen atom, and r represents an integer of 1 to 3. When r is 2 or 3, the respective R⁵ may be the same or different, and s represents 0 or a positive integer.

In the above-mentioned formulas (1) to (9), examples of the alkyl group with a carbon number of 1 to 4 may include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl and the like. Examples of the alkyl group with a carbon number of 1 to 8 may include methyl, ethyl, n-propyl, isopropyl, pentyl, hexyl, octyl and the like. Examples of the lower alkyl group may include alkyl groups with a carbon number of 1 to 8 such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and t-butyl, preferably alkyl groups with a carbon number of 1 to 4 such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and t-butyl. Examples of the lower alkoxy group may include alkoxy groups with a carbon number of 1 to 8 such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy and t-butoxy, preferably alkoxy groups with a carbon number of 1 to 4 such as methoxy, ethoxy, n-propoxy, isopropoxy and n-

butoxy. Examples of the halogen atom may include a bromine atom, a chlorine atom, a fluorine atom and the like. In the above-mentioned formula (1), the 0 or positive integer in s is preferably 0 to 15, more preferably 0 to 10. Specifically, PN-152 (manufactured by Nippon Kayaku Co., Ltd.) and the like are easily obtained from markets as commercially available products.

These phenol novolac resins are used alone or by mixing two or more kinds. The amount used of the phenol novolac resin used in the present invention is preferably 0.2 to 1.4 chemical equivalent amount, more preferably 0.3 to 0.9 chemical equivalent amount, further preferably 0.5 to 0.9 chemical equivalent amount, as the equivalent amount of the hydroxy group in the novolac resin, with respect to 1 equivalent amount of the epoxy group of the epoxy resin in the liquid crystal sealant. This amount used of the novolac resin affects the contact performance against an opposing substrate of the liquid crystal sealant.

The curing agent formed of the phenol novolac resin that is preferably used in the present invention is a compound represented by the above-mentioned formula (1). In the above-mentioned formula (1), the components wherein s is 1 or more give a high resin viscosity. Therefore, it is preferable that a component wherein $s = 0$ (binucleated form) is present, and the abundance thereof is generally about 20 to 80% by mass, preferably about 25 to 70% by mass, more preferably about 30 to 50% by mass in the phenol novolac resin (the remnant is

components wherein s is 1 or more). In the reaction of the phenol novolac resin with the epoxy resin, the phenol novolac resin having a tri- or more nucleated form (for example, a compound wherein $s = 1$ in the above-mentioned formula (1)) has a three-dimensional crosslinked structure, whereas the phenol novolac resin having a binucleated form (for example, a compound wherein $s = 0$ in the above-mentioned formula (1)) is linearly crosslinked. Therefore, flexibility is given in a rigid structure, and thus the adhesiveness against a glass substrate is improved. Furthermore, the phenol novolac resin that is preferably used in the present invention has a low resin viscosity, and thus is excellent in terms of screen-printing property. Therefore, the attachment of upper and lower glass substrates and the formation of a gap in the production of a liquid crystal display apparatus become easy.

The component (b) used in the present invention includes microparticles with each particle being formed of two layers including a core layer constituted by an acrylic polymer and a shell layer similarly constituted by an acrylic polymer. The components of the acrylic polymer used in the core layer and the components of the acrylic polymer used in the shell layer may be the same or different. Examples of the raw materials for these may include (meth)acrylate-based monomers such as *n*-propyl (meth)acrylate, *n*-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and *n*-decyl (meth)acrylate; aromatic vinyl compounds such as styrene, vinyltoluene and α -methylstyrene; vinyl cyanide compounds such as acrylonitrile and

methacrylonitrile; vinylidene cyanide, 2-hydroxyethyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 2-hydroxyethyl fumarate, hydroxybutyl vinyl ether, monobutyl maleate, butoxyethyl methacrylate; and the like. Furthermore, crosslinkable monomers having two or more reactive groups such as ethylene glycol di(meth)acrylate, butylene glycol di(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, hexanediol di(meth)acrylate, hexanediol tri(meth)acrylate, oligoethylene di(meth)acrylate and oligoethylene tri(meth)acrylate; aromatic divinyl monomers such as divinylbenzene; triallyl trimellitate, triallyl isocyanate; and the like, and one or two or more selected from these may be used. Specifically, Paraloid EXL-2655 (Rohm and Haas Company) and the like can be obtained from markets as commercially available products. Among these, microparticles each having a core layer of a polymer of n-butyl acrylate and a shell layer of a polymer of methyl methacrylate are specifically preferable. This may be obtained from markets as F-351 (Ganz Chemical Co., Ltd.).

Meanwhile, in this specification, the meth(acrylate) means either one or both of acrylate and methacrylate.

The component (c) used in the present invention is not specifically limited as long as it is a compound having a glycidyl group. Specific examples may include epoxy resins that are generally produced and sold such as bisphenol A type epoxy resins; bisphenol F type epoxy resins; bisphenol S type epoxy resins; 4,4'-biphenylphenol diglycidyl ether; 2,2',6,6' -

tetramethyl-4,4'-biphenylphenol diglycidyl ether; glycidyl ether of 2,2'-methylene-bis(4-methyl-6-tert-butylphenol); trishydroxyphenylmethane triglycidyl ether; pyrogallol triglycidyl ether; glycidyl ethers of phenols having diisopropylidene backbones; glycidyl ethers of phenols having fluorene backbones such as 1,1-di-4-hydroxyphenylfluorene; glycidyl etherated products of various novolac resins such as novolac resins containing, as raw materials, various phenols such as phenol, cresols, ethylphenols, butylphenols, octylphenols, bisphenol A, bisphenol F, bisphenol S and naphthols, xylylene backbone-containing phenol novolac resins, dicyclopentadiene backbone-containing phenol novolac resins and fluorine backbone-containing phenol novolac resins; alicyclic epoxy resins having aliphatic backbones such as cyclohexane; heterocyclic epoxy resins having hetero rings such as an isocyanuric ring and a hydantoin ring; epoxy resins obtained by glycidylating brominated bisphenol A, brominated bisphenol F, brominated bisphenol S, brominated phenol novolac and brominated cresol novolac; N,N-diglycidyl-o-toluidine; N,N-diglycidylaniline; phenyl glycidyl ether; resorcinol diglycidyl ether; 1,6-hexanediol diglycidyl ether; trimethylolpropane triglycidyl ether; polypropylene glycol diglycidyl ether; and 3,4-3',4' epoxycyclo)hexylmethylhexane carboxylate, hexahydrophthalic anhydride diglycidyl ester. Bisphenol A type epoxy resins, bisphenol F type epoxy resins, N,N-diglycidyl-o-toluidine, N,N-diglycidylaniline, (3,4-3',4' epoxycyclo)hexylmethylhexane carboxylate and

hexahydrophthalic anhydride diglycidyl ester are preferable, and bisphenol A type epoxy resins are more preferable. These epoxy resins may be used by mixing two or more kinds.

Furthermore, the above-mentioned epoxy resins are liquids or solids, and can be used by suitably mixing the epoxy resins depending on the desired viscosity.

The epoxy equivalent amount of the epoxy resin used in the present invention is preferably 230 or less, more preferably 210 or less, even more preferably 190 or less. When the epoxy equivalent amount is 230 or more, the reactivity with the curing agent becomes deteriorated, and a problem occurs in workability. Furthermore, the total chlorine amount in the liquid epoxy resin used in the present invention is preferably 1,500 ppm or less, more preferably 1,200 or less, even more preferably 1,000 or less. When the total chlorine amount is 1,500 or more, the ITO electrode of a liquid crystal cell is significantly eroded. The epoxy equivalent amount is measured by JIS K7236, and the total chlorine amount is measured by a hydrolysis process.

The component (d) used in the present invention is added aiming at lowering the viscosity so as to improve workability. Examples of the organic solvent that can be used may include alcohol-based solvents, ether-based solvents, acetate-based solvents and dimethyl esters of dibasic acids, and these may be used alone, or by mixing two or more at an optional ratio.

Examples of the alcohol-based solvents may include alkyl alcohols such as ethanol and isopropyl alcohol; alkoxy

alcohols such as 3-methyl-3-methoxybutanol, 3-methyl-3-ethoxybutanol, 3-methyl-3-n-propoxybutanol, 3-methyl-3-isopropoxybutanol, 3-methyl-3-n-butoxysibutanol, 3-methyl-3-isobutoxybutanol, 3-methyl-3-sec-butoxybutanol and 3-methyl-3-tert-butoxysibutanol; and the like.

Examples of the ether-based solvents may include monohydric alcohol ether-based solvents, alkylene glycol monoalkyl ether-based solvents, alkylene glycol dialkyl ether-based solvents, dialkylene glycol alkyl ether-based solvents, trialkylene glycol alkyl ether-based solvents and the like.

Examples of the monohydric alcohol ether-based solvents may include 3-methyl-3-methoxybutanol methyl ether, 3-methyl-3-ethoxybutanol ethyl ether, 3-methyl-3-n-butoxybutanol ethyl ether, 3-methyl-3-isobutoxybutanol propyl ether, 3-methyl-3-sec-butoxybutanol-isopropyl ether, 3-methyl-3-tert-butoxybutanol-n-butyl ether and the like.

Examples of the alkylene glycol monoalkyl ether-based solvents may include propylene glycol monomethyl ethers, propylene glycol monoethyl ethers, propylene glycol monopropyl ethers, propylene glycol monoisopropyl ethers, propylene glycol mono-n-butyl ethers, propylene glycol monoisobutyl ethers, propylene glycol mono-sec-butyl ethers, propylene glycol mono-tert-butyl ethers, ethylene glycol monomethyl ethers, ethylene glycol monoethyl ethers, ethylene glycol monopropyl ethers, ethylene glycol monoisopropyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol monoisobutyl ether, ethylene glycol mono-sec-butyl ether,

ethylene glycol mono-tert-butyl ether and the like.

Examples of the alkylene glycol dialkyl ether-based solvents may include propylene glycol dimethyl ether, propylene glycol diethyl ether, propylene glycol dipropyl ether, propylene glycol diisopropyl ether, propylene glycol di-n-butyl ether, propylene glycol diisobutyl ether, propylene glycol di-sec-butyl ether, propylene glycol di-tert-butyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dipropyl ether, ethylene glycol diisopropyl ether, ethylene glycol di-n-butyl ether, ethylene glycol diisobutyl ether, ethylene glycol di-sec-butyl ether, ethylene glycol di-tert-butyl ether, ethylene glycol dibutyl ether and the like.

Examples of the dialkylene glycol alkyl ether-based solvent may include dipropylene glycol methyl ether, dipropylene glycol ethyl ether, dipropylene glycol dipropyl ether, dipropylene glycol diisopropyl ether, dipropylene glycol di-n-butyl ether, dipropylene glycol diisobutyl ether, dipropylene glycol di-sec-butyl ether, dipropylene glycol di-tert-butyl ether, diethylene glycol dimethyl ether (diglyme), diethylene glycol diethyl ether, diethylene glycol dipropyl ether, diethylene glycol diisopropyl ether, diethylene glycol di-n-butyl ether, diethylene glycol diisobutyl ether, diethylene glycol di-sec-butyl ether, diethylene glycol di-tert-butylether and the like.

Examples of the trialkylene glycol alkyl ether-based solvents may include trialkylene glycol dialkyl ethers such as

tripropylene glycol dimethyl ether, tripropylene glycol diethyl ether, tridipropylene glycol dipropyl ether, tripropylene glycol diisopropyl ether, tripropylene glycol di-n-butyl ether, tripropylene glycol diisobutyl ether, tripropylene glycol di-sec-butyl ether, tripropylene glycol di-tert-butyl ether, triethylene glycol dimethyl ether, triethylene glycol diethyl ether, triethylene glycol dipropyl ether, triethylene glycol diisopropyl ether, triethylene glycol di-n-butyl ether, triethylene glycol diisobutyl ether, triethylene glycol di-sec-butyl ether and triethylene glycol di-tert-butylether, and the like.

Examples of the acetate-based solvents may include alkylene glycol monoalkyl ether acetates such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol monoisopropyl ether acetate, ethylene glycol mono-n-butyl ether acetate, ethylene glycol mono-sec-butyl ether acetate, ethylene glycol monoisobutyl ether acetate, ethylene glycol mono-tert-butyl ether acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monoisopropyl ether acetate, propylene glycol monopropyl ether acetate, propylene glycol mono-n-butyl ether acetate, propylene glycol mono-sec-butyl ether acetate, propylene glycol monoisobutyl ether acetate, propylene glycol mono-tert-butyl ether acetate, 3-methyl-3-methoxybutyl acetate, 3-methyl-3-ethoxybutyl acetate, 3-methyl-3-propoxybutyl acetate, 3-methyl-3-isopropoxybutyl

acetate, 3-methyl-3-n-butoxyethyl acetate, 3-methyl-3-isobutoxysibutyl acetate, 3-methyl-3-sec-butoxysibutyl acetate and 3-methyl-3-tert-butoxysibutyl acetate; and ethylene glycol diacetate, diethylene glycol diacetate, triethylene glycol diacetate, propylene glycol diacetate, dipropylene glycol diacetate, tripropylene glycol diacetate, butyl acetate and the like.

Examples of the dimethyl esters of dibasic acids may include esters represented by $\text{CH}_3\text{OCO}-(\text{-CH}_2\text{-})_n\text{-COOCH}_3$ ($n = 2$ to 4). Such esters may specifically include dimethyl glutarate, dimethyl adipate, dimethyl succinate and the like. Furthermore, two or more of these may be mixed. Furthermore, a mixture of dimethyl glutarate, dimethyl adipate and dimethyl succinate can also be obtained from markets as, for example, Rhodiasolv RPDE (manufactured by Rhodia Nicca Ltd.).

Among these organic solvents, propylene glycol diacetate, propylene glycol monoethyl ether acetate, dimethyl esters of dibasic acids and ethylene glycol dibutyl ether are preferable, and propylene glycol diacetate, propylene glycol monoethyl ether acetate, Rhodiasolv RPDE and ethylene glycol dibutyl ether are more preferable. The reason for this resides in the compatibility with component (b). Component (b) has the property of absorbing an organic solvent and a resin and swelling them step-by-step. Therefore, a liquid crystal sealant having poor storage stability is formed depending on the selection of the organic solvent. Organic solvents such as propylene glycol diacetate, propylene glycol monoethyl ether

acetate, Rhodiasolv RPDE and ethylene glycol dibutyl ether have sufficient ability to dissolve component (a), component (c) and the like, but are poor in compatibility with component (b). Therefore, the organic solvents do not precipitate insoluble components or cause layer separation due to the insufficient solution of the resin components, or do not change the properties such as viscosity of the liquid crystal sealant by swelling component (b) during storage.

The boiling point of the organic solvent is desirably in the range of from 150 to 230°C. When the boiling point is less than 150°C, the increase in the viscosity during the screen-printing of the liquid crystal sealant is significant, and thus the use time is shortened. When the boiling point is higher than 230°C, the solvent is not volatilized during solvent drying, and thus air bubbles are incorporated in the liquid crystal sealant after main curing, or the curing physical property is lowered.

As the amount used of the organic solvent, an arbitrary amount required for adjusting the viscosity of the liquid crystal sealant to a viscosity that allows application by a process such as dispensing and screen-printing (for example, 15 to 60 Pa·s (25°C)) can be used. Generally, the organic solvent is used so that the non-volatile components in the liquid crystal sealant become 70% by mass or more, preferably 85 to 95% by mass.

The liquid crystal sealant of the present invention has such a property that the gel time at 150°C is 50 seconds or

more and 200 seconds or less. When the gel time at 150°C is longer than 200 seconds, the liquid crystal sealant is cured slowly. Therefore, the defects that the liquid crystal sealant leaks from the stress due to the difference between the inner pressure and outer pressure of the liquid crystal sealant during heat pressing, and that the sealing width is disturbed by the capillary tube phenomenon, easily occur. Conversely, when the gel time is shorter than 50 seconds, the storage stability of the liquid crystal sealant itself is affected. The gel time is more preferably 70 seconds or more and 200 seconds or less, more preferably 100 seconds or more and 200 seconds or less, specifically preferably 100 seconds or more and 150 seconds or less. In this specification, the gel time is the time defined as follows: using an automatic gelation tester (manufactured by Iyo Denshi) 0.4 mL of the liquid crystal sealant is put into a measurement unit under an atmosphere with a measurement temperature of 150°C, a needle made of Teflon (registered trademark) attached to the tester is rotated on an autorotation unit at 100 rpm to thereby stir the liquid crystal sealant, and the time until a torque sensor detects a torque of 70 gcm is defined as the gel time.

The liquid crystal sealant of the present invention may also contain a cure accelerator as component (e) for the purpose of improving heat reactivity. Examples of the cure accelerator (e) used in the present invention may include imidazoles; salts of imidazoles with polyvalent carboxylic acids such as phthalic acid, isophthalic acid, telephthalic

acid, trimellitic acid, pyromellitic acid, naphthalene dicarboxylic acid, maleic acid and oxalic acid; amides such as dicyandiamide; salts of the amides with phenols, the above-mentioned polyvalent carboxylic acids, or phosphinic acids; diaza compounds such as 1,8-diaza-bicyclo(5.4.0)undecene-7; salts of the diaza compounds with phenols, the above-mentioned polyvalent carboxylic acids, or phosphinic acids; phosphines such as triphenylphosphine and tetraphenylphosphonium tetraphenylborate; phenols such as 2,4,6-trisaminomethylphenol; amine adducts, and the like. Specifically, 2-methylimidazole, 2-phenylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-phenyl-4-methylimidazole, 1-benzyl-2-phenylimidazole, 1-benzyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-cyanoethyl-2-undecylimidazole, 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-undecylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-ethyl,4-methylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine-isocyanuric acid adduct, 2:3 adduct of 2-methylimidazole isocyanurate, 2-phenylimidazole isocyanurate adduct, 2-phenyl-3,5-dihydroxymethylimidazole, 2-phenyl-4-hydroxymethyl-5-methylimidazole, 1-cyanoethyl-2-phenyl-3,5-dicyanoethoxymethylimidazole and the like may be included.

Among these cure accelerators, preferable ones may include salts of imidazoles with polyvalent carboxylic acids and amine adducts, and specifically preferable ones may

include 2,4-diamino-6-[2'-methylimidazolyl-(1')]-ethyl-s-triazine isocyanurate adduct and epoxy resin-amine adducts. The reason for this is that these cure accelerators are difficult to dissolve in solvents and have high latent performance, and thus give a long pot life to the liquid crystal sealant and are rapidly cured when being heated at 100°C or more to thereby prevent the leaking of the liquid crystal sealant by the stress due to the difference between the inner pressure and outer pressure of the liquid crystal sealant in the step of forming a gap in a liquid crystal panel. These compounds can be obtained from markets as MY-H (manufactured by Ajinomoto Fine-Techno Co., Inc.) and 2MAOK-PW (manufactured by Shikoku Chemicals Corporation). The amount of the cure accelerator added is preferably 0.5 to 20 parts by mass, more preferably 1 to 18 parts by mass with respect to 100 parts by mass of the epoxy resin.

It is more preferable to use these cure accelerators in the forms of latent cure accelerators since they have advantages such as improvement of workability (extension of pot life). Latent cure accelerators have the property that they are solids at room temperature, and dissolve and react as cure accelerators only after being melted by heating, and examples may include microcapsule-type cure accelerators obtained by forming these cure accelerators into microcapsules, solid-dispersing type cure accelerators that are difficult to dissolve in solvents and epoxy resins (for example, imidazoles), amine adducts and the like.

Among these cure accelerators, solid-dispersing type latent cure accelerators have average particle sizes of preferably 6 μm or less, more preferably 4 μm or less, even more preferably 3 μm or less, measured by a laser process. When a latent cure accelerator having an average particle size larger than 6 μm is used application with a dispenser is difficult, and the shape after application is not even, and thus the shape of the seal after sealing is also not even. Furthermore, rough coarseness and fineness of a filler is confirmed in the seal part after sealing the liquid crystal sealant in which the cure accelerator having an average particle size of larger than 6 μm is used.

The liquid crystal sealant of the present invention may contain a coupling agent as a component (f) for the purpose of further improving adhesiveness. Examples of the coupling agent may include silane-based coupling agents such as 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-aminopropyl methyltrimethoxysilane, 3-aminopropyl triethoxysilane, 3-mercaptopropyl trimethoxysilane, vinyltrimethoxysilane, N-(2-(vinylbenzylamino)ethyl)-3-aminopropyl trimethoxysilane hydrochloride, 3-methacryloxypropyl trimethoxysilane, 3-chloropropyl methyldimethoxysilane and 3-chloropropyl trimethoxysilane; titanium-based coupling agents such as

isopropyl (N-ethylaminoethylamino) titanate, isopropyl triisostearoyl titanate, titanium di(dioctylpyrrophosphate) oxyacetate, tetraisopropyl di(dioctylphosphite) titanate and neoalkoxy tri(p-N-(β -aminoethyl)aminophenyl) titanate; zirconium-based coupling agents such as Zr-acetylacetonate, Zr-methacrylate, Zr-propionate, neoalkoxy zirconate, neoalkoxy trisneodecanoyl zirconate, neoalkoxy tris(dodecanoyl) benzenesulfonyl zirconate, neoalkoxy tris(ethylenediaminoethyl) zirconate, neoalkoxy tris(m-aminophenyl) zirconate and ammonium zirconium carbonate; aluminum-based coupling agents such as Al-acetylacetonate, Al-methacrylate and Al-propionate; and the like, and silane-based coupling agents are preferable, and epoxysilane coupling agents are more preferable. By using the coupling agent, a liquid crystal sealant having excellent reliability of humidity resistance and small decrease in adhesiveness after moisture absorption can be obtained. Specifically, Sila-Ace S-510 (manufactured by Chisso Corporation) and the like can be obtained from markets.

In the liquid crystal sealant of the present invention, a component (g), an inorganic filler may be used to seek improvement of the adhesiveness and improvement of the reliability of humidity resistance. Examples of this inorganic filler (g) may include molten silica, crystalline silica, silicon carbide, silicon nitride, boron nitride, calcium carbide, magnesium carbide, 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 fibers, carbon fibers, molybdenum disulfide, asbestos and the like, and molten silica, crystalline silica, silicon nitride, boron nitride, calcium carbide, barium sulfate, calcium sulfate, mica, talc, clay, alumina, aluminum hydroxide, calcium silicate and aluminum silicate are preferable, and molten silica, crystalline silica, alumina and talc are more preferable. These inorganic fillers may be used in a mixture of two or more kinds. If the average particle diameter is too great, a defect factor is created in such a way that a gap cannot be formed well when the upper and 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 in the liquid crystal sealant of the inorganic filler as the component (g), which can be used in the liquid crystal sealant of the present invention, is generally from 10 to 60 parts by mass, preferably from 20 to 50 parts by mass with respect to 100 parts by mass of the total amount of the liquid crystal sealant of the present invention. If the content of the inorganic filler is less than 10 parts by mass, the adhesiveness with respect to a glass

substrate decreases, and the reliability of humidity resistance is also poor, and thus the adhesiveness after moisture absorption may significantly decrease. On the other hand, if the content of the inorganic filler is more than 60 parts by mass, it is hard to perform crushing and formation of the gap of the liquid crystal cell may become impossible.

Where necessary, additives such as organic fillers, pigments, leveling agents and defoaming agents can be incorporated in the liquid crystal sealant of the present invention.

As one example of a method for obtaining the liquid crystal sealant of the present invention, there is a method described below. First, component (a), component (c) and component (d) are dissolved by mixing, component (f) and component (g), and an organic filler, a defoaming agent, a leveling agent and the like as necessary are added thereto, and the mixture is uniformly mixed with a known mixing apparatus, for example, a three-roller milling machine, a sand mill, a ball mill or the like, component (b) and component (e) are then added, the mixture is uniformly mixed with a three-roller milling machine or a planetary mixer, and filtered with a metal mesh, whereby the liquid crystal sealant of the present invention can be obtained.

The liquid crystal display cell of the present invention is obtained by disposing a pair of substrates on which prescribed electrodes are formed facing each other 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 formed of glass, quartz, plastic, silicon or the like, in which at least one of the substrates is light-transmitting. As the manufacturing method thereof, a spacer, such as glass fibers (space control material), is added to the liquid crystal sealant of the present invention, 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 for 3 to 30 minutes. Then, the other glass substrate is superposed, and gap formation is performed under heating. After the gap formation, curing is performed at 100 to 180°C for 30 minutes to 3 hours, whereby an empty cell can be obtained. A liquid crystal is injected into this empty cell from a cut (injection port) that has been formed in advance in the liquid crystal sealant, in vacuum, whereby the liquid crystal display cell of the present invention can be obtained. The liquid crystal display cell of the present invention obtained in this way is excellent in adhesiveness and flexibility, and thus is highly resistant against impacts such as falling. Furthermore, the liquid crystal display cell is excellent in reliability of humidity resistance. Examples of the spacer include glass fibers, silica beads, polymer beads and the like. The diameter thereof varies depending on the purpose, and is generally 2 to

8 μm , and preferably 4 to 7 μm . The amount used is generally about from 0.1 to 4 parts by mass, preferably about from 0.5 to 2 parts by mass, more preferably about from 0.9 to 1.5 parts by mass with respect to 100 parts by mass of the liquid crystal sealant of the present invention.

The liquid crystal sealant of the present invention is very excellent in workability. Namely, the liquid crystal sealant has good coating workability by dispensing, screen-printing or the like, and the viscosity thereof increases to a predetermined viscosity in preliminary heating and then is stabilized. Therefore, the liquid crystal sealant is easily used. Furthermore, since the liquid crystal sealant is excellent in contact performance against an opposing substrate, the substrates are not peeled off from each other during transportation. In addition, since the liquid crystal sealant has a very good heat-curing property, it is rapidly cured in the heating step. Therefore, it is possible to decrease the display defects of a liquid crystal display cell without leaving uncured components and with extremely little elution of the constitutional components into the liquid crystal. Furthermore, since a cured product thereof is also excellent in terms of various properties of the cured product, such as adhesiveness, heat-resistance and humidity resistance, a liquid crystal display cell that is excellent in reliability can be prepared by using the liquid crystal sealant of the present invention. Furthermore, the liquid crystal display cell prepared by using the liquid crystal sealant of the

present invention also satisfies the properties required for a liquid crystal display cell such as a high voltage retention rate and a low ion density.

EXAMPLES

Hereinafter, the present invention is further specifically described with 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.

(Preparation of liquid crystal sealant)

Respective resin components (component (a) and component (c)) and an organic solvent (component (d)) were mixed at the ratio shown in the following Table 1 and dissolved by heating. After cooling to room temperature, a coupling agent (component (f)), an inorganic filler (component (g)) and the like were suitably added as necessary, an acrylic polymer having a core-shell structure (component (b)), and a cure accelerator (component (e)), as necessary, were added, the mixture was homogeneously mixed by a three-roll milling machine and filtered by a metal mesh. By this way, the liquid crystal sealants of Examples 1 to 8 and Comparative Examples 1 to 4 were prepared.

(Gel time)

Using an automatic gelation tester (manufactured by Iyo

Denshi), 0.4 mL of the liquid crystal sealant was put into a measurement unit under an atmosphere with a measurement temperature of 150°C, a needle made of Teflon (registered trademark) attached to the tester was rotated on an autorotation unit at 100 rpm to thereby stir the sealant, and the time until a torque sensor detected a torque of 70 gcm was deemed as the gel time. The result is shown in Table 1.

(Measurement of viscosity)

The viscosity at 25°C and 10 rpm was measured by using a type E viscometer (VISCONIC EHD type, cone 3° × R14: manufactured by Tokyo Seiki Kosakusho, Ltd.). The result is shown in Table 1.

(Thixo ratio)

Viscosities at 10 rpm and 1 rpm at 25°C were measured by using a type E viscometer (VISCONIC EHD type, cone 3° × R14: manufactured by Tokyo Seiki Kosakusho, Ltd.), and the value of the viscosity at 1 rpm/the viscosity at 10 rpm was deemed as the thixo ratio. The result is shown in Table 1.

(Test for storage stability)

The liquid crystal sealant prepared was retained in a 25°C atmosphere for 48 hours. The viscosity at 25°C and 10 rpm was measured by a type E viscometer (VISCONIC EHD type, cone 3° × R14: manufactured by Tokyo Seiki Kosakusho, Ltd.), and the viscosity increased from the initial viscosity was calculated

and deemed as the thickening rate after 48 hours. The calculation formula was $\{(\text{the viscosity after 48 hours} - \text{the initial viscosity}) / (\text{the initial viscosity})\} \times 100$. The result is shown in Table 1.

(Test for adhesiveness)

A liquid crystal sealant to which 5 μm glass fibers (PF-50S: manufactured by Nippon Electric Glass Co., Ltd.) had been added to the amount of 1 mass% with respect to the liquid crystal sealant was applied onto a 1.5 cm $\times$ 3 cm glass substrate having an ITO film, which had been washed, so that the diameter when the liquid crystal sealant is crushed to a thickness of 5 μm became 0.8 to 1.2 mm. Preliminary heating was performed for 10 minutes on a hot plate that had been preset to 90°C. As an opposing substrate, a 1.5 cm $\times$ 3 cm glass substrate having an ITO film, which had been washed, was attached to the substrate in a cross shape so that the side of the ITO plane faced the side of the liquid crystal sealant, and two portions were clipped with binder clips No. 155 (manufactured by Lion Office Products Corporation) to thereby fix the substrates. This test piece was put into an electric drier that had been preset to 150°C, and cooled to room temperature. The test piece was pulled under the tensile mode of a bond tester (SS-30WD: manufactured by Seishin Trading Co. Ltd.) at a velocity of 3.3 mm/sec, and the strength in the tensile direction was measured. The strength was converted to a value per a unit surface area of the seal and deemed as

adhesiveness. The criteria for the evaluation are as shown below. The result is shown in Table 1.

A: 16 MPa or more of the adhesiveness

B: 10 MPa or more and less than 16 MPa of the adhesiveness

C: Less than 10 MPa of the adhesiveness

(Test for moisture-resistant adhesiveness)

A test piece was prepared in a similar procedure to that mentioned above (Test for adhesiveness). The test piece was then put into a thermo-hygrostat bath (HPAV-80-20: manufactured by Isuzu Seisakusho Co. Ltd.) that had been preset to 60°C and 90%, for 12 hours, and cooled at room temperature to give a measurement test piece. The test piece was pulled under the tensile mode of a bond tester (SS-30WD: manufactured by Seishin Trading Co. Ltd.) at a velocity of 3.3 mm/sec, and the strength in the tensile direction was measured. The strength was converted to a value per unit surface area of the seal and deemed as moisture-resistant adhesiveness. The evaluation criteria are as shown below. The result is shown in Table 1.

A: 16 MPa or more of the moisture-resistant adhesiveness

B: 10 MPa or more and less than 16 MPa of the moisture-resistant adhesiveness

C: Less than 10 MPa of the moisture-resistant adhesiveness

(Contact performance against opposing substrate)

The liquid crystal sealant was applied onto a 5 cm × 5 cm glass substrate by a dispenser into a pattern with an injection port so as to give a cross-sectional surface of 5,000 μm^2 , and solvent drying (precuring) was performed for 10 minutes in an electric drier that had been preset to 90°C. The substrate was cooled to a room temperature atmosphere, an opposing glass substrate of 5 cm × 5 cm was superposed thereon, and a weight of 10 kg was put thereon for 30 seconds. The crushing property of the liquid crystal sealant was observed under an optical microscope, and the width of the liquid crystal sealant was measured. The measurement was performed in two directions: from the side of the glass substrate with the liquid crystal sealant applied thereon and from the opposing substrate, and the degree of the crushing was evaluated by comparing the width of the liquid crystal sealant on the side with the liquid crystal sealant applied thereon and the width of the liquid crystal sealant on the side of the opposing substrate. The evaluation criteria are as shown below. The result is shown in Table 1.

S: The width of the liquid crystal sealant on the opposing glass substrate was 70% or more of the width of the liquid crystal sealant on the substrate with the liquid crystal sealant applied thereon

A: The width of the liquid crystal sealant on the opposing glass substrate was 40% or more and less than 70% of the width of the liquid crystal sealant on the substrate with

the liquid crystal sealant applied thereon

B: The width of the liquid crystal sealant on the opposing glass substrate was 10% or more and less than 40% of the width of the liquid crystal sealant on the substrate with the liquid crystal sealant applied thereon

C: The width of the liquid crystal sealant on the opposing glass substrate was less than 10% of the width of the liquid crystal sealant on the substrate with the liquid crystal sealant applied thereon, or the substrates were not in contact with each other at all

(Test for seepage of constitutional components of liquid crystal sealant after pressing)

The liquid crystal sealant was applied onto a 5 cm × 5 cm glass substrate by a dispenser into a pattern with an injection port so as to give a cross-sectional surface of 5,000 μm^2 , and solvent drying (precuring) was performed for 10 minutes in an electric drier that had been preset to 90°C. The substrate was cooled to a room temperature atmosphere, a 5 cm × 5 cm opposing glass substrate was superposed thereon, the four sides were clipped with binder clips No. 155 (manufactured by Lion Office Products Corporation), and the substrates were put into an electric drier that had been preset to 150°C. The substrates were cooled to room temperature, and the appearance of the liquid crystal sealant in the substrates was observed under an optical microscope. In this test, the presence or absence of the seepage of the resin components (the presence

or absence of the phase separation of the resin components and filler component) is confirmed from the effects of curability and the like. The evaluation criteria are as shown below. The result is shown in Table 1.

A: Seepage of the resin components was not found.

C: Seepage of the resin components was found.

(Test for printing property)

The liquid crystal sealant as prepared was applied by printing onto a glass substrate by a screen printer (LS-150: manufactured by Newlong Seimitsu Kogyo Co., Ltd.). This was confirmed by visual observation. The presence or absence of blur, cutting of the liquid crystal sealant, and the like was observed. The evaluation criteria are as shown below. The result is shown in Table 1.

A: Blur and discontinuity were not found.

C: Blur and discontinuity were found.

(Test for dispense property)

The liquid crystal sealant as prepared was filled into a syringe and degassed, and then was applied onto a glass substrate with a dispenser (SHOT MASTER 300 manufactured by Musashi Engineering, Inc.) at 30 mm/sec, the shape was confirmed by visual observation. The presence or absence of blur, cutting of the liquid crystal sealant, and the like was observed. The evaluation criteria are as shown below. The result is shown in Table 1.

A: Blur and discontinuity were not found.

C: Blur and discontinuity were found.

(Test for measurement of specific resistance value)

About 100 mg of the liquid crystal sealant as prepared was homogeneously applied onto the bottom of a 10 mL sample vial, and solvent drying (precuring) was performed in an electric drier that had been preset to 90°C. Thereafter the liquid crystal sealant was cured for 60 minutes in an electric drier that had been preset to 150°C. The liquid crystal sealant was cooled to room temperature, and a liquid crystal (MLC-6866-100: manufactured by Merck & Co., Inc.) was added in a ten-fold amount based on the weight of the liquid crystal sealant. Heating was performed for 24 hours in an electric drier that had been preset to 90°C, and cooling was performed for 30 minutes. Each of the supernatant liquids was isolated with decantation, and the value of specific resistance was measured with a digital ultra ohmmeter (R8340: manufactured by Advantest Corporation). Evaluation was performed as described below. The result is shown in Table 1.

A: $1.0 \times 10^E + 12$ or more of the value of specific resistance

C: less than $1.0 \times 10^E + 12$ of the value of specific resistance

Meanwhile, " $1.0E + 12$ " of the value of specific resistance represents " 1.0×10^{12} ". The same applies to the other descriptions.

(Water absorption rate)

The liquid crystal sealant as prepared was applied onto a 5 cm × 7 cm glass substrate by using an applicator with a clearance of 25 μm. Solvent drying was performed for 10 minutes in an electric drier that had been preset to 90°C, and curing was performed for 60 minutes in an electric drier that had been preset to 150°C. The liquid crystal sealant was put into a thermo-hygrostat bath (HPAV-80-20: manufactured by Isuzu Seisakusho Co. Ltd.) that had been preset to 60°C and 90% for 24 hours and cooled at room temperature, and the water absorption rate was calculated from the change in weight from this liquid crystal sealant to the liquid crystal sealant immediately after the curing. The calculation formula was $\{(\text{the weight of the sealant after water absorption} - \text{the weight of the sealant before water absorption}) / (\text{the weight of the sealant before water absorption})\} \times 100$. The result is shown in Table 1.

[Table 1]

			Example 1	Example 2	Example 3
Component (a)	#1	PN-152	38 parts	38 parts	38 parts
	#2	PN-80			
Component (b)	#3	F-351	10 parts	10 parts	10 parts
	#4	Paraloid EXL-2655			
Component (c)	#5	RE-310S	100 parts	100 parts	100 parts
Component (d)	#6	Propylene glycol diacetate	31 parts		
	#7	Rhodiasolv RPDE		30 parts	
	#8	Propylene glycol monoethyl ether acetate			29 parts
	#9	Ethylene glycol dibutyl ether			
	#10	Butyl cellosolve			
Component (e)	#11	MY-H	10 parts	10 parts	10 parts
	#12	2MAOK-PW			
Component (f)	#13	Sila-Ace S-510	2 parts	2 parts	2 parts
Component (g)	#14	X-24-9163A	10 parts	10 parts	10 parts
	#15	Nanotech Alumina SP-C	30 parts	30 parts	30 parts
Gel time (sec)			138	145	132
Initial viscosity (Pa·S)			27	28	29
Thixo ratio			1.4	1.5	1.4
Storage stability (Thickening rate after 48 hours)			15	12	17
Adhesiveness test (MPa)			A	A	A
Moisture-resistant adhesiveness test (MPa)			A	A	A
Adhesiveness against opposing substrate			S	S	S
Seepage test			A	A	A
Printing property test			A	A	A
Dispense property test			A	A	A
Measurement of specific resistance value			4.1E+12	3.2E+12	3.6E+12
Water absorption rate			1.2	1.3	1.2

			Example 4	Example 5	Example 6
Component (a)	#1	PN-152	38 parts	38 parts	38 parts
	#2	PN-80			
Component (b)	#3	F-351	10 parts	10 parts	10 parts
	#4	Paraloid EXL-2655			
Component (c)	#5	RE-310S	100 parts	100 parts	100 parts
Component (d)	#6	Propylene glycol diacetate		30 parts	
	#7	Rhodiasolv RPDE			
	#8	Propylene glycol monoethyl ether acetate			
	#9	Ethylene glycol dibutyl ether	29 parts		
	#10	Butyl cellosolve			29 parts
Component (e)	#11	MY-H	10 parts		10 parts
	#12	2MAOK-PW		10 parts	
Component (f)	#13	Sila-Ace S-310	2 parts	2 parts	2 parts
Component (g)	#14	X-24-9163A	10 parts	10 parts	10 parts
	#15	Nanotech Alumina SP-C	30 parts	30 parts	30 parts
Gel time (sec)			142	127	134
Initial viscosity (Pa·S)			28	29	28
Thixo ratio			1.4	1.4	1.4
Storage stability (Thickening rate after 48 hours)			15	15	40
Adhesiveness test (MPa)			A	A	A
Moisture-resistant adhesiveness test (MPa)			A	A	A
Adhesiveness against opposing substrate			S	S	S
Seepage test			A	A	A
Printing property test			A	A	A
Dispense property test			A	A	A
Measurement of specific resistance value			4.0E+12	7.4E+12	3.3E+12
Water absorption rate			1.2	1.4	1.3

			Example 7	Example 8	Comparative Example 1
Component	#1	PN-152	38 parts	54 parts	38 parts
(a)	#2	PN-80			
Component	#3	F-351		10 parts	
(b)	#4	Paraloid EXL-2655	10 parts		
Component	#5	RE-310S	100 parts	100 parts	100 parts
Component (d)	#6	Propylene glycol diacetate	28 parts	38 parts	26 parts
	#7	Rhodiasolv RPDE			
	#8	Propylene glycol monoethyl ether acetate			
	#9	Ethylene glycol dibutyl ether			
	#10	Butyl cellosolve			
Component	#11	MY-H	10 parts	10 parts	10 parts
(e)	#12	2MAOK-PW			
Component (f)	#13	Sila-Ace S-510	2 parts	2 parts	2 parts
Component	#14	X-24-9163A	10 parts	10 parts	10 parts
(g)	#15	Nanotech Alumina SP-C	30 parts	30 parts	30 parts
Gel time (sec)			146	152	149
Initial viscosity (Pa·S)			27	29	26
Thixo ratio			1.4	1.3	1.4
Storage stability (Thickening rate after 48 hours)			16	16	15
Adhesiveness test (MPa)			A	A	B
Moisture-resistant adhesiveness test (MPa)			B	A	C
Adhesiveness against opposing substrate			S	B	S
Seepage test			A	A	A
Printing property test			A	A	A
Dispense property test			A	A	A
Measurement of specific resistance value			5.1E+12	4.6E+12	4.0E+12
Water absorption rate			1.1	1.2	1.1

			Comparative Example 2	Comparative Example 3	Comparative Example 4
Component (a)	#1	PN-152			38 parts
	#2	PN-80		38 parts	
Component (b)	#3	F-351	10 parts	10 parts	10 parts
	#4	Paraloid EXL-2655			
Component (c)	#5	RE-310S	100 parts	100 parts	100 parts
Component (d)	#6	Propylene glycol diacetate	9 parts	42 parts	27 parts
	#7	Rhodiasolv RPDE			
	#8	Propylene glycol monoethyl ether acetate			
	#9	Ethylene glycol dibutyl ether			
	#10	Butyl cellosolve			
Component (e)	#11	MY-H	10 parts	10 parts	5 parts
	#12	2MAOK-PW			
Component (f)	#13	Sila-Ace S-510	2 parts	2 parts	2 parts
Component (g)	#14	X-24-9163A	10 parts	10 parts	10 parts
	#15	Nanotech Alumina SP-C	30 parts	30 parts	30 parts
Gel time (sec)			121	141	221
Initial viscosity (Pa·S)			29	31	27
Thixo ratio			1.5	1.4	1.4
Storage stability (Thickening rate after 48 hours)			21	15	12
Adhesiveness test (MPa)			C	B	A
Moisture-resistant adhesiveness test (MPa)			*	C	B
Adhesiveness against opposing substrate			S	C	S
Seepage test			A	A	C
Printing property test			A	A	A
Dispense property test			A	A	A
Measurement of specific resistance value			4.5E+11	3.5E+12	2.8E+12
Water absorption rate			2.5	1.3	1.2

* : Measurement was impossible since peeling off occurred after test

#1 : Manufactured by Nippon Kayaku Co., Ltd. (Phenol novolac having softening point of 50°C)

#2 : Manufactured by Nippon Kayaku Co., Ltd. (Phenol novolac having softening point of 80°C)

#3 : Manufactured by Ganz Chemical Co., Ltd.

#4 : Manufactured by Rohm and Haas Company

#5 : Manufactured by Nippon Kayaku Co., Ltd. (Bisphenol A type epoxy resin)

#6 : Manufactured by Inoue Perfumery MFG. Co., Ltd.

#7 : Manufactured by Rhodia Nicca Ltd. (Arcosolv RPDE)

#8 : Manufactured by Kuraray Co., Ltd.

#9 : Manufactured by Wako Pure Chemical Industries, Ltd.

#10 : Manufactured by Wako Pure Chemical Industries, Ltd.

#11 : Manufactured by Ajinomoto Fine-Techno Co., Inc.
(epoxy resin-amine adduct)

#12 : Manufactured by Shikoku Chemicals Corporation (2,4-diamino-6-[2'-methylimidazolyl-(1')]-ethyl-s-triazineisocyanuric acid adduct)

#13 : Manufactured by Chisso Corporation (3-glycidoxypropyltrimethoxysilane)

#14 : Manufactured by Shin-Etsu Chemical Co., Ltd.
(silica)

#15 : Manufactured by C. I. Kasei Co., Ltd. (alumina)

From the results in Table 1, the liquid crystal sealant of the present invention was excellent in printing property, dispense property and contact performance against an opposing substrate, and was also excellent in workability during the manufacture of a liquid crystal panel. Furthermore, the seal shape was not disturbed even after the lamination and pressing, and excellent values were shown in the adhesiveness, moisture-resistant adhesiveness and liquid crystal contamination. On the other hand, with respect to Comparative Examples, some

were excellent in printing property and dispense property but had poor contact performance against an opposing substrate, some had good workability but poor adhesiveness, or some caused seepage after the pressing.

Therefore, it can be considered that the liquid crystal sealant of the present invention causes no problem in workability throughout the steps, and thus is a sealant that is very excellent in terms of reliability.

INDUSTRIAL APPLICABILITY

The liquid crystal sealant of the present invention is excellent in terms of coating workability, contact performance against an opposing substrate, and viscosity stability after preliminary heating, and is extremely excellent in terms of adhesiveness and flexibility after curing. Therefore, the liquid crystal sealant enables easy production of a liquid crystal display cell having high reliability.

CLAIMS

1. A liquid crystal sealant comprising (a) a solid phenol novolac resin having a softening point of 75°C or less, (b) an acrylic polymer having a core-shell structure, (c) an epoxy resin, and (d) an organic solvent, and having a gel time at 150°C of 50 seconds or more and 200 seconds or less.
2. The liquid crystal sealant according to claim 1, wherein the core layer of the component (b) is a polymer of n-butyl acrylate, and the shell layer is a polymer of methyl methacrylate.
3. The liquid crystal sealant according to claim 1 or 2, wherein the component (d) is one or more organic solvent(s) selected from the group consisting of propylene glycol diacetate, dimethyl esters of dibasic acids, propylene glycol monoethyl ether acetate and ethylene glycol dibutyl ether.
4. The liquid crystal sealant according to any one of claims 1 to 3, wherein the component (a) is a compound represented by the following formula (1):



5. The liquid crystal sealant according to any one of claims 1 to 4, wherein the equivalent amount of the hydroxy group of the component (a) with respect to 1 equivalent amount of the epoxy group of the component (c) is 0.2 to 1.4 chemical equivalent amount.

7. The liquid crystal sealant according to any one of claims 1 to 6, further comprising (e) a cure accelerator.

8. The liquid crystal sealant according to claim 7, wherein

the component (e) is at least one selected from 2,4-diamino-6-[2'-methylimidazolyl-(1')]-ethyl-s-triazine isocyanuric acid adduct and epoxy resin amine adducts.

9. The liquid crystal sealant according to any one of claims 1 to 8, further comprising (f) a coupling agent.

10. The liquid crystal sealant according to claim 9, wherein the component (f) is an epoxysilane coupling agent.

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

12. A liquid crystal display cell, which has been sealed by a cured product obtained by curing the liquid crystal sealant according to any one of claims 1 to 11.