

METHOD FOR MANUFACTURING LIQUID-CRYSTAL DISPLAY CELLS AND
LIQUID-CRYSTAL DISPLAY CELLS OBTAINED VIA SAID METHOD

TECHNICAL FIELD

[0001]

The present invention relates to a method of manufacturing liquid crystal display cells and liquid crystal display cells manufactured by the method. More specifically, the present invention relates to a method of stably manufacturing liquid crystal display cells without the insertion of liquid crystal into a liquid crystal sealant during the manufacturing process and liquid crystal display cells manufactured by the method.

BACKGROUND ART

[0002]

In order to cope with the upsizing of liquid crystal display cells in recent years, as a method of manufacturing a liquid crystal display cell, a so-called one drop fill process having higher productivity is proposed (Patent Documents 1 and 2). Specifically, the one drop fill process is a manufacturing method in which liquid crystal is added dropwise to an inner side of a weir made of a liquid crystal sealant formed on one substrate, then the other substrate is bonded thereto and thereafter the liquid crystal sealant is cured.

[0003]

However, in the one drop fill process, since the liquid

crystal and the liquid crystal sealant are brought into contact with each other before the curing of the liquid crystal sealant, an insertion phenomenon occurs in the liquid crystal sealant due to a pressure caused by the liquid crystal, and in the worst case, the weir formed of the liquid crystal sealant is broken, with the result that the liquid crystal may disadvantageously leak. This problem occurs even in the one drop fill process using both light and heat, in a case where there is a part to which sufficient ultraviolet rays are not applied due to shadowing by cables and the like. This problem is particularly serious in a case where only heat is used to cure the liquid crystal sealant without the application of ultraviolet rays. Although it is necessary to increase the accuracy of the amount of liquid crystal added dropwise in order to solve this problem, since the liquid crystal is swollen at the time of heating, which is the step of curing the liquid crystal sealant, it is difficult to completely prevent the insertion phenomenon described above.

[0004]

In order to solve this problem, various technologies relating to liquid crystal sealants are proposed.

Patent Document 3 attempts to solve the problem with organic bentonite. This method has given effects on the insertion of liquid crystal but they are not sufficient.

Patent Document 4 discloses a method of using a liquid crystal sealant formed with fumed silica and polythiol to perform B-stage processing on the liquid crystal sealant.

However, this method is disadvantageous in that the step is prolonged and thus it is necessary to use a device for the step.

Patent Document 5 discloses a liquid crystal sealant for one drop fill process that uses a heat radical polymerization initiator to increase a curing rate and thus prevent the insertion.

[0005]

As described above, solution of the above problem has been sought only with improvement of the liquid crystal sealant, and it is difficult to practically achieve it. Hence, improvements in two aspects: the design of the liquid crystal display cell; and the design of the liquid crystal sealant in accordance thereto are needed. However, a method for solving the above mentioned problem has not been proposed yet, and a method of manufacturing a liquid crystal display cell in which the insertion of liquid crystal into a liquid crystal sealant is sufficiently reduced is not established.

[0006]

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 Unexamined Patent Application, Publication No. 2010-14771

Patent Document 4: Japanese Unexamined Patent Application, Publication No. 2011-150181

Patent Document 5: PCT International Publication No.
WO2011/061910

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0007]

The present invention relates to liquid crystal display cells and a method of manufacturing the same. More specifically, the present invention proposes a method of stably manufacturing liquid crystal display cells without the insertion of liquid crystal into liquid crystal sealant during the manufacturing process and a liquid crystal display cell manufactured by the method.

Means for Solving the Problems

[0008]

As a result of thorough studies, the present inventors have found that when a given relationship between the cell gap of a liquid crystal display cell configured of two substrates and the average grain diameter of an organic filler contained in a liquid crystal sealant is achieved, it is possible to realize a method of manufacturing a liquid crystal display cell without the insertion of liquid crystal into the liquid crystal sealant, and thereby completed the present invention.

In the present specification, "(meth)acrylic" means "acrylic and/or methacrylic", and a (meth)acryloyl group means an "acryloyl group and/or a methacryloyl group".

Although in the present specification, the average

particle diameter may be referred to as the average grain diameter, they both have the same meaning.

[0009]

Specifically, the present invention relates to 1) to 6) below.

1)

A method of manufacturing a liquid crystal display cell in which, in a liquid crystal display cell configured of two substrates, a liquid crystal is added dropwise to an inner side of a weir made of a liquid crystal sealant formed on one substrate, thereafter the other substrate is bonded thereto and then the liquid crystal sealant is cured only with heat,

where the liquid crystal sealant contains an (a) organic filler which, provided that an average particle diameter of the (a) organic filler is A (μm) and a cell gap of the liquid crystal display cell is B (μm), satisfies formula (1) below:

$1.0 \mu\text{m} \leq A - B \leq 6.0 \mu\text{m}$ (1) and an average amount of compression of the (a) organic filler by the two substrates after being bonded in-between is A-B (μm).

2)

The method of manufacturing a liquid crystal display cell according to the above item 1), where a step of curing the liquid crystal sealant is performed only with heat.

3)

The method of manufacturing a liquid crystal display cell according to the above item 1) or 2), where the liquid crystal sealant further contains a (b) heat radical polymerization initiator and a (c) curable compound having a (meth)acryloyl

group.

4)

The method of manufacturing a liquid crystal display cell according to any one of the above items 1) to 3), where the (a) organic filler is rubber fine particles.

5)

The method of manufacturing a liquid crystal display cell according to the above item 4), where the rubber fine particles are formed of acrylic rubber, styrene rubber, styrene-olefin rubber or silicone rubber.

6)

A liquid crystal display cell that is manufactured by the method of manufacturing a liquid crystal display cell according to any one of the above items 1) to 5).

Effects of the Invention

[0010]

In the method of manufacturing the liquid crystal display cell according to the present invention, since liquid crystal is not inserted into the liquid crystal sealant during the manufacturing process, it is possible to extremely stably manufacture the liquid crystal display cell. Since it is possible to reduce the production takt time, it is possible to further realize the enhancement of productivity.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0011]

A method of manufacturing a liquid crystal display cell

according to the present invention relates to a manufacturing method in which, in a liquid crystal display cell configured of two substrates, liquid crystal is added dropwise to the inner side of a weir made of a liquid crystal sealant formed on one substrate, thereafter the other substrate is bonded and then the liquid crystal sealant is cured with ultraviolet rays and/or heat. In other words, it relates to the one drop fill process.

As also described in Background Art section, in the one drop fill process, since the liquid crystal and the liquid crystal sealant are brought into contact with each other before the curing of the liquid crystal sealant, an insertion phenomenon occurs in the liquid crystal sealant due to a pressure caused by the liquid crystal, and the weir formed of the liquid crystal sealant is broken, with the result that the liquid crystal may disadvantageously leak.

[0012]

In the one drop fill process, when a given relationship between the average particle diameter A (μm) of an organic filler contained in the liquid crystal sealant and the cell gap B (μm) of the liquid crystal display cell is maintained, the insertion of the liquid crystal into the liquid crystal sealant is greatly reduced. This is considered to be because the organic filler compressed by a pressure between the upper and lower substrates acts as the weir, and resists the pressure of the expansion of the liquid crystal.

The given relationship is a relationship that is

represented by formula (1) described above. When the value of $A - B$ is less than $1.0\text{ }\mu\text{m}$, the compression of the organic filler is insufficient, whereas when it is greater than $9.0\text{ }\mu\text{m}$, the cell gap of the liquid crystal display cell may be prevented from being broken so as to be the intended gap. The value of $A - B$ is further preferably at least $2.0\text{ }\mu\text{m}$ and no greater than $8.0\text{ }\mu\text{m}$, and is particularly preferably at least $2.0\text{ }\mu\text{m}$ and no greater than $6.0\text{ }\mu\text{m}$.

Here, the average grain diameter of the organic filler can be measured with a laser diffraction/scattering particle size distribution measuring device (dry) (Seishin Enterprise Co., Ltd.; LMS-30) and the like.

[0013]

The liquid crystal sealant used in the method of manufacturing the liquid crystal display cell according to the present invention contains (a) the organic filler (hereinafter also referred to as component (a)). The (a) organic filler is not particularly limited as long as it satisfies the above-mentioned conditions of the average grain diameter. Examples thereof include: polyamide fine particles such as nylon 6, nylon 12 and nylon 66; fluorine-based fine particles such as tetrafluoroethylene and vinylidene fluoride; olefin-based fine particles such as polyethylene and polypropylene; polyester-based fine particles such as polyethylene terephthalate and polyethylene naphthalate; and rubber fine particles such as natural rubber, isoprene rubber and acrylic rubber.

[0014]

The (a) organic filler is preferably rubber fine particles. Examples of the rubber fine particles include natural rubber (NR), isoprene rubber (IR), butadiene rubber (BR), styrene-butadiene rubber (SBR), butyl rubber (IIR), nitrile rubber (NBR), ethylene propylene rubber (EPM, EP), chloroprene rubber (CR), acrylic rubber (ACM, ANM), chlorosulfonated polyethylene rubber (CSM), urethane rubber (PUR), silicone rubber (Si, SR), fluoro rubber (FKM, FPM) and polysulfide rubber (thiokol); a single type of rubber fine particles may be used or two or more types may be used to form a core shell structure. In addition, two or more types of rubber fine particles may be used together. Among them, acrylic rubber, styrene rubber, styrene-olefin rubber and silicone rubber are preferable, and acrylic rubber and silicone rubber are particularly preferable.

When acrylic rubber is used, acrylic rubber having a core shell structure formed with two types of acrylic rubbers is preferable, and acrylic rubber whose core layer is n-butyl acrylate and whose shell layer is methyl methacrylate is particularly preferable. This is sold as ZEFLAC^{RTM} F-351 by AICA Kogyo Co., Ltd.

Examples of the silicone rubber include organopolysiloxane cross-linked product powder and linear dimethyl polysiloxane cross-linked product powder. Examples of the composite silicone rubber include composite silicone rubber in which the surface of the silicone rubber described above is coated with silicone resin (for example,

polyorganosilsesquioxane resin). Among these rubber fine particles, the silicone rubber of the linear dimethyl polysiloxane cross-linked powder and the composite silicone rubber fine particles of the silicon resin-coated linear dimethyl polysiloxane cross-linked powder are particularly preferable. These may be used singly or two or more types may be used together. The shape of the rubber powder is preferably spherical because its viscosity after addition is increased by a small amount.

Specific examples of the organic filler (a) described above can include: silicone rubber such as KMP594, KMP597 and KMP598 (made by Shin-Etsu Chemical Co., Ltd.) and EP2001 (made by Dow Corning Toray Co., Ltd.); urethane rubber such as JB-800T and HB-800BK (made by Negami Kogyo Co., Ltd.); acrylic rubber such as AFX-8 (made by Sekisui Plastics Co., Ltd.), F351S (made by Aica Kogyo Co., Ltd.) and W-341 and the meta Bren series (made by Mitsubishi Rayon Co., Ltd.); styrene rubber such as the RABALON series (made by Mitsubishi Chemical Corporation); and styrene-olefin rubber such as the TR series (made by JSR Co., Ltd.) and Septon series (made by Kuraray Co., Ltd.). However, the present invention is not limited thereto.

The content of the (a) organic filler in the liquid crystal sealant used in the present invention is, with the assumption that the total amount of liquid crystal sealant is 100 mass parts, 5 to 50 mass parts, and is preferably 5 to 40 mass parts.

[0015]

In order for the configuration of the present invention to be realized, a classification operation is performed on the organic filler, and thus it is possible to obtain an organic filler having the desired average particle diameter. This operation is useful for removing coarse particles, and thus it is possible to prepare an organic filler having a sharp particle size distribution. Since coarse particles easily cause a cell gap failure on liquid crystal, this classification operation is preferably performed.

For example, crushing is performed with a jet mill JM-0202 (made by Seishin Enterprise Co., Ltd.), and thereafter the classification operation can be performed with an air classifier machine CLASSIEL N05 (made by Seishin Enterprise Co., Ltd.). In order for this operation to be performed more efficiently, a dispersant or the like may be used.

[0016]

Since the method of manufacturing the liquid crystal display cell according to the present invention causes very little insertion of liquid crystal into the liquid crystal sealant, it can also be applied to the one drop fill process only by heat. In terms of the production takt time and the like, the one drop fill process only by heat is more preferable.

[0017]

As long as the liquid crystal sealant used in the method of manufacturing the liquid crystal display cell according to the present invention contains the (a) organic filler

satisfying the conditions described above, the other constituent components are not particularly limited; however (b) a heat radical polymerization initiator and (c) a curable compound having a (meth)acryloyl group are particularly preferably contained.

[0018]

There is no limitation on the (b) heat radical polymerization initiator as long as it is a compound that produces a radical by heating to start a chain polymerization reaction. Examples thereof include an organic peroxide, an azo compound, a benzoin compound, a benzoin ether compound, an acetophenone compound and benzopinacol, and benzopinacol is preferably used. Examples of the organic peroxide include: Kayamec^{RTM} A, M, R, L, LH, SP-30C, Perkadox CH-50L, BC-FF, Kadox B-40ES, Perkadox 14, Trigono^{RTM} 22-70E, 23-C70, 121, 121-50E, 121-LS50E, 21-LS50E, 42, 42LS, Kayaester^{RTM} P-70, TMPO-70, CND-C70, OO-50E, AN, Kayabutyl^{RTM} B, Perkadox 16, Kayacarbon^{RTM} BIC-75 and AIC-75 (made by Kayaku Akzo Corporation); and Permec^{RTM} N, H, S, F, D, G, Perhexa^{RTM} H, HC, Pa TMH, C, V, 22, MC, Percure^{RTM} AH, AL, HB, Perbutyl^{RTM} H, C, ND, L, Percumyl^{RTM} H, D, Peroyl^{RTM} IB, IPP and Perocta^{RTM} ND (made by NOF Corporation), and these are all commercially available. Examples of commercially available azo compound include VA-044, V-070, VPE-0201 and VSP-1001 (made by Wako Pure Chemical Industries, Ltd.)

In the present specification, the superscript "RTM" means a registered trademark. As the (b) heat radical polymerization

initiator, a heat radical polymerization initiator that does not contain, within a molecule, an oxygen-oxygen bond (-O-O-) or a nitrogen-nitrogen bond (-N=N-) is preferable. Since a heat radical polymerization initiator that has, within a molecule, an oxygen-oxygen bond (-O-O-) or a nitrogen-nitrogen bond (-N=N-) emits a large amount of oxygen or nitrogen when a radical is generated, there is a possibility that it is cured with bubbles left in the liquid crystal sealant to deteriorate properties such as the adhesive strength. A benzopinacol-based heat radical polymerization initiator (including those obtained by chemically modifying benzopinacol) is particularly preferable. Specific examples include benzopinacol; 1,2-dimethoxy-1,1,2,2-tetraphenyl ethane; 1,2-diethoxy-1,1,2,2-tetraphenyl ethane; 1,2-diphenoxy-1,1,2,2-tetraphenyl ethane; 1,2-dimethoxy-1,1,2,2-tetra(4-methylphenyl) ethane; 1,2-diphenoxy-1,1,2,2-tetra(4-methoxyphenyl) ethane; 1,2-bis(trimethylsiloxy)-1,1,2,2-tetraphenyl ethane; 1,2-bis(triethylsiloxy)-1,1,2,2-tetraphenyl ethane; 1,2-bis(t-butyltrimethylsiloxy)-1,1,2,2-tetraphenyl ethane; 1-hydroxy-2-trimethylsiloxy-1,1,2,2-tetraphenyl ethane; 1-hydroxy-2-triethylsiloxy-1,1,2,2-tetraphenyl ethane; and 1-hydroxy-2-t-butyltrimethylsiloxy-1,1,2,2-tetraphenylethane. 1-hydroxy-2-trimethylsiloxy-1,1,2,2-tetraphenyl ethane; 1-hydroxy-2-triethylsiloxy-1,1,2,2-tetraphenyl ethane; 1-hydroxy-2-t-butyltrimethylsiloxy-1,1,2,2-tetra-phenyl ethane; and 1,2-bis(trimethylsiloxy)-1,1,2,2-tetraphenyl ethane are preferable. 1-hydroxy-2-trimethylsiloxy-1,1,2,2-tetraphenyl ethane and

1,2-bis (trimethylsiloxy)-1,1,2,2-tetraphenyl ethane are further preferable. 1,2-bis(trimethylsiloxy)-1,1,2,2-tetraphenylethane is particularly preferable.

The benzopinacol described above is commercially available from Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd. and the like. It is possible to easily perform such synthesis by a known method in which the hydroxy group of benzopinacol is etherified. In addition, it is possible to perform such synthesis by a method of heating, under a basic catalyst such as pyridine, the corresponding benzopinacol and various types of silylating agents such that the hydroxy group of benzopinacol is silyl etherified. Examples of the silylating agent include: generally known trimethylsilylating agents such as trimethylchlorosilane (TMCS), hexamethyldisilazane (HMDS) and N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA); triethylsilylating agents such as triethylchlorosilane (TECS); and t-butyl dimethylsilylating agents such as t-butyl methyl silane (TBMS). These reagents are easily available from the market of silicon derivative manufacturers and the like. The silylating agent reaction amount is preferably 1.0 to 5.0 times moles with respect to one mole of a hydroxyl group of a target compound. The silylating agent reaction amount is more preferably 1.5 to 3.0 times moles. When the silylating agent reaction amount is less than 1.0 times moles, the reaction efficiency is poor, the reaction time is prolonged and thus thermal decomposition is facilitated. When the silylating

agent reaction amount is more than 5.0 times moles, separation at the time of collection may be degraded or purification may be difficult to perform.

[0019]

Preferably, in the (b) heat radical polymerization initiator, the diameter of the grains is reduced and they are uniformly dispersed. Since an excessively large average grain diameter may cause a failure such as unsatisfactory gap formation upon bonding of the upper and lower glass substrates at the time of manufacturing the liquid crystal display cell having a narrow gap, the average grain diameter is preferably no greater than 5 μm , and is more preferably no greater than 3 μm . Although there is no limitation on the refinement of the average grain diameter, a lower limit is normally about 0.1 μm . The grain diameter can be measured with the laser diffraction/scattering particle size distribution measuring device (dry) (Seishin Enterprise Co., Ltd.; LMS-30).

[0020]

The content of the (b) heat radical polymerization initiator in the liquid crystal sealant used in the present invention is preferably, with the assumption that the total amount of liquid crystal sealant is 100 mass parts, 0.0001 to 10 mass parts, is more preferably 0.0005 to 5 mass parts, and is particularly preferably 0.001 to 3 mass parts.

[0021]

Examples of the (c) curable compound having a (meth)acryloyl group can include (meth) acrylic ester and

epoxy (meth) acrylate, for example. Examples of the (meth) acrylic ester can include benzyl methacrylate, cyclohexyl methacrylate, glycerol dimethacrylate, glycerol triacrylate, EO-modified glycerol triacrylate, pentaerythritol acrylate, trimethylolpropane triacrylate, tris (acryloxyethyl) isocyanurate, dipentaerythritol hexaacrylate and phloroglucinol triacrylate. The epoxy (meth) acrylate can be obtained by a known method through a reaction between an epoxy resin and a (meth) acrylic acid. The epoxy resin serving as a raw material is not particularly limited, and an epoxy resin having two or more functional groups is preferable. Examples thereof can include bisphenol A type epoxy resin, bisphenol F type epoxy resin, bisphenol S type epoxy resin, phenol novolak type epoxy resin, cresol novolak type epoxy resin, bisphenol A novolac type epoxy resin, bisphenol F novolak type epoxy resin, alicyclic epoxy resin, aliphatic chain epoxy resin, glycidyl ester type epoxy resin, glycidyl amine type epoxy resin, hydantoin type epoxy resin, isocyanurate type epoxy resin and phenol novolak type epoxy resin having a triphenol methane skeleton; diglycidyl ether compounds of bifunctional phenols such as catechol and resorcinol; diglycidyl ether products of bifunctional alcohols; and halides and hydrogen additives thereof. Among them, in terms of contamination of liquid crystal, epoxy resin having a resorcinol skeleton is preferable, and examples thereof include resorcinol diglycidyl ether. The ratio between the epoxy group and the (meth) acryloyl group is not limited, and is appropriately selected

in terms of process compatibility and contamination of liquid crystal. Hence, the preferable curable compound having a (meth)acryloyl group is a curable compound that has a (meth)acryloyl group and further has a resorcinol skeleton.

Examples thereof include acrylic acid ester of resorcinol diglycidyl ether and methacrylic acid ester of resorcinol diglycidyl ether.

The content of the (c) curable compound having a (meth)acryloyl group in the liquid crystal sealant used in the present invention is preferably, with the assumption that the total amount of liquid crystal sealant is 100 mass parts, in the range of 30 to 90 mass parts, and is more preferably 40 to 80 mass parts.

[0022]

The above (c) curable compound having a (meth)acryloyl group preferably contains a compound having three or more (meth)acryloyl groups in one molecule. In the compound having three or more (meth)acryloyl groups in one molecule, the cross-linking rate (reaction rate) is fast, and thus it is possible to realize excellent resistance to the insertion. When this method is used, unlike a method of increasing the amount of heat radical polymerization initiator or the like to enhance the reactivity, the handling property is also excellent.

Examples of the compound having three or more (meth)acryloyl groups in one molecule can include: KAYARAD^{RTM}PET-30, DPHA, DPCA-20, DPCA-30, DPCA-60, DPCA-120,

DPEA-12, GPO-303, TMPTA, THE-330, TPA-320, TPA-330, D-310, D-330, RP-1040, UX-5000 and DPHA-40H (made by Nippon Kayaku Co., Ltd.); NK ester^{RTM} A-9300, A-9300-1CL, A-GLY-9E, A-GLY-20E, A-TMM-3, A-TMM-3LM-N, A-TMPT, AD-TMP, ATM-35E, A-TMMT, A-9550 and A-DPH (made by Shin-Nakamura Chemical Co., Ltd.); and SR295, SR350, SR355, SR399, SR494, CD501, SR502, CD9021, SR9035 and SR9041 (made by Sartomer Company Inc.). Among them, the mole average molecular weight is preferably 800 or more, and for example, KAYARAD^{RTM} DPCA-20, DPCA-30 and DPEA-12 are preferable. A curable compound containing a C1-C4 alkylene oxide (-O-R-O-) in its molecule is preferable, and KAYARAD^{RTM} DPEA-12 is particularly preferable.

[0023]

In addition to the component (a) described above and the components (b) and (c) contained when necessary, the liquid crystal sealant used in the method of manufacturing the liquid crystal display cell according to the present invention may contain a curable resin having an epoxy group, a thermal curing agent, a silane coupling agent, an inorganic filler, a curing accelerator, a pigment, a leveling agent, a defoamer and a solvent.

[0024]

By using the curable resin having an epoxy group described above, it is possible to enhance the adhesive strength. The curable resin having an epoxy group is not particularly limited, and an epoxy resin having two or more functional groups is preferable. Examples thereof can include

bisphenol A type epoxy resin, bisphenol F type epoxy resin, bisphenol S type epoxy resin, phenol novolak type epoxy resin, cresol novolak type epoxy resin, bisphenol A novolac type epoxy resin, bisphenol F novolak type epoxy resin, alicyclic epoxy resin, aliphatic chain epoxy resin, glycidyl ester type epoxy resin, glycidyl amine type epoxy resin, hydantoin type epoxy resin, isocyanurate type epoxy resin and phenol novolak type epoxy resin having a triphenol methane skeleton; diglycidyl ether compounds of bifunctional phenols; diglycidyl ether compounds of bifunctional alcohols; and halides and hydrogen additives thereof. Among them, in terms of contamination of liquid crystal, bisphenol type epoxy resin and novolak type epoxy resin are preferable. The content of the curable resin having an epoxy group in the liquid crystal sealant used in the present invention is, with the assumption that the total amount of liquid crystal sealant is 100 mass parts, about 1 to 30 mass parts.

[0025]

The above thermal curing agent is not particularly limited; examples thereof can include polyvalent amines, polyhydric phenols, a hydrazide compound, and the like, and solid organic acid hydrazide is particularly preferably used. Examples thereof can include salicylic acid hydrazide that is aromatic hydrazide, benzoic hydrazide, hydrazide 1-naphthoic acid, 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 and pyromellitic acid tetrahydrazide. If the compound is an aliphatic hydrazide compound, examples thereof include holm hydrazide, acetohydrazide, propionic acid hydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, dihydrazide succinate, glutaric acid dihydrazide, adipic acid dihydrazide, pimelic acid dihydrazide, sebacic acid dihydrazide, 1,4-cyclohexane dihydrazide, tartaric dihydrazide, malic acid dihydrazide, iminodiacetic acid dihydrazide, N,N'-hexamethylenebis semicarbazide, citric acid trihydrazide, nitriloacetic acid trihydrazide, cyclohexanetricarboxylic acid trihydrazide, dihydrazide compounds having a hydantoin skeleton such as 1,3-bis(hydrazinocarboethyl)-5-isopropyl hydantoin and preferably a valine hydantoin skeleton (skeleton obtained by replacing the carbon atom of a hydantoin ring with an isopropyl group), tris(1-hydrazinocarbonyl-methyl) isocyanurate, tris(2-hydrazinocarbonyl-ethyl) isocyanurate, tris(3-hydrazinocarbonyl-propyl) isocyanurate and bis(2-hydrazinocarbonyl-ethyl) isocyanurate. The thermal curing agents may be used singly or two or more types may be mixed. In terms of a balance between curing reactivity and potential, isophthalic acid dihydrazide, malonic acid dihydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, tris(1-hydrazinocarbonyl-methyl) isocyanurate, tris(2-hydrazinocarbonyl-ethyl) isocyanurate, tris(2-hydrazinocarbonyl-ethyl) isocyanurate and tris(3-hydrazinocarbonyl propyl) isocyanurate are preferable, and malonic acid dihydrazide and sebacic acid dihydrazide are

particularly preferable. The content of the thermal curing agent used is, with the assumption that the total amount of liquid crystal sealant is 100 mass parts, about 1 to 30 mass parts.

[0026]

Using the silane coupling agent described above makes it possible to enhance the adhesive strength and the moisture resistance reliability. Examples of the silane coupling agent include 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyl methyl dimethoxy silane, 3-glycidoxypropyl methyl diethoxy silane, 2-(3,4-epoxycyclohexyl) ethyl trimethoxy silane, N-phenyl- γ -aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyl methyl dimethoxy silane, N-(2-aminoethyl)-3-aminopropyl methyl trimethoxy silane, 3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, vinyltrimethoxysilane, N-(2-(vinylbenzyl-amino) ethyl) 3-aminopropyltrimethoxysilane hydrochloride, 3-methacryloxypropyl trimethoxy silane, 3-chloropropyl methyl dimethoxy silane and 3-chloro-propyl trimethoxysilane. Since these silane coupling agents are sold as a KBM series, KBE series and the like by Shin-Etsu Chemical Co., Ltd. and the like, they are easily available on the market. The content of the silane coupling agent in the liquid crystal sealant is, with the assumption that the total amount of liquid crystal sealant used in the present invention is 100 mass parts, about 0.05 to 3 mass parts.

[0027]

Using the inorganic filler described above makes it possible to enhance the adhesive strength and the moisture resistance reliability. Examples of the inorganic filler include fused 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 silicate aluminum, zirconium silicate, barium titanate, glass fiber, carbon fiber, molybdenum disulfide and asbestos. Fused silica, crystalline silica, silicon nitride, boron nitride, calcium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, aluminum hydroxide, calcium silicate and aluminum silicate are preferable, and fused silica, crystalline silica, alumina and talc are more preferable. Two or more types of the inorganic fillers described above may be mixed and used. Since an excessively large average grain diameter may cause a failure such as unsatisfactory gap formation upon bonding of the upper and lower glass substrates at the time of manufacturing the liquid crystal display cell having a narrow gap, the adequate average grain diameter is no greater than 3 μm , and is preferably no greater than 2 μm . The grain diameter can be measured with the laser diffraction/scattering particle size distribution measuring device (dry) (Seishin Enterprise Co., Ltd.; LMS-30). The content of the inorganic filler in the liquid crystal sealant is normally, with the assumption that the total amount

of liquid crystal sealant used in the present invention is 100 mass parts, 1 to 60 mass parts, and is preferably 1 to 40 mass parts. When the content of the inorganic filler is excessively low, the adhesive strength to the glass substrate is decreased, and the moisture resistance reliability is degraded, with the result that a significant decrease in the adhesive strength after the moisture absorption may be produced. On the other hand, when the content of the inorganic filler is excessively high, it is unlikely to be broken, with the result that there is a possibility that it is impossible to perform the gap formation on the liquid crystal cell.

[0028]

Examples of the curing accelerator can include an organic acid and an imidazole.

Examples of the organic acid include an organic carboxylic acid and an organic phosphoric acid, and an organic carboxylic acid is preferable. Specific examples thereof can include aromatic carboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, benzophenonetetracarboxylic acid and furandicarboxylic acid; succinic acid; adipic acid; dodecanedioic acid, sebacic acid; thiodipropionic acid; cyclohexanedicarboxylic acid; tris(2-carboxymethyl) isocyanurate; tris(2-carboxyethyl) isocyanurate; tris(2-carboxypropyl) isocyanurate; and bis(2-carboxyethyl) isocyanurate.

Examples of the imidazole compound can include 2-methylimidazole, 2-phenyl imidazole, 2-undecyl imidazole, 2-

heptadecyl imidazole, 2-phenyl-4-methylimidazole, 1-benzyl-2-phenyl imidazole, 1-benzyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-phenyl imidazole, 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-methyl imidazole isocyanuric acid, 2-phenyl imidazole isocyanuric acid adduct, 2-phenyl-3,5-dihydroxy methyl imidazole, 2-phenyl-4-hydroxy-methyl-5-methyl imidazole and 1-cyanoethyl-2-phenyl-3,5-dicyano ethoxymethyl imidazole.

The content of the curing accelerator in the liquid crystal sealant is normally, with the assumption that the total amount of liquid crystal sealant is 100 mass parts, 0.1 to 10 mass parts, and is preferably 0.5 to 5 mass parts.

[0029]

In the liquid crystal display cell of the present invention, a pair of substrates on which predetermined electrodes are formed are arranged at a predetermined distance opposite each other, and the surrounding area thereof is sealed with the liquid crystal sealant and the liquid crystal is inserted into the gap. The type of liquid crystal inserted is not particularly limited. Here, the substrate is configured of a combined substrate which is formed of glass, quartz, plastic, silicon or the like and at least one side of the

substrate has optical transparency. The production method thereof is as follows. A spacer (gap control material) such as glass fiber and the like is added to the liquid crystal sealant, thereafter one of the pair of the substrates is coated with the liquid crystal sealant using a dispenser, a screen printing device or the like and then, as necessary, temporary curing is performed at 80 to 120°C. Thereafter, the liquid crystal is added dropwise to the inner side of a weir formed of the liquid crystal sealant, the other glass substrate is stacked in a vacuum and gap formation is performed. Although depending on the situation, the liquid crystal may be dropped to the substrate that is not coated with the liquid crystal sealant, the effects of the present invention are not affected in either case. Preferably, in order to realize an appropriate cell gap, one substrate is previously coated with a planar spacer (for example, a Natoco spacer). After the gap formation, as necessary, ultraviolet rays of 1000 to 6000 mJ/cm² are applied, and thereafter curing is performed at 90 to 130°C for 1 to 2 hours, with the result that it is possible to obtain the liquid crystal display cell of the present invention.

[0030]

The liquid crystal sealant used in the method of manufacturing the liquid crystal display cell according to the present invention can be obtained by, for example, the following method. First, as necessary, the curable resin having an epoxy group is dissolved and mixed in the (c)

component. Then, as necessary, the silane coupling agent is dissolved in this mixture. Then, the (a) component, the (b) component and, as necessary, a heat curing agent, an inorganic filler, an anti-foaming agent, a leveling agent, a solvent and the like are added, are uniformly mixed with a known mixing device such as a three-roll mill, a sand mill or a ball mill and are filtered with a metal mesh.

[0031]

In the method of manufacturing the liquid crystal display cell according to the present invention, since in the manufacturing process, liquid crystal is not inserted into the liquid crystal sealant, it is possible to extremely stably manufacture the liquid crystal display cell. Since it is possible to reduce the production takt time, it is possible to further realize the enhancement of productivity.

In the liquid crystal display cell of the present invention, properties necessary for the liquid crystal display cell in which the voltage retention rate is high and the ion density is low are sufficiently provided.

EXAMPLES

[0032]

Although the present invention will be described in further detail below using synthesis examples, manufacturing examples and examples, the present invention is not limited to the examples. Unless otherwise particularly specified, "part" and "%" in the text are based on mass.

[0033]

[Synthesis example 1]

[Synthesis of 1,2-bis (trimethylsiloxy)-1,1,2,2-tetraphenylethane]

100 parts (0.28 moles) of commercially available benzopinacol (made by Tokyo Kasei Kogyo Co., Ltd.) was dissolved in 350 parts of dimethyl formaldehyde. 32 parts (0.4 moles) of pyridine serving as a base catalyst and 150 parts (0.58 moles) of BSTFA (made by Shin-Etsu Chemical Co., Ltd.) serving as a silylating agent were added to this mixture, were increased to 70°C and were agitated for 2 hours. The obtained reaction solution was cooled, 200 parts of water was added while being agitated and the product was precipitated and the unreacted silylating agent was deactivated. The precipitated product was filtered and separated, and was then sufficiently washed with water. Then, the obtained product was dissolved in acetone, water was added to perform recrystallization and purification was performed. 105.6 parts (88.3% yield) of 1,2-bis(trimethylsiloxy)-1,1,2,2-tetraphenylethane, which was the target, was obtained.

As a result of analysis by HPLC (high performance liquid chromatography), the purity was 99.0% (area percentage).

[0034]

[Synthesis example 2]

[Synthesis of all-acrylic product of resorcinol diglycidyl ether]

181.2 g (EX-201: made by Nagase ChemteX Corporation) of

resorcinol diglycidyl ether was dissolved in 266.8 g of toluene, 0.8 g of dibutylhydroxytoluene was added as a polymerization inhibitor to this mixture and the temperature thereof was increased to 60°C. Thereafter, 117.5 g of acrylic acid having an equivalent weight of 100% to an epoxy group was added, the temperature was further increased to 80°C, 0.6 g of trimethyl ammonium chloride serving as a reaction catalyst was added thereto and agitation was performed at 98°C for about 30 hours, with the result that a reaction solution was obtained. The reaction solution was washed with water, and thus toluene was distilled, with the result that 293 g of epoxy acrylate of resorcinol diglycidyl ether, which was the target, was obtained. The reactive group equivalent weight of the obtained epoxy acrylate was 183 as a theoretical value.

[0035]

[Manufacturing examples 1 to 5 of liquid crystal sealant]

The amounts of components (a), (b) and (c) and the like shown in Table 1 below were used to manufacture liquid crystal sealants. The manufacturing method is described below.

A curable resin having an epoxy group was first heated, dissolved and mixed in the (c) component. After the mixture was cooled to a room temperature, a silane coupling agent, the (a) component, the (b) component, a heat curing agent, an inorganic filler and a curing accelerator were sequentially added, were uniformly mixed with a three-roll mill and were filtered with a metal mesh (635 meshes).

[0036]

[Table 1]

		Manufacturing example 1	Manufacturing example 2	Manufacturing example 3	Manufacturing example 4	Manufacturing example 5
Component(a)	Organic filler (a)-1	90 parts				
	Organic filler (a)-2		90 parts			
	Organic filler (a)-3			90 parts		
	Organic filler (a)-4				90 parts	
	Organic filler (a)-5					90 parts
Component(b)	Heat radical polymerization initiator	4 parts	4 parts	4 parts	4 parts	4 parts
Component(c)	Curable compound having a (meth) acryloyl group (c)-1	140 parts	140 parts	140 parts	140 parts	140 parts
	Curable compound having a (meth) acryloyl group (c)-2	30 parts	30 parts	30 parts	30 parts	30 parts
Other components	Curable resin having an epoxy group	30 parts	30 parts	30 parts	30 parts	30 parts
	Heat curing agent	12 parts	12 parts	12 parts	12 parts	12 parts
	Silane coupling agent-1	3 parts	3 parts	3 parts	3 parts	3 parts
	Silane coupling agent-2	3 parts	3 parts	3 parts	3 parts	3 parts
	Curing accelerator	3 parts	3 parts	3 parts	3 parts	3 parts
	Inorganic filler	18 parts	18 parts	18 parts	18 parts	18 parts

Component(a)-1 : Silicone rubber powder

(Made by Shin-Etsu Chemical Co., Ltd.: KMP-594; Average grain diameter of 5 μm)

Component(a)-2 : Silicone rubber powder

(Made by Shin-Etsu Chemical Co., Ltd.: KMP-598; Average grain diameter of 13 μm)

Component(a)-3 : Urethane rubber

(Negami Industrial Co., Ltd.: JB-800T; Average grain diameter of 6 μm)

Component(a)-4 : Urethane rubber

(Negami Industrial Co., Ltd.: HB-800BK; Average grain diameter of 8 μm)

Component(a)-5 : Acrylic rubber

(Sekisui Chemical Industry Co., Ltd.: AFX-8; Average grain diameter of 8 μm)

Component(b) : 1,2-bis(trimethylsiloxy)-1,1,2,2-tetraphenylethane

(Synthesis example 1 product obtained by being pulverized with a jet mill to have an average grain diameter of 1.9 μm)

Component(c)-1 : All-acrylic product of resorcinol diglycidyl ether (Synthesis example 2)

Component(c)-2 : Ethylene oxide-modified dipentaerythritol hexaacrylate

(Made by Nippon Kayaku Co., Ltd.: DPEA-12)

Curable resin having an epoxy group : Ethylene oxide addition bisphenol S-type epoxy resin

(Synthesized by a method described in Patent No. 4211942)

Heat curing agent : Product obtained by pulverizing tris(2-hydrazinocarbonyl ethyl) isocyanurate

(Made by Nippon Finechem Co., Ltd.: HCIC, pulverized with a jet mill to have an average grain diameter of 1.5 μm)

Silane coupling agent-1 : 3-glycidyloxypropyltrimethoxysilane

(Made by Chisso Corporation: Sila-Ace S-510)

Silane coupling agent-2 : N-2 (aminoethyl) 3-aminopropyltriethoxysilane

(Made by Shin-Etsu Chemical Co., Ltd.: KBM-603)

Curing accelerator : Tris(3-carboxyethyl) isocyanurate

(Made by Shikoku Chemicals Corporation: CIC acid, pulverized with a jet mill to have an average grain diameter of 1.5 μm)

Inorganic filler : Spherical silica

(Made by Shin-Etsu Chemical Co., Ltd.: X-24-9163A; Average grain diameter of 110 μm)

[0037]

[Evaluation for resistance to insertion of liquid crystal]

With the liquid crystal sealants manufactured in
manufacturing examples 1 to 5 of the liquid crystal sealant,

three types of liquid crystal display cells having cell gaps of 3 μm , 4 μm and 5 μm were produced, and the insertion property was observed. A test method is described below.

As a spacer, 1 g of a glass fiber (PF-30S, PF-40S or PF-50S made by Nippon Electric Glass Co., Ltd.) having a diameter of 3 μm , 4 μm or 5 μm was added to 100 g of each of the liquid crystal sealants, mixing, agitation and defoaming were performed and the mixture was put into a syringe. The liquid crystal sealant previously put into the syringe was applied to a glass substrate with an ITO transparent electrode using a dispenser (SHOTMASTER300 made by Musashi Engineering Co., Ltd.) in a seal pattern and a dummy seal pattern, and then the droplets of a liquid crystal (MLC-3007 made by Merck Co., Ltd.) were dropped into the frame of the seal pattern. A planar spacer (Natoco spacer KSEB-310F, KSEB-410NPF or KSEB-525F; made by Natoco Co., Ltd.; a gap width after the bonding was 3 μm , 4 μm and 5 μm) was sprayed and was thermally fixed to one further rubbing-processed glass substrate, and it was bonded with a bonding device in a vacuum to the substrate to which the liquid crystal was already dropped. After a gap was formed by being opened to the atmosphere, the resulting substrate was left for 10 minutes, was put into an oven of 120°C, was heated and cured for 1 hour, then an interface between the seal and the liquid crystal was observed with a polarizing microscope and evaluation was made according to the following criteria. The results are shown in Table 2.

O: Insertion of liquid crystal into sealant was not

observed

Δ: Slight insertion of liquid crystal into sealant was
observed

×: Insertion of liquid crystal into sealant was observed
[0038]

[Table 2]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 1	Comparative Example 2
Liquid crystal display cell Cell gap (B)	3 μ m	4 μ m	4 μ m	5 μ m	3 μ m	4 μ m	5 μ m	5 μ m	5 μ m	3 μ m	5 μ m
Liquid crystal *In parentheses average grain diameter (A) of (a) component	Manufacturing example 1 (5 μ m)	Manufacturing example 1 (5 μ m)	Manufacturing example 2 (13 μ m)	Manufacturing example 2 (13 μ m)	Manufacturing example 3 (6 μ m)	Manufacturing example 3 (6 μ m)	Manufacturing example 3 (6 μ m)	Manufacturing example 4 (8 μ m)	Manufacturing example 5 (8 μ m)	Manufacturing example 2 (13 μ m)	Manufacturing example 1 (5 μ m)
A—B	2 μ m	1 μ m	9 μ m	8 μ m	3 μ m	2 μ m	1 μ m	3 μ m	3 μ m	10 μ m	0 μ m
Insertion resistance evaluation	○	○	○	○	○	○	○	○	○	※	×

*Cell gap was uneven, and thus it was impossible to form liquid crystal display cell

[0039]

It is found from the results of table 2 that in examples 1 to 9, the liquid crystal display cells were manufactured without insertion of the liquid crystal, but in comparative examples 1 and 2, the liquid crystal display cells were not manufactured due to an insertion or gap failure. Hence, it is possible to confirm the advantage of the present invention.

INDUSTRIAL APPLICABILITY

[0040]

In the method of manufacturing the liquid crystal display cell according to the present invention, since in the manufacturing process, liquid crystal is not inserted into the liquid crystal sealant, it is possible to extremely stably manufacture the liquid crystal display cell. Since it is also possible to reduce the production takt time, it is possible to realize the further enhancement of productivity.

CLAIMS

1. A method of manufacturing a liquid crystal display cell in which, in a liquid crystal display cell configured of two substrates, a liquid crystal is added dropwise to an inner side of a weir made of a liquid crystal sealant formed on one substrate, thereafter the other substrate is bonded thereto and then the liquid crystal sealant is cured only with heat,

wherein the liquid crystal sealant contains an (a) organic filler which, provided that an average particle diameter of the (a) organic filler is A (μm) and a cell gap of the liquid crystal display cell is B (μm), satisfies formula (1) below:

$$1.0 \mu\text{m} \leq A - B \leq 6.0 \mu\text{m} \quad (1)$$

and an average amount of compression of the (a) organic filler by the two substrates after being bonded in-between is A-B (μm).

2. The method of manufacturing a liquid crystal display cell according to claim 1, wherein the liquid crystal sealant further contains a (b) heat radical polymerization initiator and a (c) curable compound having a (meth)acryloyl group.

3. The method of manufacturing a liquid crystal display cell according to claim 2, wherein the (c) curable compound having a (meth)acryloyl group is (meth) acrylic acid ester of resorcinol diglycidyl ether.

4. The method of manufacturing a liquid crystal display cell according to any one of claims 1 to 3, wherein the (a) organic filler is rubber fine particles.

5. The method of manufacturing a liquid crystal display cell according to claim 4, wherein the rubber fine particles are one or more rubber fine particle(s) selected from the group consisting of acrylic rubber, styrene rubber, styrene-olefin rubber, urethane rubber and silicone rubber.

6. The method of manufacturing a liquid crystal display cell according to claim 4, wherein the rubber fine particles are one or more rubber fine particle(s) selected from the group consisting of acrylic rubber and urethane rubber.

7. A liquid crystal display cell, wherein the liquid crystal display cell is manufactured by the method of manufacturing a liquid crystal display cell according to any one of claims 1 to 6.