

DESCRIPTION

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

Technical Field

The present invention relates to a liquid crystal sealing agent and a liquid crystal display cell using the same. More particularly, the present invention relates to a liquid crystal sealing agent suitable for manufacture of a liquid crystal display cell by the liquid crystal dropping process, and a liquid crystal display cell manufactured using the same.

Background Art

Along with recent upsizing of liquid crystal display cells, the so-called liquid crystal dropping process, which has a higher mass productivity as a manufacturing method of liquid crystal display cells, is prevalent. In the liquid crystal dropping process, a liquid crystal is dropped inside a weir of a liquid crystal sealing agent formed on one substrate, and then the other substrate is laminated thereon, thus manufacturing a liquid crystal display cell in which the liquid crystal is sealed. However, the liquid crystal dropping process, since an uncured liquid crystal sealing agent and a liquid crystal are brought into direct contact, essentially has a problem that components of the liquid crystal sealing agent are extracted in the liquid crystal and contaminate the display region of the liquid crystal, therefore, a less contaminating sealing agent is demanded in view of improving the reliability of liquid crystal display cells.

In the liquid crystal dropping process, as a curing method of the liquid crystal sealing agent, three methods of a thermosetting method, a photocuring method and a

combined photo- and thermosetting method are considered. The thermosetting method has problems that the shape of the seal is hardly held because the viscosity of the sealing agent becomes low on heating and that the liquid crystal is liable to be contaminated because the uncured liquid crystal sealing agent and the liquid crystal are brought into contact while heating.

On the other hand, liquid crystal sealing agents used in the photocuring method include two types of cationic polymerization and radical polymerization depending on types of photopolymerization initiators. The liquid crystal sealing agents of the cationic polymerization type have a drawback of being inferior in reliability, since cationic components generated on photocuring contaminate the liquid crystal and decrease the specific resistance of the liquid crystal. Besides, the liquid crystal sealing agents of the radical polymerization type have a problem of being insufficient in adhesive strength, since the curing shrinkage during photocuring is large. Further, a problematic point related to both photocuring methods of the cationic polymerization type and the radical polymerization type involves a problem that metal wiring parts of an array substrate of a liquid crystal display cell and black matrix parts of a color filter substrate generate light-shielded parts in the liquid crystal sealing agent where light does not enter, causing the light-shielded parts to become uncured.

The thermosetting method and the photocuring method thus hold such problems, respectively, and actually the combined photo- and thermosetting method is prevalent as a practical curing system. The combined photo- and thermosetting method is characterized in that a liquid crystal sealing agent interposed between substrates is subjected to a primary curing by light irradiation, and thereafter to a secondary curing by heating (see Patent Document 1). Merits of thermosetting include the remarkable improvement in adhesive strength and moisture resistance reliability, the curability by thermosetting even with light-shielded parts, and the like.

An important characteristic required for a liquid crystal sealing agent used in the combined photo- and thermosetting method is that the liquid crystal sealing agent does not contaminate the liquid crystal in each process before and after light irradiation and heat curing. Further, the liquid crystal sealing agent desirably has little viscosity change during use at room temperature and a favorable pot life in view of workability, while low-temperature curing generally below 130°C and within 1 hour is demanded in view of characteristics of an enclosed liquid crystal and costs.

The curing resin system used for a liquid crystal sealing agent by the combined photo- and thermosetting method generally uses a curing resin system having both reactive groups of an epoxy group which has thermosettability, and a (meth)acryloyl group which has photocurability. In such a curing resin system, a mixed resin system of an epoxy resin and an epoxy (meth)acrylate resin, or a partially (meth)acryloylated epoxy resin is used. The curing resin system essentially contains further a photopolymerization initiator component to photocure the (meth)acryloyl group and a curing agent component to thermoset the epoxy group. The curing agent components generally used are hydrazide compounds, such as adipic acid dihydrazide, sebacic acid dihydrazide, isophthalic acid dihydrazide and Amicure VDH (dihydrazides having a valine hydantoin skeleton, made by Ajinomoto Fine-Techno Co., Inc.). However, hydrazide compounds are suitable for curing light-shielded parts because they react not only with an epoxy group but also with a (meth)acryloyl group, but they cause the time-dependent changes in viscosity etc. at room temperature. Therefore, the selection of curing agents is an important factor largely influencing on the possibility of contaminating liquid crystals and the workability such as pot life of a liquid crystal sealing agent. Among the hydrazides, a sealing agent using adipic acid dihydrazide, sebacic acid dihydrazide, dodecanedioic acid dihydrazide, isophthalic acid dihydrazide or the like

is relatively excellent but insufficient in preservation stability, and a sealing agent having a longer pot life and a stable workability is demanded.

As described above, a liquid crystal sealing agent for the liquid crystal dropping process having a low possibility of contaminating liquid crystals and excellent pot life at room temperature, low-temperature curability and the like, is demanded.

Meanwhile, with respect to a resin composition using a hydrazide compound, Patent Document 2 discloses tris(2-hydrazinocarbonylethyl) isocyanate being a hydrazide compound related to the present invention, and contends that it is useful as an epoxy resin curing agent. However, there is no description about the preservation stability, curing characteristics and the like of the epoxy resin composition and also no description of the possibility of application to a curing agent of a liquid crystal sealing agent. Patent Document 3 discloses that in a curing system of an epoxy resin and a hydrazide curing agent, polycarboxylic acids are effective as a curing promoter, but also does not describe the possibility of application to a liquid crystal sealing agent.

Patent Document 1: Japanese Patent No. 2846842

Patent Document 2: Japanese Patent Application Laying Open (KOKAI) No. 2002-371069

Patent Document 3: Japanese Patent Application Laying Open (KOKAI) No. 62-172014

The present invention relates to a liquid crystal sealing agent and a liquid crystal display cell using the same, and more particularly, to a liquid crystal sealing agent suitable for manufacture of a liquid crystal display cell by the liquid crystal dropping process, and a liquid crystal display cell manufactured using the same. It is an object of the present invention especially to propose a liquid crystal sealing agent remarkably improved in pot life at room temperature and simultaneously

excellent in low-temperature curability, liquid crystal contamination, dispense workability, laminatability and adhesive strength.

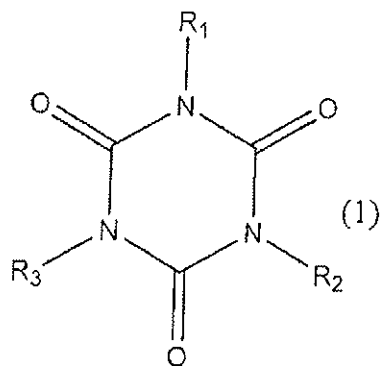
Disclosure of the Invention

As a result of exhaustive studies to solve the above-mentioned problems, the present inventors have found that a resin composition having a specific composition achieves the object. This has led to the completion of the present invention.

That is, the present invention relates to the following (1) to (9).

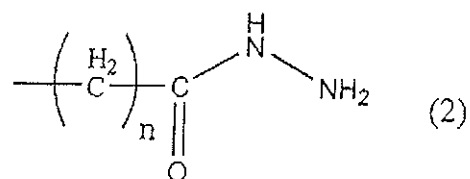
- (1) A liquid crystal sealing agent comprising (a) a hydrazide compound having an isocyanuric ring skeleton represented by the general formula (1) described below and (b) one or more curable resins selected from epoxy resins, (meth)acrylated epoxy resins and partially (meth)acrylated epoxy resins:

[Chemical Formula 1]



wherein R¹ to R³ each independently represents hydrogen or a molecular skeleton represented by the following formula (2):

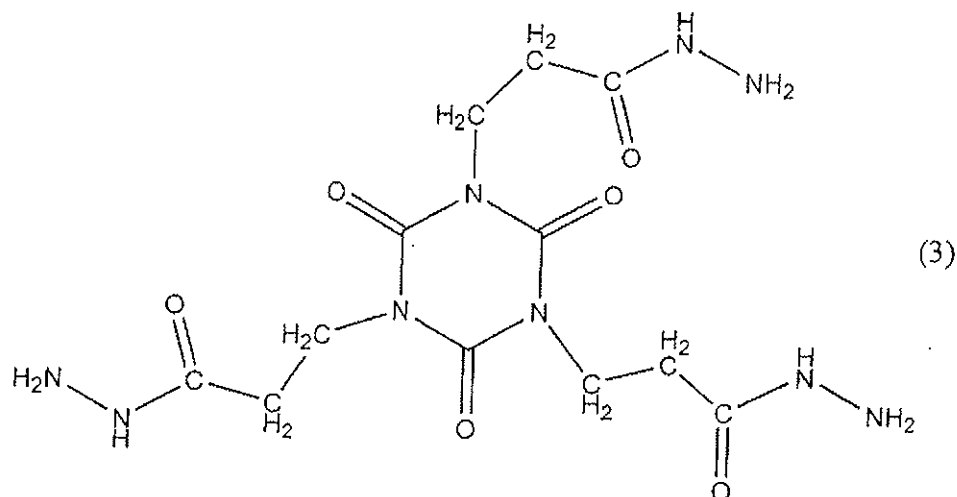
[Chemical Formula 2]



wherein n is an integer of 1 to 6.

(2) The liquid crystal sealing agent according to (1), wherein the hydrazide compound (a) is a compound represented by the following formula (3):

[Chemical Formula 3].

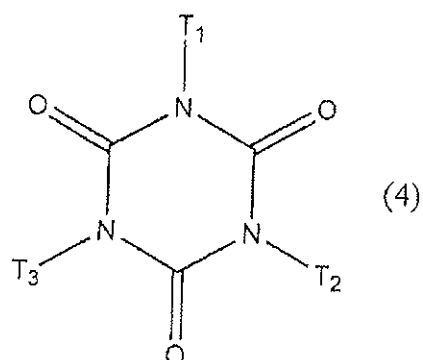


(3) The liquid crystal sealing agent according to claim 1 or 2, wherein the curable resin (b) is a mixture of an epoxy resin and a (meth)acrylated epoxy resin.

(4) The liquid crystal sealing agent according to claims 1 to 3, further comprising (c) a polycarboxylic acid as a curing promoter.

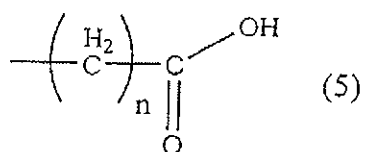
(5) The liquid crystal sealing agent according to any one of (1) to (4), wherein the polycarboxylic acid has in its molecule an isocyanuric ring skeleton represented by the general formula (4) described below:

[Chemical Formula 4]



wherein T¹ to T³ each independently represents hydrogen or a molecular skeleton represented by the following formula (5):

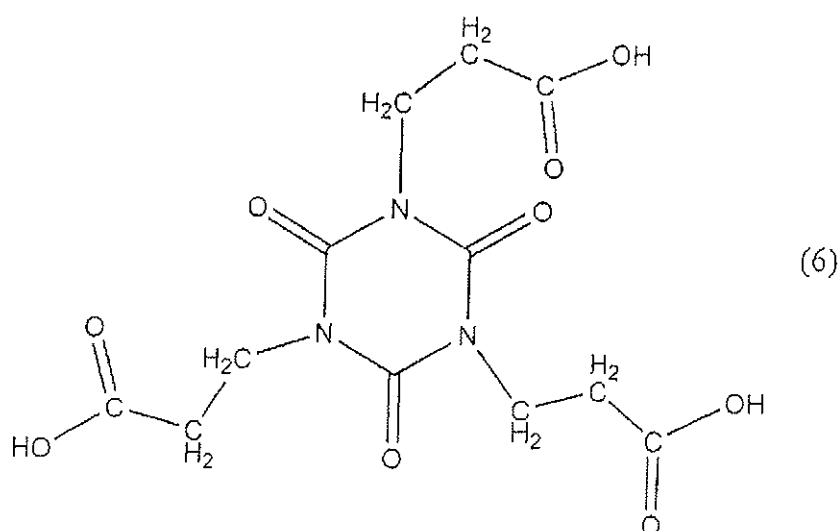
[Chemical Formula 5]



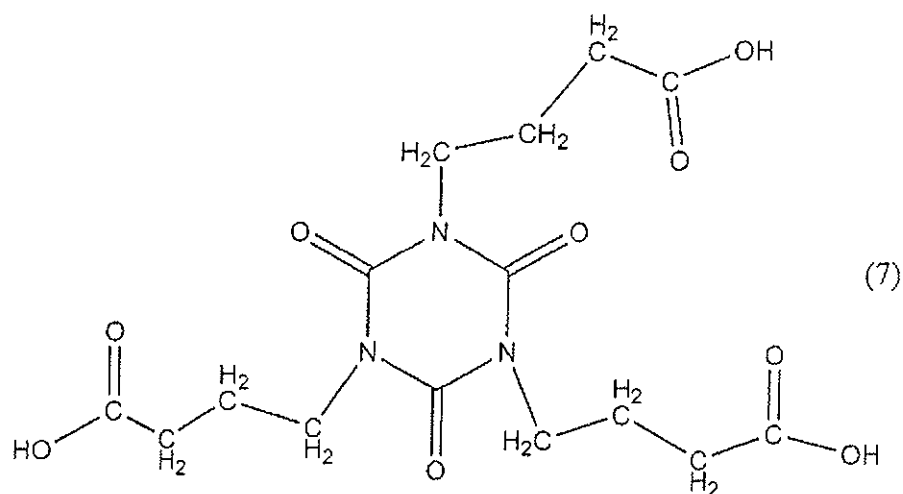
wherein n is an integer of 1 to 6.

(6) The liquid crystal sealing agent according to (5), wherein the polycarboxylic acid (c) is a compound represented by the following formula (6):

[Chemical Formula 6].



- (7) The liquid crystal sealing agent according to (5), wherein the polycarboxylic acid (c) is a compound represented by the following formula (7):
[Chemical Formula 7].



- (8) A liquid crystal display cell sealed with a cured substance of the liquid crystal sealing agent according to any one of (1) to (7).
- (9) A method for manufacturing a liquid crystal display cell comprising two substrates, characterized by dropping a liquid crystal inside a weir of the liquid crystal sealing agent according to any one of (1) to (7), formed on one of the

substrates, thereafter laminating the other substrate on the one substrate, and then curing the liquid crystal sealing agent.

Effects of the Invention

The liquid crystal sealing agent of the present invention has excellent dispense workability and laminatability to a substrate, a long pot life, a large adhesive strength, a low possibility of contaminating liquid crystals, and an excellent gap formability. Use of the liquid crystal sealing agent of the present invention in the liquid crystal dropping process allows the improvements in the yield and productivity in manufacture of the liquid crystal display cell.

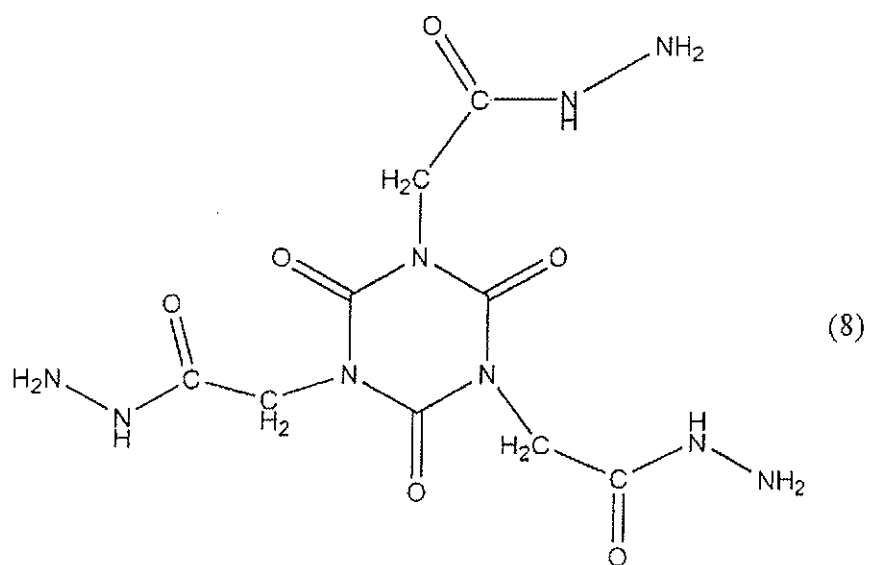
Best Mode for Carrying Out the Invention

Hereinafter, the present invention will be described in detail.

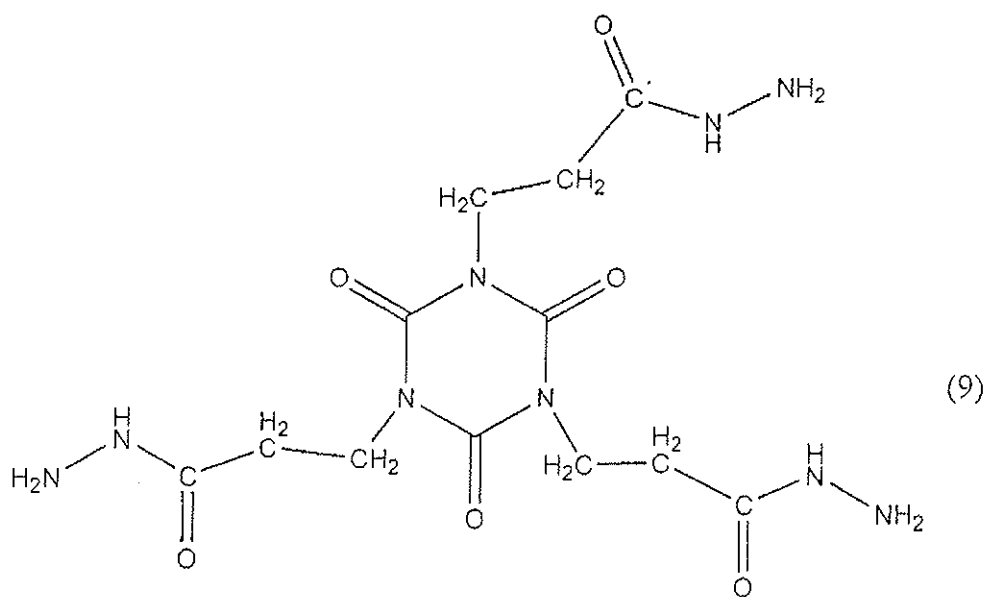
The liquid crystal sealing agent used in the present invention contains a hydrazide compound (a) as a curing agent, which has an isocyanuric ring skeleton represented by the general formula (1) described before.

The hydrazide compound having an isocyanuric ring skeleton can be synthesized by a common method such as esterifying a carboxylic acid compound having the skeleton and further reacting it with hydrated hydrazine under heating. Specific examples of the hydrazide compounds include tris(2-hydrazinocarbonylmethyl) isocyanurate (the following formula (8)), tris(2-hydrazinocarbonylethyl) isocyanurate (the following formula (9)), tris(2-hydrazinocarbonylpropyl) isocyanurate (the following formula (10)) and bis(2-hydrazinocarbonylethyl) isocyanurate (the following formula (11)), but are not especially limited thereto. Tris(2-hydrazinocarbonylethyl) isocyanurate is commercially available as trade name, HCIC, from Japan Finechem Co., Inc.

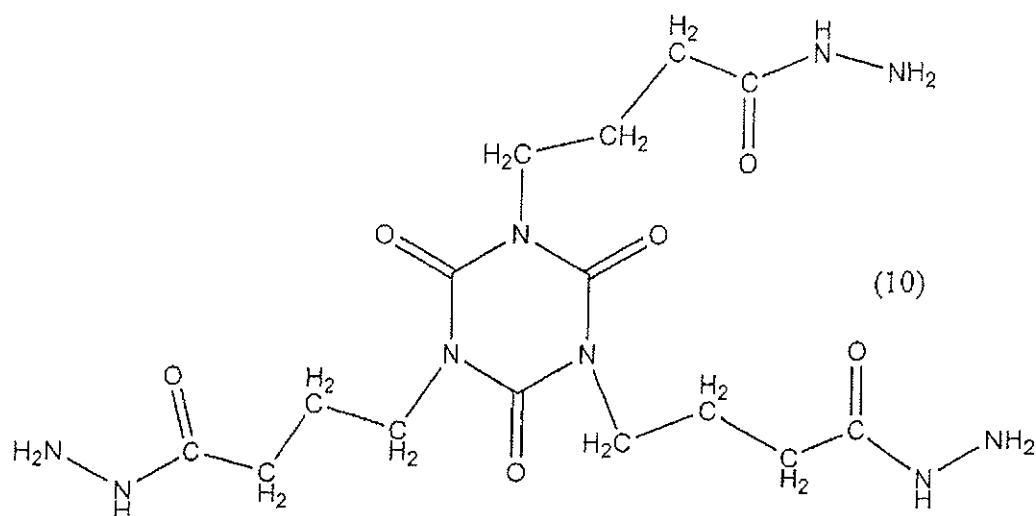
[Chemical Formula 8]



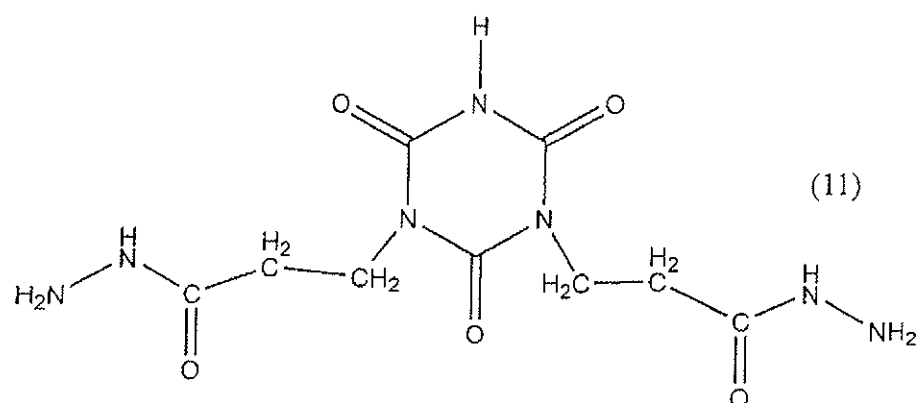
[Chemical Formula 9]



[Chemical Formula 10]



[Chemical Formula 11]



With respect to a curing agent of a liquid crystal sealing agent of the liquid crystal dropping system, it is important that a liquid crystal sealing agent starts the reaction homogeneously and promptly without contaminating a liquid crystal on heating after light irradiation, and has little viscosity change and a favorable pot life at room temperature during use. In the case of a solid-dispersed latent thermosetting agent, if the agent has a nonuniform and large particle size, and an insufficient and deviated dispersion, the display faults of a liquid crystal panel are generated due to nonuniform curing causing a faulty cell gap and a contaminated liquid crystal. In consideration of this point, the hydrazide compound having an isocyanuric ring skeleton used in the present invention is preferably one finely

pulverized into not more than 3 μm , more preferably not more than 2 μm , in average particle size as measured by a laser diffraction/scattering particle size distribution analyzer. The lower limit of the average particle size is about 0.1 μm . The maximum particle size is preferably not more than 8 μm , more preferably not more than 5 μm . A sealing agent using a hydrazide compound having an isocyanuric ring skeleton has a very favorable pot life at room temperature, while it exhibits a moderate curability even under the condition of 120°C for 1 hour. The hydrazide compound having an isocyanuric ring skeleton has almost no solubility to a liquid crystal, resulting in the enclosed liquid crystal exhibiting a very low contamination.

The using amount of the hydrazide compound (a) having an isocyanuric ring skeleton as a curing agent is preferably not less than 1 part by weight and not more than 20 parts by weight to 100 parts by weight of the curable resin (b).

The curable resin of the present invention to be used is one or more curable resins (b) selected from epoxy resins, (meth)acrylated epoxy resins and partially (meth)acrylated epoxy resins. It includes, for example, an epoxy resin, a mixture of an epoxy resin and a (meth)acrylated epoxy resin, a (meth)acrylated epoxy resin, and a partially (meth)acrylated epoxy resin. (Here, “(meth)acryl” means “acryl” and/or “methacryl”. Hereinafter, same as this.) Any curable resin used in the present invention is preferably one having low contamination and solubility to a liquid crystal, and examples of suitable epoxy resins include bisphenol S epoxy resins, resorcinol diglycidyl ether multimers and diglycidyl ethers of ethylene oxide addition bisphenol S, but are not limited thereto. A (meth)acrylated epoxy resin and a partially (meth)acrylated epoxy resin are obtained by reaction of an epoxy resin and a (meth)acrylic acid. An epoxy resin as a raw material is not especially limited, but is preferably di- or more functional epoxy resins, and includes, for example, bisphenol A epoxy resins, bisphenol F epoxy resins, bisphenol S epoxy resins, phenol novolac epoxy resins, cresol novolac epoxy resins, bisphenol A novolac epoxy resins,

bisphenol F novolac epoxy resins, cycloaliphatic epoxy resins, aliphatic chain epoxy resins, glycidyl ester epoxy resins, glycidyl amine epoxy resins, hydantoin epoxy resins, isocyanurate epoxy resins, phenol novolac epoxy resins having a triphenolmethane skeleton, and additionally diglycidyl-etherified di-functional phenols, diglycidyl-etherified di-functional alcohols, halides thereof, and those hydrogenated. Among these, bisphenol epoxy resins and novolac epoxy resins are more preferable in view of the liquid crystal contamination. The ratio of an epoxy group and a (meth)acryloyl group is not limited, and is suitably selected in view of the process adaptability and the liquid crystal contamination.

As the curable resin, further, monomers and/or oligomers of (meth)acrylates esters may be used for controlling the reactivity and the viscosity. Such monomers and oligomers include, for example, reaction products of dipentaerythritol and (meth)acrylic acid, and reaction products of dipentaerythritol caprolactone and (meth)acrylic acid, but are not especially limited as long as they have a low possibility of contamination to a liquid crystal.

The using amount of the curable resin (b) is suitably determined in consideration of workability and properties of an obtained liquid crystal sealing agent, and usually about 25 to 80% by weight in the liquid crystal sealing agent, preferably 25 to 75% by weight.

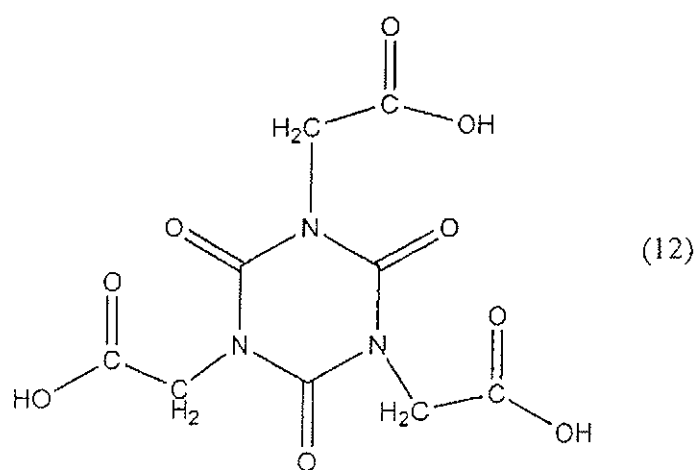
When a curable resin containing a (meth)acryloyl group is used for the liquid crystal sealing agent of the present invention, a radically reactive photopolymerization initiator is used for imparting photocurability. Any initiator can be used as long as it has a sensitivity nearly to the i line (365 nm), which has a relative small influence on liquid crystal characteristics, and a low liquid crystal contamination. Specific examples of radically reactive photopolymerization initiators to be usable include benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, diethylthioxanthone, benzophenone, 2-ethylanthraquinone, 2-hydroxy-2-

methylpropiohenone, 2-methyl-[4-(methylthio)phenyl]-2-morpholino-1-propane, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, a reaction product of 2-hydroxyethyl acrylate, isophorone diisocyanate and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methylpropan-1-one, and a reaction product of 2-isocyanatoethyl methacrylate and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methylpropan-1-one.

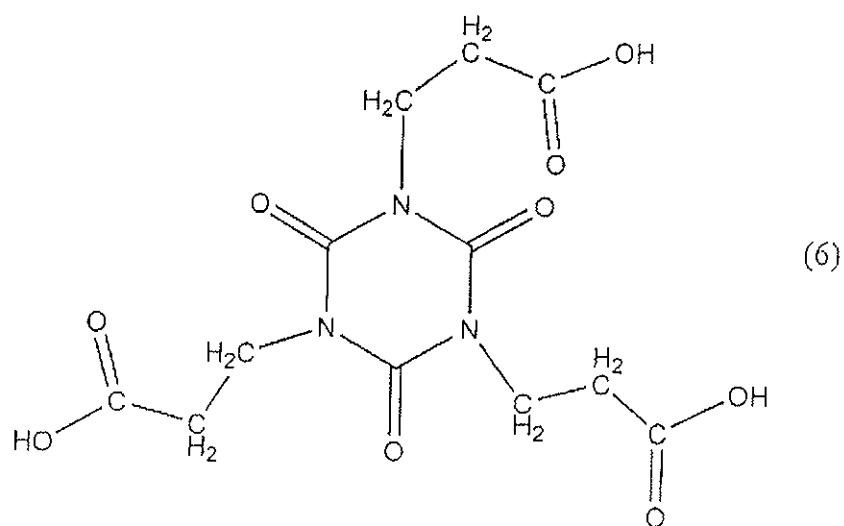
When a radically reactive photopolymerization initiator is added, the using amount is about 0.1 to 10 parts by weight in a liquid crystal sealing agent.

In the liquid crystal sealing agent of the present invention, a polycarboxylic acid (c) as a curing promoter is desirably formulated for improvement of low-temperature curability. Specific examples of polycarboxylic acids include aromatic carboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid and benzophenone tetracarboxylic acid, aliphatic carboxylic acids such as decanedioic acid and dodecanedioic acid, and polycarboxylic acids having an isocyanuric ring skeleton represented by the general formula (4) described before. Polycarboxylic acids having an isocyanuric ring skeleton represented by the general formula (4) specifically include tris(2-carboxymethyl) isocyanurate (the following formula (12)), tris(2-carboxyethyl) isocyanurate (the following formula (6)), tris(2-carboxypropyl) isocyanurate (the following formula (7)) and bis(2-carboxyethyl) isocyanurate (the following formula (13)).

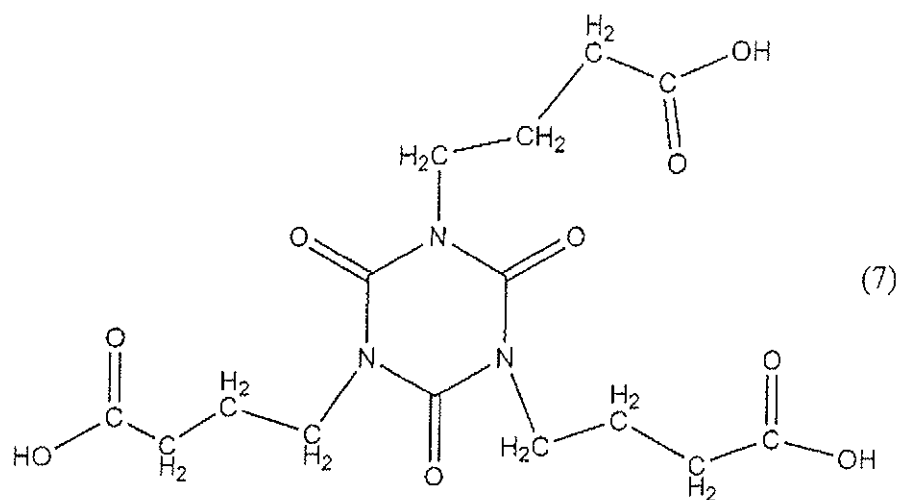
[Chemical Formula 12]



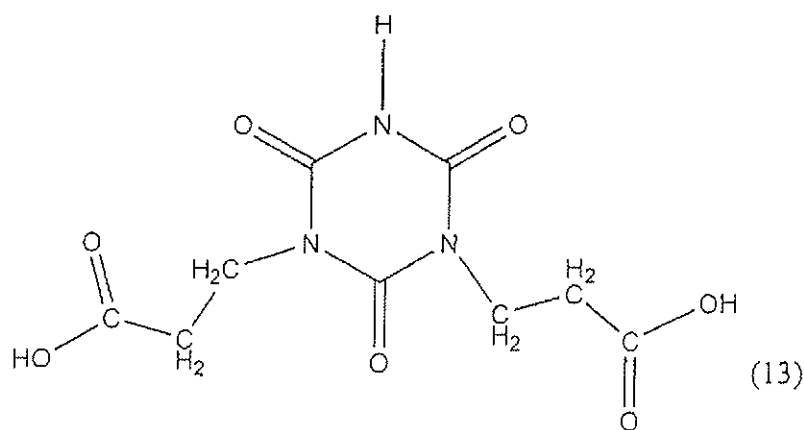
[Chemical Formula 13]



[Chemical Formula 14]



[Chemical Formula 15]



Among these curing promoters, preferable in the present invention are polycarboxylic acids having an isocyanuric ring skeleton in view of the stability with time and the liquid crystal contamination.

The adding amount of a curing promoter is preferably not less than 0.1 part by weight and not more than 10 parts by weight to 100 parts by weight of a curable resin (b).

Inorganic fillers may be formulated to the liquid crystal sealing agent of the present invention for improvement of adhesive strength, moisture resistance and the like. The inorganic fillers to be useable are not especially limited, but specifically

include spherical silica, fused silica, crystal silica, titanium oxide, titanium black, silicon carbide, silicon nitride, boron nitride, calcium carbonate, magnesium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, magnesium oxide, zirconium oxide, aluminum hydroxide, magnesium hydroxide, calcium silicate, aluminum silicate, lithium aluminum silicate, zirconium silicate, barium titanate, glass fiber, carbon fiber, molybdenum disulfide and asbestos. They are preferably spherical silica, fused silica, crystal silica, titanium oxide, titanium black, silicon nitride, boron nitride, calcium carbonate, barium sulfate, calcium sulfate, mica, talc, clay, alumina, aluminum hydroxide, calcium silicate and aluminum silicate. These inorganic fillers may be used as a mixture of two or more.

The inorganic filler used in the present invention preferably has an average particle size of not more than 3 μm . With the average particle size of more than 3 μm , the gap formation has trouble in some case on laminating upper and lower glass substrates during manufacture of a liquid crystal cell. The lowest limit of the average particle size of an inorganic filler is usually about 0.01 μm .

The content of the inorganic filler used in the present invention is usually 2 to 60% by weight, preferably 5 to 50% by weight in a liquid crystal sealing agent. With the content of a filler of lower than 2% by weight, since the sealing agent has a decreased adhesive strength to a glass substrate and an inferior moisture resistance reliability, the adhesive strength after moisture absorption largely decreases in some case. By contrast, with the content of the filler of more than 60% by weight, since the filler content is too much, the sealing agent is hardly squashed and the gap of a liquid crystal cell may not be formed.

Organic fillers may further be added in the liquid crystal sealing agent of the present invention in the range of not affecting characteristics of the liquid crystal sealing agent. The organic fillers include polymer beads and core-shell type rubber fillers. These fillers may be used as a mixture of two or more.

The liquid crystal sealing agent of the present invention preferably contains a silane coupling agent for improvement of the adhesive strength. The silane coupling agents to be usable include, for example, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane, N-(2-aminoethyl)3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)3-aminopropylmethyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, vinyltrimethoxysilane, N-(2-(vinylbenzylamino)ethyl)3-aminopropyltrimethoxysilane hydrochloride, 3-methacryloxypropyltrimethoxysilane, 3-chloropropylmethyldimethoxysilane and 3-chloropropyltrimethoxysilane. These silane coupling agents may be used as a mixture of two or more. Among these, silane coupling agents having an amino group are preferable for providing a more favorable adhesive strength. Use of a silane coupling agent can provide a liquid crystal sealing agent having an improved adhesive strength and an excellent moisture resistance reliability.

In the case of adding a coupling agent, the using amount thereof is usually about 0.1 to 5% by weight in a liquid crystal sealing agent.

Further as required, additives such as an organic solvent, a pigment, a leveling agent and a defoaming agent can be formulated to the liquid crystal sealing agent of the present invention.

The liquid crystal sealing agent of the present invention can be manufactured by homogeneously mixing melted and mixed resin components with filler components and a thermosetting agent by a well-known mixing apparatus, for example, a three-roll mill, a sand mill, a ball mill or a planetary mixer. After the mixing, the liquid crystal sealing agent is preferably subjected to a filtering process for removing foreign substances.

The liquid crystal cell of the present invention is one in which a pair of substrates on each of which a predetermined electrode is formed are arranged oppositely with a predetermined gap; the periphery thereof is sealed with the liquid crystal sealing agent of the present invention; and a liquid crystal is enclosed in the gap. Types of enclosed liquid crystals are not especially limited. Here, the substrates are constituted of a combination of substrates composed of glass, quartz, plastic, silicon or the like, at least one of the substrates having light transmissivity. The manufacturing method involves, for example, adding a spacer (gap control material) such as glass fibers to the liquid crystal sealing agent of the present invention, thereafter applying the liquid crystal sealing agent in a weir shape on one of the pair of substrates by a dispenser or the like, then dropping a liquid crystal inside the weir of the liquid crystal sealing agent, and superposing the other glass substrate on the one substrate in vacuo to form a gap. After the gap formation, the liquid crystal sealing portion is irradiated with ultraviolet rays by an ultraviolet irradiation apparatus to photocure the liquid crystal sealing portion. The ultraviolet irradiation amount is usually 200 mJ/cm^2 to $6,000 \text{ mJ/cm}^2$, preferably 500 mJ/cm^2 to $4,000 \text{ mJ/cm}^2$. Thereafter, the liquid crystal sealing portion is cured at 90 to 140°C for 1 to 2 hours to provide the liquid crystal display cell of the present invention. The spacer includes, for example, glass fibers, silica beads and polymer beads. The diameters are different depending on the purposes, but usually 2 to $8 \text{ }\mu\text{m}$, preferably 4 to $7 \text{ }\mu\text{m}$. The using amount is usually 0.1 to 4 parts by weight, preferably 0.5 to 2 parts by weight to 100 parts by weight of the liquid crystal sealing agent of the present invention.

The liquid crystal sealing agent of the present invention exhibits a remarkably low contamination to a liquid crystal through the manufacturing process, and is excellent in dispense workability to a substrate, laminatability, adhesive strength, pot life at room temperature, and low-temperature curability. The liquid crystal display

cell of the present invention thus obtained has no display faults due to liquid crystal contamination and has an excellent adhesive strength and moisture resistance reliability.

Examples

Hereinafter, the present invention will be described further in detail by way of Examples.

Example 1

75 parts by weight of an epoxy acrylate resin, KAYARAD R-94220 (an epoxy acrylate of a bisphenol F epoxy resin, made by Nippon Kayaku Co., Ltd.), 25 parts by weight of an epoxy resin RE-203 (an ethylene oxide addition bisphenol S epoxy resin; epoxy equivalent: 233 g/eq., made by Nippon Kayaku Co., Ltd.), 5 parts by weight of a photopolymerization initiator, KAYACURE RPI-4 (a reaction product of 2-isocyanatoethyl methacrylate and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methylpropan-1-one, made by Nippon Kayaku Co., Ltd.), and 1.5 parts by weight of a silane coupling agent, Sila-Ace S-510 (3-glycidoxypyrpyltrimethoxysilane, made by Chisso Corp.) were mixed to obtain a resin solution. Then, as fillers, 17.5 parts by weight of NanoTek Alumina SPC (spherical alumina, average particle size: 50 nm, made by C.I. Kasei Co., Ltd.), and 1.5 parts by weight of a butadiene/alkyl methacrylate/styrene copolymer (Paraloid EXL-2655, made by Rohm and Haas Co.) were homogeneously mixed therewith in a bead mill; and further 14 parts by weight of a finely pulverized product of tris(2-hydrazinocarbonyl ethyl) isocyanurate (a product obtained by finely pulverizing HCIC into 1.5 μm in average particle size and 5 μm in maximum particle size by a jet mill, made by Japan Finechem Co., Inc.), and 3 parts by weight of a pulverized product of dodecanedioic acid (a product obtained by finely pulverizing dodecanedioic acid into 1.5 μm in average particle size and 5 μm in maximum particle size by a jet mill, made by Ube Industries, Ltd.) were mixed therewith, and the resultant mixture was kneaded by a three-roll mill to obtain a

liquid crystal sealing agent of the present invention. The viscosity (25°C) of the liquid crystal sealing agent was 300 Pa·s (25°C, R-type viscometer (made by Toki Sangyo Co., Ltd.).

Example 2

75 parts by weight of an epoxy acrylate resin, KAYARAD R-94220 (an epoxy acrylate of a bisphenol F epoxy resin, made by Nippon Kayaku Co., Ltd.), 25 parts by weight of an epoxy resin RE-203 (an ethylene oxide addition bisphenol S epoxy resin; epoxy equivalent: 233 g/eq., made by Nippon Kayaku Co., Ltd.), 5 parts by weight of a photopolymerization initiator, KAYACURE RPI-4 (a reaction product of 2-isocyanatoethyl methacrylate and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methylpropan-1-one, made by Nippon Kayaku Co., Ltd.), and 1.5 parts by weight of a silane coupling agent, Sila-Ace S-510 (3-glycidoxypentyltrimethoxysilane, made by Chisso Corp.) were mixed to obtain a resin solution. Then, as fillers, 17.5 parts by weight of NanoTek Alumina SPC (spherical alumina, average particle size: 50 nm, made by C.I. Kasei Co., Ltd.), and 1.5 parts by weight of a butadiene-alkyl methacrylate-styrene copolymer (Paraloid EXL-2655, made by Rohm and Haas Co.) were homogeneously mixed therewith in a bead mill; and further 14 parts by weight of a finely pulverized product of tris(2-hydrazinocarbonyl) isocyanurate (a product obtained by finely pulverizing HCIC into 1.5 µm in average particle size and 5 µm in maximum particle size by a jet mill, made by Japan Finechem Co., Inc.), and 3 parts by weight of a pulverized product of tris(2-carboxyethyl) isocyanurate (a product obtained by finely pulverizing CIC acid into 1.5 µm in average particle size and 5 µm in maximum particle size by a jet mill, made by Shikoku Chemicals Corp.) were mixed therewith, and the resultant mixture was kneaded by a three-roll mill to obtain a liquid crystal sealing agent of the present invention. The viscosity (25°C) of the liquid crystal sealing agent was 250 Pa·s (25°C, R-type viscometer (made by Toki Sangyo Co., Ltd.).

Example 3

75 parts by weight of an epoxy acrylate resin, KAYARAD R-94220 (an epoxy acrylate of a bisphenol F epoxy resin, made by Nippon Kayaku Co., Ltd.), 25 parts by weight of an epoxy resin RE-203 (an ethylene oxide addition bisphenol S epoxy resin; epoxy equivalent: 233 g/eq., made by Nippon Kayaku Co., Ltd.), 5 parts by weight of a photopolymerization initiator, KAYACURE RPI-4 (a reaction product of 2-isocyanatoethyl methacrylate and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methylpropan-1-one, made by Nippon Kayaku Co., Ltd.), and 1.5 parts by weight of a silane coupling agent, Sila-Ace S-510 (3-glycidoxypyrpyltrimethoxysilane, made by Chisso Corp.) were mixed to obtain a resin solution. Then, as fillers, 17.5 parts by weight of NanoTek Alumina SPC (spherical alumina, average particle size: 50 nm, made by C.I. Kasei Co., Ltd.), and 1.5 parts by weight of a butadiene-alkyl methacrylate-styrene copolymer (Paraloid EXL-2655, made by Rohm and Haas Co.) were homogeneously mixed therewith in a bead mill; and further 14 parts by weight of a finely pulverized product of tris(2-hydrazinocarbonylethyl) isocyanurate (a product obtained by finely pulverizing HCIC into 1.5 μm in average particle size and 5 μm in maximum particle size by a jet mill, made by Japan Finechem Co., Inc.), and 3 parts by weight of a pulverized product of tris(2-carboxypropyl) isocyanurate (a product obtained by finely pulverizing C3-CIC acid into 1.5 μm in average particle size and 5 μm in maximum particle size by a jet mill, made by Shikoku Chemicals Corp.) were mixed therewith, and the resultant mixture was kneaded by a three-roll mill to obtain a liquid crystal sealing agent of the present invention. The viscosity (25°C) of the liquid crystal sealing agent was 350 Pa·s (25°C, R-type viscometer (made by Toki Sangyo Co., Ltd.).

Liquid crystal contamination (UV irradiation and thermosetting)

0.5 g of the liquid crystal sealing agent was charged in a sample bottle; 1 g of a liquid crystal (MLC-6866-100, made by Merck & Co., Ltd.) was added thereto;

thereafter, ultraviolet rays of 3,000 mJ/cm² were irradiated to the sample bottle by a UV irradiation apparatus; then, the sample bottle was put in an oven of 120°C for 1 hour. The sample bottle was allowed to stand at room temperature for 30 min, and then, the liquid crystal was taken out the sample bottle and the elution amount (ppm) of the sealing agent components was quantitatively determined by gas chromatography. The results are shown in Table 1.

[Table 1]

Table 1 Liquid Crystal Contamination (UV irradiation and thermosetting): Elution Amount (ppm)

Component Names	Example 1	Example 2	Example 3
Epoxy Acrylate (KAYARAD R-94220)	120	120	120
Epoxy Resin (RE-203)	520	270	360
Photopolymerization Initiator (KAYACURE RPI-4)	not detected	not detected	not detected
Curing Agent (HCIC)	not detected	not detected	not detected
Curing Promoter A (dodecanedioic acid)	70	-	-
Curing Promoter B (CIC acid)	-	4	-
Curing Promoter C (C3-CIC acid)	-	-	22

Liquid crystal contamination (thermosetting alone)

0.5 g of the liquid crystal sealing agent was charged in a sample bottle; 1 g of a liquid crystal (MLC-6866-100, made by Merck & Co., Ltd.) was added thereto; thereafter, the sample bottle was put in an oven of 120°C for 1 hour. The sample bottle was taken out the oven, and immediately, the liquid crystal was taken out from the sample bottle and the elution amount (ppm) of the sealing agent components was quantitatively determined by gas chromatography. The results are shown in Table 2.

[Table 2]

Table 2 Liquid Crystal Contamination (thermosetting alone): Elution Amount (ppm)

Component Names	Example 1	Example 2	Example 3
Epoxy Acrylate (KAYARAD R-94220)	4500	3400	3000
Epoxy Resin (RE-203)	1600	800	1100
Photopolymerization Initiator (KAYACURE RPI-4)	not detected	not detected	not detected
Curing Agent (HCIC)	not detected	not detected	not detected
Curing Promoter A (dodecanedioic acid)	180	-	-
Curing Promoter B (CIC acid)	-	4	-
Curing Promoter C (C3-CIC acid)	-	-	21

Adhesive strength

1 g of a glass fiber of 5 μm as a spacer was added to 100 g of the obtained liquid crystal sealing agent, and stirred for mixing. The resultant liquid crystal sealing agent was applied on a glass substrate of 50 mm $\times$ 50 mm; a glass piece of 1.5 mm $\times$ 1.5 mm was laminated on the liquid crystal sealing agent; the liquid crystal sealing agent was irradiated with ultraviolet rays of 3 J/cm² by a UV irradiation apparatus, and then put it in an oven for thermosetting. The thermosetting conditions were two conditions of 100°C for 1 hour and 120°C for 1 hour. The shear bond strength of the glass piece was measured by a bond tester made by Seishin Trading Co., Ltd. The results are shown in Table 3.

Pot life

The change in viscosity at 25°C of the obtained liquid crystal sealing agent was measured. The viscosity increasing rates (%) to the initial viscosities are shown in Table 3.

[Table 3]

Table 3 Adhesive strength and Pot Life

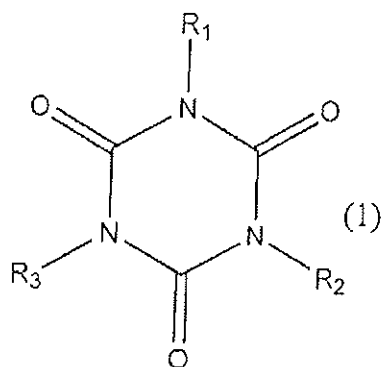
Evaluation Items	Example 1	Example 2	Example 3
Adhesive strength (MPa)			
Curing Condition 3 J/cm ² + 100°C × 1 hr	45	69	65
Curing Condition 3 J/cm ² + 120°C × 1 hr	81	88	87
Pot Life (viscosity increase % to initial value)			
After 2 days	11	5	4
After 4 days	34	19	15

As shown in Tables 1, 2 and 3, the sealing agents of Examples according to the present invention have a low possibility of contaminating liquid crystal, an excellent adhesive property, little viscosity change and favorable workability. Especially the polycarboxylic acid having an isocyanuric ring skeleton used in Examples 2 and 3 hardly elutes into the liquid crystal, therefore, the obtained panel can be said to be excellent in reliability.

CLAIMS

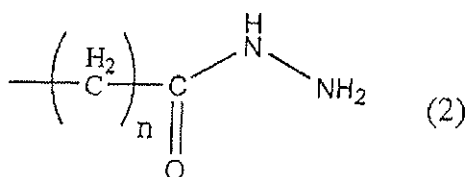
1. A liquid crystal sealing agent comprising (a) a hydrazide compound having an isocyanuric ring skeleton represented by the general formula (1) described below and (b) one or more curable resins selected from epoxy resins, (meth)acrylated epoxy resins and partially (meth)acrylated epoxy resins:

[Chemical Formula 16]



wherein R¹ to R³ each independently represents hydrogen or a molecular skeleton represented by the following formula (2):

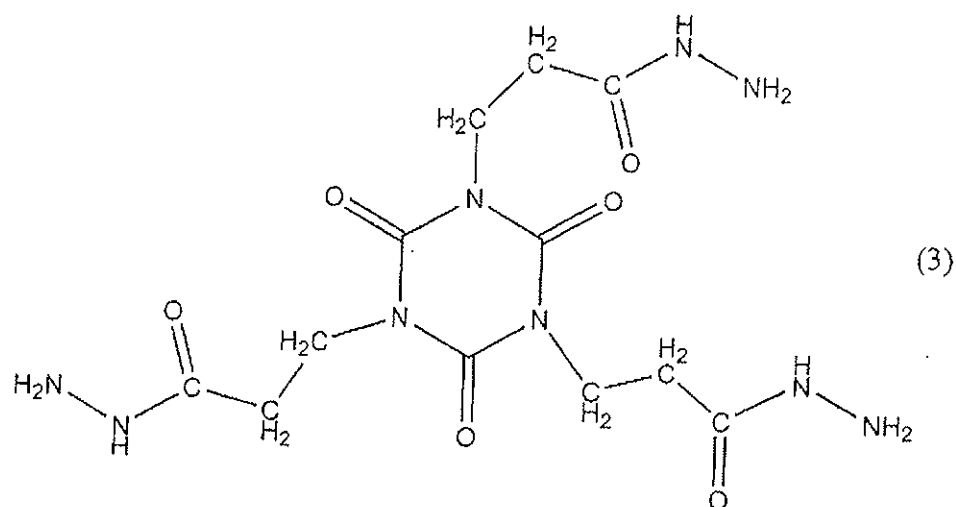
[Chemical Formula 17]



wherein n is an integer of 1 to 6.

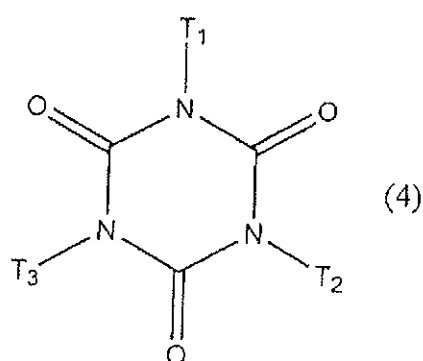
2. The liquid crystal sealing agent according to claim 1, wherein the hydrazide compound (a) is a compound represented by the following formula (3):

[Chemical Formula 18].



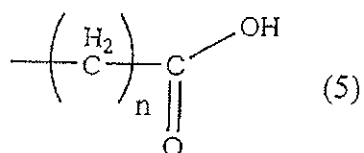
3. The liquid crystal sealing agent according to claim 1 or 2, wherein the curable resin (b) is a mixture of an epoxy resin and a (meth)acrylated epoxy resin.
4. The liquid crystal sealing agent according to any one of claims 1 to 3, further comprising (c) a polycarboxylic acid as a curing promoter.
5. The liquid crystal sealing agent according to any one of claims 1 to 4, wherein the polycarboxylic acid (c) has in its molecule an isocyanuric ring skeleton represented by the general formula (4) described below:

[Chemical Formula 19]



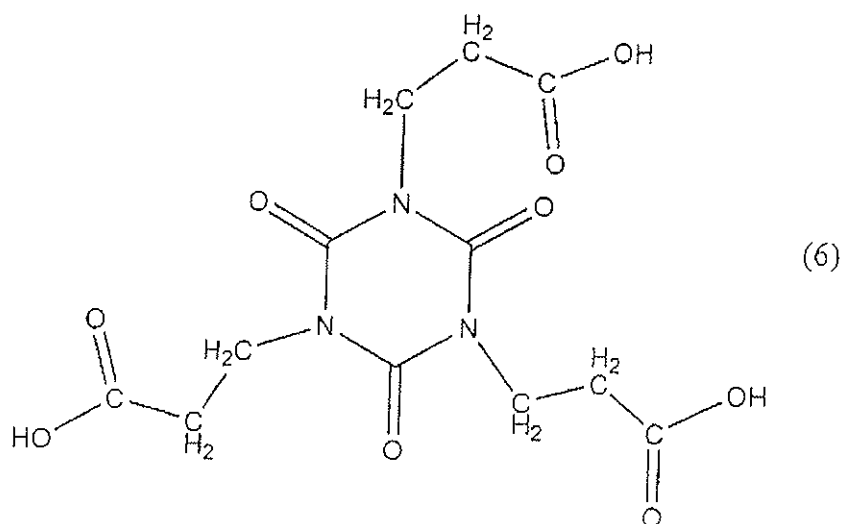
wherein T^1 to T^3 each independently represents hydrogen or a molecular skeleton represented by the following formula (5):

[Chemical Formula 20]

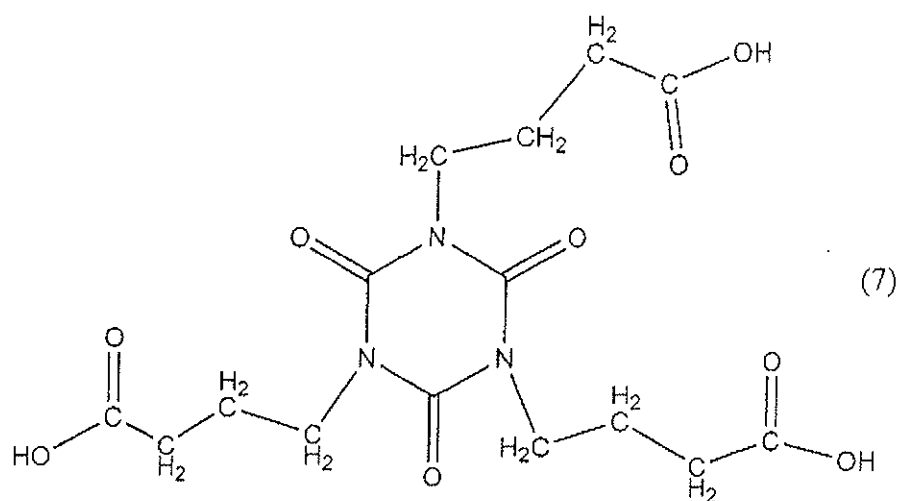


wherein n is an integer of 1 to 6.

6. The liquid crystal sealing agent according to claim 5, wherein the polycarboxylic acid (c) is a compound represented by the following formula (6):
[Chemical Formula 21].



7. The liquid crystal sealing agent according to claim 5, wherein the polycarboxylic acid (c) is a compound represented by the following formula (7):
[Chemical Formula 22].



8. A liquid crystal display cell sealed with a cured substance of the liquid crystal sealing agent according to any one of claims 1 to 7.
9. A method for manufacturing a liquid crystal display cell comprising two substrates, characterized by dropping a liquid crystal inside a weir of the liquid crystal sealing agent according to any one of claims 1 to 7, formed on one of the substrates, thereafter laminating the other substrate on the one substrate, and then curing the liquid crystal sealing agent.