

SPACER FOR DISPLAY PANELS, RADIATION SENSITIVE RESIN
COMPOSITION AND LIQUID CRYSTAL DISPLAY DEVICE

Field of the Invention

5 The present invention relates to a spacer for display panels, a radiation sensitive resin composition and a liquid crystal display device. More specifically, it relates to a spacer for display panels which is used in liquid crystal display panels, touch panels, etc., a radiation sensitive
10 resin composition used to form the spacer, and a liquid crystal display device comprising the spacer.

Description of the Prior Art

 Heretofore, spacer particles such as glass beads or
15 plastic beads having a predetermined diameter have been used in liquid crystal display panels to keep the gap width between two substrates constant. However, as the spacer particles are sprayed over a substrate at random, when they are existent in an effective pixel area, they are imaged or scatter
20 incident light, thereby reducing the contrast of the liquid crystal display panel.

 Therefore, a spacer is formed by photolithography. In this technique, a substrate is coated with a photosensitive resin, exposed to ultraviolet radiation through a
25 predetermined mask and developed to form a dot-like or stripe-like spacer. According to this technique, a spacer can be formed in an area other than the effective pixel area and the above problem which is encountered when the spacer particles are sprayed can be solved. Further, since the cell
30 gap can be controlled by the coating thickness of the photosensitive resin in this technique, the control of the gap width is easy and high accuracy is obtained.

 The gap width between the substrates of a liquid crystal display panel is maintained at a fixed value by a spacer

interposed between the substrates at normal temperature, whereby the thickness of a liquid crystal layer between the substrates is kept constant. However, when the liquid crystal display panel is left at a high temperature in the annealing step after the injection and sealing of liquid crystals in the production process of a liquid crystal display panel and a high-temperature shelf test for evaluating the reliability of a liquid crystal display panel, liquid crystals filled between the substrates thermally expand and the gap width is changed by the expansion pressure, whereby the substrates are distorted and the thickness of the liquid crystal layer becomes partially nonuniform. Therefore, display contrast becomes nonuniform and display quality deteriorates. Particularly in a large-sized liquid crystal display panel having a large substrate area, the distortion of the substrates caused by the thermal expansion of the liquid crystals tends to be marked. Since a liquid crystal display panel for TV's is becoming bigger in size, nonuniform display contrast caused by the thermal expansion of liquid crystals is becoming a serious problem to be solved.

Various proposals have already been made to reduce nonuniform display contrast caused by the thermal expansion of liquid crystals.

JP-A 8-15708 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") discloses a method making use of a plurality of spherical spacers which differ in diameter and elasticity. With regard to process conditions for assembling a display panel, JP-A 2002-49041 discloses a method of controlling the scattering density of spherical spacers. JP-A 2001-147437 discloses the arrangement of columnar spacers.

However, when a liquid crystal display panel is inclined from a horizontal direction at a high temperature, as the spherical spacer particles do not adhere to the surface

of a substrate, the particles move in the liquid crystal layer and are unevenly distributed, thereby causing nonuniform display. The specification of the arrangement of columnar spacers limits the design freedom of a panel, which is not
5 advisable because the design of a liquid crystal display panel will become more and more diverse in the future.

Summary of the Invention

It is an object of the present invention to provide a
10 spacer for display panels which has a specific linear thermal expansion coefficient, can keep the gap width between substrate constant at normal temperature and high temperatures and can always ensure excellent display quality without being affected by temperature variations, a
15 radiation sensitive resin composition used to form the spacer and a liquid crystal display device comprising the spacer.

Other objects and advantages of the present invention will become apparent from the following description.

According to the present invention, firstly, the above
20 objects and advantages of the present invention are attained by a spacer for display panels which has a linear thermal expansion coefficient of higher than $2.0 \times 10^{-4}/^{\circ}\text{C}$ and $8.0 \times 10^{-4}/^{\circ}\text{C}$ or lower.

According to the present invention, secondly, the above
25 objects and advantages of the present invention are attained by a radiation sensitive resin composition comprising [A] a copolymer of (a1) an unsaturated carboxylic acid and/or an unsaturated carboxylic anhydride and (a2) an unsaturated compound other than the component (a1), [B] a polyfunctional
30 unsaturated monomer and [C] a radiation sensitive polymerization initiator, wherein a cured film of the radiation sensitive resin composition has a linear thermal expansion coefficient of higher than $2.0 \times 10^{-4}/^{\circ}\text{C}$ and $8.0 \times 10^{-4}/^{\circ}\text{C}$ or lower and the radiation sensitive resin

composition is used to form the spacer for display panels set forth in claim 1.

According to the present invention, thirdly, the above objects and advantages of the present invention are attained
5 by a liquid crystal display device comprising the spacer for display panels of the present invention.

Detailed Description of the Preferred Embodiments

The present invention will be described in detail
10 hereinafter.

Spacer for display panels

The linear thermal expansion coefficient of the spacer for display panels of the present invention is higher than $2.0 \times 10^{-4}/^{\circ}\text{C}$ and $8.0 \times 10^{-4}/^{\circ}\text{C}$ or lower, preferably $(3.0 \text{ to } 8.0) \times 10^{-4}/^{\circ}\text{C}$, more preferably $(4.0 \text{ to } 8.0) \times 10^{-4}/^{\circ}\text{C}$,
15 particularly preferably $(5.0 \text{ to } 8.0) \times 10^{-4}/^{\circ}\text{C}$.

The spacer for display panels of the present invention can keep the gap width between substrates constant at normal temperature and high temperatures, can always ensure
20 excellent display quality without being affected by temperature variations and can be advantageously used in liquid crystal display panels, touch panels, etc., without restrictions on its shape and position and on the design freedom of a panel when its linear thermal expansion
25 coefficient falls within the above range.

Radiation sensitive resin composition

The material used to form the spacer for display panels of the present invention is not particularly limited as far
30 as it has the above linear thermal expansion coefficient and required strength, surface hardness, heat resistance and chemical resistance as a spacer and can form a spacer having a predetermined shape. The preferred material is a radiation sensitive resin composition which comprises [A] a copolymer

(to be referred to as "copolymer [A]" hereinafter) of (a1) an unsaturated carboxylic acid and/or an unsaturated carboxylic anhydride (to be referred to as "acid unsaturated compound (a1)" hereinafter) and (a2) an unsaturated compound
 5 other than the above component (a1) (to be referred to as "other unsaturated compound (a2)" hereinafter), [B] a polyfunctional unsaturated monomer and [C] a radiation sensitive polymerization initiator and which has a linear thermal expansion coefficient of a cured film obtained
 10 therefrom of higher than $2.0 \times 10^{-4}/^{\circ}\text{C}$ and $8.0 \times 10^{-4}/^{\circ}\text{C}$ or lower.

- copolymer [A] -

Examples of the acid unsaturated compound (a1) used in
 15 the copolymer [A] include unsaturated monocarboxylic acids such as (meth)acrylic acid and crotonic acid; unsaturated dicarboxylic acids such as maleic acid, fumaric acid, citraconic acid, mesaconic acid and itaconic acid; and anhydrides of these unsaturated dicarboxylic acids.

20 Out of these acid unsaturated compounds (a1), acrylic acid, methacrylic acid and maleic anhydride are preferred from the viewpoints of copolymerization reactivity and easy acquisition.

The above acid unsaturated compounds (a1) may be used
 25 alone or in admixture of two or more.

Examples of the other unsaturated compound (a2) used in the copolymer [A] include alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl
 30 (meth)acrylate, i-butyl (meth)acrylate, sec-butyl (meth)acrylate and t-butyl (meth)acrylate; alicyclic (meth)acrylates such as cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-methylcyclohexyl (meth)acrylate, tricyclo[5.2.1.0^{2,6}]decan-8-yl

(meth)acrylate, 2-dicyclopentanyloxyethyl (meth)acrylate and isobornyl (meth)acrylate; aryl (meth)acrylates such as phenyl (meth)acrylate and benzyl (meth)acrylate; hydroxyalkyl (meth)acrylates such as 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate; epoxy group-containing (meth)acrylates such as glycidyl (meth)acrylate, 3,4-epoxybutyl (meth)acrylate, 6,7-epoxyheptyl (meth)acrylate, 2,3-epoxycyclopentyl (meth)acrylate and 3,4-epoxycyclohexyl (meth)acrylate; 10 unsaturated dicarboxylic diesters such as diethyl maleate, diethyl fumarate and diethyl itaconate; unsaturated imide compounds such as N-phenylmaleimide, N-benzylmaleimide and N-cyclohexylmaleimide; vinyl cyanide compounds such as (meth)acrylonitrile, α -chloroacrylonitrile and vinylidene cyanide; 15 unsaturated amide compounds such as (meth)acrylamide and N,N-dimethyl (meth)acrylamide; aromatic vinyl compounds such as styrene, α -methylstyrene, m-methylstyrene, p-methylstyrene, vinyltoluene and p-methoxystyrene; indene derivatives such as indene and 20 1-methylindene; conjugated diene compounds such as 1,3-butadiene, isoprene and 2,3-dimethyl-1,3-butadiene; and vinyl chloride, vinylidene chloride and vinyl acetate.

Out of these other unsaturated compounds (a2), alkyl (meth)acrylates such as n-butyl (meth)acrylate, alicyclic (meth)acrylates such as tricyclo[5.2.1.0^{2,6}]decan-8-yl, aryl (meth)acrylates such as benzyl (meth)acrylate, epoxy group-containing (meth)acrylates such as glycidyl (meth)acrylate, styrene and 1,3-butadiene are preferred from the viewpoint of copolymerization reactivity.

30 The above other unsaturated compounds (a2) may be used alone or in admixture of two or more.

The content of a recurring unit derived from the acid unsaturated compound (a1) in the copolymer [A] is preferably 5 to 50 wt%, particularly preferably 10 to 40 wt%. When the

content of the recurring unit is lower than 5 wt%, the heat resistance, chemical resistance and surface hardness of the spacer may deteriorate and when the content is higher than 50 wt%, the storage stability of the composition may lower.

5 The weight average molecular weight in terms of polystyrene (to be referred to as "Mw" hereinafter) of the copolymer [A] is preferably 2,000 to 500,000, more preferably 5,000 to 100,000. When Mw of the copolymer [A] is lower than 2,000, the heat resistance and surface hardness may lower
10 and when Mw is higher than 500,000, the developability may deteriorate.

 In the present invention, the copolymers [A] may be used alone or in admixture of two or more.

 The copolymer [A] may be produced by polymerizing the
15 acid unsaturated compound (a1) and the other unsaturated compound (a2) in a solvent in the presence of a polymerization initiator.

 Examples of the solvent used for the production of the copolymer [A] include alcohols such as methanol and ethanol;
20 ethers such as tetrahydrofuran and dioxane; ethylene glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono-n-propyl ether and ethylene glycol mono-n-butyl ether; ethylene glycol alkyl ether acetates such as ethylene glycol methyl ether
25 acetate, ethylene glycol ethyl ether acetate, ethylene glycol-n-propyl ether acetate and ethylene glycol-n-butyl ether acetate; diethylene glycol ethers such as diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl
30 ether and diethylene glycol ethyl methyl ether; diethylene glycol alkyl ether acetates such as diethylene glycol methyl ether acetate, diethylene glycol ethyl ether acetate, diethylene glycol-n-propyl ether acetate and diethylene glycol-n-butyl ether acetate; propylene glycol ethers such

as propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-n-butyl ether; propylene glycol alkyl ether acetates such as propylene glycol methyl ether acetate, propylene glycol ethyl ether acetate, propylene glycol-n-propyl ether acetate and propylene glycol-n-butyl ether acetate; propylene glycol alkyl ether propionates such as propylene glycol methyl ether propionate, propylene glycol ethyl ether propionate, propylene glycol-n-propyl ether propionate and propylene glycol-n-butyl ether propionate; aromatic hydrocarbons such as toluene and xylene; ketones such as methyl ethyl ketone, cyclohexanone, 4-hydroxy-4-methyl-2-pentanone and methyl isoamyl ketone; and other esters such as methyl acetate, ethyl acetate, n-propyl acetate, n-butyl acetate, methyl hydroxyacetate, ethyl hydroxyacetate, n-propyl hydroxyacetate, n-butyl hydroxyacetate, methyl methoxyacetate, ethyl methoxyacetate, n-propyl methoxyacetate, n-butyl methoxyacetate, methyl ethoxyacetate, ethyl ethoxyacetate, n-propyl ethoxyacetate, n-butyl ethoxyacetate, methyl n-propoxyacetate, ethyl n-propoxyacetate, n-propyl n-propoxyacetate, n-butyl n-propoxyacetate, methyl n-butoxyacetate, ethyl n-butoxyacetate, n-propyl n-butoxyacetate, n-butyl n-butoxyacetate, methyl lactate, ethyl lactate, n-propyl lactate, n-butyl lactate, methyl 3-hydroxypropionate, ethyl 3-hydroxypropionate, n-propyl 3-hydroxypropionate, n-butyl 3-hydroxypropionate, methyl 2-methoxypropionate, ethyl 2-methoxypropionate, n-propyl 2-methoxypropionate, n-butyl 2-methoxypropionate, methyl 2-ethoxypropionate, ethyl 2-ethoxypropionate, n-propyl 2-ethoxypropionate, n-butyl 2-ethoxypropionate, methyl 2-n-propoxypropionate, ethyl 2-n-propoxypropionate, n-propyl 2-n-propoxypropionate, n-butyl 2-n-propoxypropionate, methyl 2-n-butoxypropionate, ethyl 2-n-butoxypropionate, n-propyl 2-n-butoxypropionate,

n-butyl 2-n-butoxypropionate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, n-propyl 3-methoxypropionate, n-butyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, n-propyl 3-ethoxypropionate,
 5 n-butyl 3-ethoxypropionate, methyl 3-n-propoxypropionate, ethyl 3-n-propoxypropionate, n-propyl 3-n-propoxypropionate, n-butyl 3-n-propoxypropionate, methyl 3-n-butoxypropionate, ethyl 3-n-butoxypropionate, n-propyl 3-n-butoxypropionate, n-butyl
 10 3-n-butoxypropionate, methyl 2-hydroxy-2-methylpropionate, ethyl 2-hydroxy-2-methylpropionate and methyl 2-hydroxy-3-methylbutanoate.

These solvents may be used alone or in admixture of two or more.

15 As the polymerization initiator used for the synthesis of the copolymer [A] may be used a generally known radical polymerization initiator. Examples of the radical polymerization initiator include azo compounds such as 2,2'-azobisisobutyronitrile,
 20 2,2'-azobis-(2,4-dimethylvaleronitrile) and 2,2'-azobis-(4-methoxy-2,4-dimethylvaleronitrile); organic peroxides such as benzoyl peroxide, lauroyl peroxide, t-butylperoxy pyvarate and 1,1'-bis(t-butylperoxy)cyclohexane; hydrogen peroxide; and
 25 redox polymerization initiators comprising one of the above peroxides and a reducer.

These polymerization initiators may be used alone or in admixture of two or more.

30 - [B] polyfunctional unsaturated monomer -

The polyfunctional unsaturated monomer is a monomer having two or more polymerizable unsaturated bonds. Preferred examples of this polyfunctional unsaturated monomer include polyfunctional (meth)acrylic esters which

may have a urethane bond.

Out of the above polyfunctional (meth)acrylic esters, bifunctional (meth)acrylic esters include ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 5 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, diethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate and bisphenoxyethanol full orange (meth)acrylate.

10 Commercially available products of the bifunctional (meth)acrylic ester include Aronix M-210, 240 and 6200 (of Toagosei Chemical Industry Co., Ltd.), KAYARAD HDDA, HX-220, and R-604 (of Nippon Kayaku Co., Ltd.) and Biscoat 260, 312 and 335HP (of Osaka Yuki Kagaku Co., Ltd.), and those of the 15 bifunctional (meth)acrylic ester having a urethane bond include Aronix M-1100, 1200, 1210, 1310 and 1600 (of Toagosei Chemical Industry Co., Ltd.), R-1000 series, 1204, 1211 and 1213 (of Dai-ichi Kogyo Seiyaku Co., Ltd.), and AH-600, AT-600 and UA-306H (of Kyoeisha Kagaku Co., Ltd.).

20 (Meth)acrylic esters having a functionality of 3 or more include trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate and 25 tri[2-(meth)acryloyloxyethyl]phosphate.

Commercially available products of the (meth)acrylic ester having a functionality of 3 or more include Aronix M-309, 400, 402, 405, 450, 7100, 8030, 8060, 1310, 1600, 1960, 8100, 8530, 8560 and 9050, and Aronix TO-1450 (of Toagosei Chemical 30 Industry Co., Ltd.), KAYARAD TMPTA, DPHA, DPCA-20, DPCA-30, DPCA-60, DPCA-120 and MAX-3510 (of Nippon Kayaku Co., Ltd.), and Biscoat 295, 300, 360, 400, GPT and 3PA (of Osaka Yuki Kagaku Co., Ltd.); those of trifunctional (meth)acrylic ester having a urethane bond include R-1000 series, 1301,

1302, 1303, 1304, 1306 and 1308 (of Dai-ichi Kogyo Seiyaku Co., Ltd.); and those of (meth)acrylic ester having a functionality of 4 or more and having a urethane bond include Aronix M-1960 (of Toagosei Chemical Industry Co., Ltd.), and
5 R-1150 (of Dai-ichi Kogyo Seiyaku Co., Ltd.).

In the present invention, the above polyfunctional unsaturated monomers may be used alone or in admixture of two or more. The polyfunctional unsaturated monomer preferably contains a polyfunctional (meth)acrylic ester
10 having a urethane bond and more preferably is a mixture of a polyfunctional (meth)acrylic ester having a urethane bond and a polyfunctional (meth)acrylic ester having no urethane bond. A radiation sensitive resin composition having a high linear thermal expansion coefficient can be obtained by using
15 a polyfunctional unsaturated monomer containing a polyfunctional (meth)acrylic ester having a urethane bond.

In the polyfunctional unsaturated monomer containing a polyfunctional (meth)acrylic ester having a urethane bond, the amount of the polyfunctional (meth)acrylic ester having
20 a urethane bond is preferably 10 to 50 wt%, more preferably 15 to 50 wt%, particularly preferably 25 to 50 wt%. When the polyfunctional (meth)acrylic ester having a urethane bond is contained in that amount, the characteristic properties such as sensitivity at the time of exposure, developability
25 and strength of a spacer are not impaired.

- [C] radiation sensitive polymerization initiator -

The radiation sensitive polymerization initiator responds to radiation to produce active species capable of
30 initiating the polymerization of the polyfunctional unsaturated monomer [B].

The radiation sensitive polymerization initiator is preferably a radiation sensitive radical polymerization initiator.

Examples of the above radiation sensitive radical polymerization initiator include α -diketones such as benzyl and diacetyl; acyloins such as benzoin; acyloin ethers such as benzoin methyl ether, benzoin ethyl ether and benzoin isopropyl ether; benzophenones such as thioxanthone, 2,4-diethylthioxanthone, thioxanthone-4-sulfonic acid, benzophenone, 4,4'-bis(dimethylamino)benzophenone and 4,4'-bis(diethylamino)benzophenone; acetophenones such as acetophenone, p-dimethylaminoacetophenone, 4-(α,α' -dimethoxyacetoxy)benzophenone, 2,2'-dimethoxy-2-phenylacetophenone, p-methoxyacetophenone, 2-methyl-2-morpholino-1-(4-methylthiophenyl)-1-propanone and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one; quinones such as anthraquinone and 1,4-naphthoquinone; halogen compounds such as phenacyl chloride, tribromomethylphenyl sulfone and tris(trichloromethyl)-s-triazine; acylphosphine oxides such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide; and peroxides such as di-t-butyl peroxide.

Commercially available products of the radiation sensitive radical polymerization initiator include IRGACURE-124, 149, 184, 369, 500, 651, 819, 907, 1000, 1700, 1800, 1850 and 2959, and Darocur-1116, 1173, 1664, 2959 and 4043 (of Ciba Specialty Chemicals Co., Ltd.), KAYACURE-DETX, -MBP, -DMBI, -EPA and -OA (of Nippon Kayaku Co., Ltd.), LUCIRIN TPO (of BASF Co., Ltd.), VICURE-10 and 55 (of STAUFFER Co., Ltd.), TRIGGNALP1 (of AKZO Co., Ltd.), SANDORAY 1000 (of SANDOZ AG), DEAP (of APJOHN Co., Ltd.), and QUANTACURE-PDO, -ITX and -EPD (of WARD BLEKINSOP Co., Ltd.).

These radiation sensitive radical polymerization

initiators may be used alone or in admixture of two or more.

A radiation sensitive resin composition which has high sensitivity and is rarely deactivated by oxygen contained in air can be obtained by using at least one radiation
5 sensitizier in conjunction with the above radiation sensitive radical polymerization initiator.

As for the amount of each component of the radiation sensitive resin composition of the present invention, the amount of the polyfunctional monomer [B] is preferably 10
10 to 150 parts by weight, more preferably 20 to 120 parts by weight based on 100 parts by weight of the copolymer [A], and the amount of the radiation sensitive polymerization initiator [C] is preferably 1 to 40 parts by weight, more preferably 3 to 35 parts by weight based on 100 parts by weight
15 of the copolymer [A].

When the amount of the polyfunctional monomer [B] is smaller than 10 parts by weight, it may be difficult to form a film uniform in thickness and when the amount is larger than 150 parts by weight, the adhesion to a substrate may
20 lower. When the amount of the radiation sensitive polymerization initiator [C] is smaller than 1 part by weight, the heat resistance, surface hardness and chemical resistance may deteriorate and when the amount is larger than 40 parts by weight, the transparency may lower.

25

- other additives -

The radiation sensitive resin composition of the present invention may contain other additives such as a surfactant and adhesion aid in limits that do not impair the
30 object of the present invention.

The above surfactant is used to improve coatability.

The above surfactant is preferably a fluorine-based surfactant or silicone-based surfactant.

The fluorine-based surfactant is preferably a compound

having a fluoroalkyl group or fluoroalkylene group at any one of its terminal, main chain and side chain. Examples of the fluorine-based surfactant include

1,1,2,2-tetrafluoropropyl(1,1,2,2-tetrafluorooctyl)ether,
 5 hexyl(1,1,2,2-tetrafluorooctyl)ether, octaethylene glycol di(1,1,2,2-tetrafluorobutyl)ether, hexaethylene glycol di(1,1,2,2,3,3-hexafluoropentyl)ether, octapropylene glycol di(1,1,2,2-tetrafluorobutyl)ether, hexapropylene glycol di(1,1,2,2,3,3-hexafluoropentyl)ether, sodium
 10 perfluorododecylsulfonate,
 1,1,2,2,8,8,9,9,10,10-decafluorododecane,
 1,1,2,2,3,3-hexafluorodecane, sodium fluoroalkylbenzenesulfonate, sodium fluoroalkylphosphonate, sodium fluoroalkylcarbonate, fluoroalkylpolyoxyethylene
 15 ether, diglycerin tetrakis(fluoroalkylpolyoxyethylene ether), fluoroalkylammonium iodide, fluoroalkyl betaine, fluoroalkylpolyoxyethylene ether, perfluoroalkylpolyoxyethanol, perfluoroalkyl alkoxylate and fluorine-based alkyl esters.

20 Commercially available products of the fluorine-based surfactant include BM-1000 and 1100 (of BM CHEMIE Co., Ltd.), Megafac F142D, F172, F173, F178, F183, F191, F471 and F476 (of Dainippon Ink and Chemicals, Inc.), Florade FC-170C, 171, 430 and 431 (of Sumitomo 3M Limited), Surflon S-112, 113,
 25 131, 141, 145 and 382 and Surflon SC-101, 102, 103, 104, 105 and 106 (of Asahi Glass Co., Ltd.), F Top EF301, 303 and 352 (of Shin Akita Kasei Co., Ltd.), and Futargent FT-100, 110, 140A, 150, 250, 251, 300, 310 and 400S and Futargent FTX-251 and 218 (of Neos Co., Ltd.).

30 Commercially available products of the above silicone-based surfactant include Toray Silicone DC3PA, DC7PA, SH11PA, SH21PA, SH28PA, SH29PA, SH30PA, SH-190, SH-193, SZ-6032, SF-8428, DC-57 and DC-190 (of Toray Dow Corning Silicone Co., Ltd.), and TSF-4300, 4440, 4445, 4446,

4452 and 4460 (of GE Toshiba Silicone Co., Ltd.).

Other surfactants include nonionic surfactants including polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether
5 and polyoxyethylene oleyl ether; polyoxyethylene aryl ethers such as polyoxyethylene-n-octylphenyl ether and polyoxyethylene-n-nonylphenyl ether; and polyoxyethylene dialkyl esters such as polyoxyethylene dilaurate and polyoxyethylene distearate; and KP341 organosiloxane
10 polymer (of Shin-Etsu Chemical Co., Ltd.) and Polyflow No. 57 and No. 95 (meth)acrylic acid-based copolymers (of Kyoeisha Kagaku Co., Ltd.).

These surfactants may be used alone or in admixture of two or more.

15 The amount of the surfactant is preferably 5 parts or less by weight, more preferably 2 parts or less by weight based on 100 parts by weight of the copolymer [A]. When the amount of the surfactant is larger than 5 parts by weight, the film may be roughened at the time of application.

20 The above adhesion aid is used to improve adhesion to the substrate.

The adhesion aid is preferably a silane coupling agent having a functional group, specifically a silane coupling agent having a functional group such as carboxyl group,
25 methacryloyl group, isocyanate group or epoxy group. Examples of the adhesion aid include trimethoxysilyl benzoic acid, γ -methacryloxypropyltrimethoxysilane, vinyltriacetoxysilane, vinyltrimethoxysilane, γ -isocyanatepropyltriethoxysilane,
30 γ -glycidoxypropyltrimethoxysilane and β -(3,4-epoxycyclohexyl)ethyl trimethoxysilane.

These adhesion aids may be used alone or in admixture of two or more.

The amount of the adhesion aid is preferably 20 parts

or less by weight, more preferably 15 parts or less by weight based on 100 parts by weight of the copolymer [A]. When the amount of the adhesion aid is larger than 20 parts by weight, the heat resistance may lower.

5 In the radiation sensitive resin composition of the present invention, the copolymer [A], polyfunctional unsaturated monomer [B], radiation sensitive polymerization initiator [C] and other additives and the amounts of these components are suitably selected to ensure that the linear
10 thermal expansion coefficient of a cured film obtained therefrom becomes higher than $2.0 \times 10^{-4}/^{\circ}\text{C}$ and $8.0 \times 10^{-4}/^{\circ}\text{C}$ or lower, preferably $(3.0 \text{ to } 8.0) \times 10^{-4}/^{\circ}\text{C}$, more preferably $(4.0 \text{ to } 8.0) \times 10^{-4}/^{\circ}\text{C}$, particularly preferably $(5.0 \text{ to } 8.0) \times 10^{-4}/^{\circ}\text{C}$.

15

Preparation of radiation sensitive resin composition

The radiation sensitive resin composition of the present invention is preferably prepared as a composition solution by mixing together the above copolymer [A],
20 polyfunctional monomer [B], radiation sensitive polymerization initiator [C] and optionally other additives and dissolving these components in a suitable solvent.

The above solvent used to prepare the above composition solution preferably dissolves these components and does not
25 react with these components.

Examples of the solvent are the same as those listed as the solvent used for the production of the above copolymer [A].

Out of these solvents, ethylene glycol ethers, ethylene
30 glycol alkyl ether acetates, diethylene glycol ethers, propylene glycol alkyl ether acetates and other esters are preferred from the viewpoints of solubility, reactivity with each components and ease of forming a coating film.

The above solvents may be used alone or in admixture

of two or more.

A high-boiling solvent may be used in conjunction with the above solvent.

Examples of the high-boiling solvent include

5 N-methylformamide, N,N-dimethylformamide,
N-methylformanilide, N-methylacetamide,
N,N-dimethylacetamide, N-methylpyrrolidone, dimethyl
sulfoxide, benzyl ethyl ether, dihexyl ether,
acetonylacetone, isophorone, caproic acid, caprylic acid,
10 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl
benzoate, diethyl oxalate, diethyl maleate, γ -butyrolactone,
ethylene carbonate, propylene carbonate and phenyl
cellosolve acetate.

The above high-boiling solvents may be used alone or
15 in admixture of two or more.

The composition solution prepared as described above
is filtered with a millipore filter having an opening diameter
of about 0.2 to 0.5 μ m before use.

20 Method of forming a spacer for display panels

A description is subsequently given of the method of
forming the spacer for display panels of the present invention
from the radiation sensitive resin composition of the present
invention.

25 The above composition solution is first applied to the
surface of a substrate to form a coating film.

The composition solution may be applied by suitable
means such as spraying, roll coating, rotational coating,
bar coating or ink jet coating.

30 Thereafter, a film having no fluidity is obtained by
prebaking this coating film to evaporate the solvent.

The prebaking conditions which differ according to the
type and amount of each component are generally a temperature
of 60 to 120°C and a time of 10 to 600 sec.

The film is then exposed to radiation through a mask having a predetermined pattern and developed with a developer to remove unnecessary portions.

The radiation used for exposure is visible radiation, 5 ultraviolet radiation, far ultraviolet radiation, electron radiation, X-radiation, etc., preferably ultraviolet radiation having a wavelength of 190 to 450 nm.

The amount of exposure is preferably 100 to 20,000 J/m², more preferably 150 to 10,000 J/m².

10 The developer may be an alkaline aqueous solution of an inorganic alkali such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate or ammonia water; primary amine such as ethylamine or n-propylamine; secondary amine such as 15 diethylamine or di-n-propylamine; tertiary amine such as triethylamine, methyldiethylamine or N-methylpyrrolidone; alcohol amine such as dimethylethanolamine or triethanolamine; quaternary ammonium salt such as tetramethylammonium hydroxide, tetraethylammonium 20 hydroxide or choline; or cyclic amine such as pyrrole, piperidine, 1,8-diazabicyclo[5.4.0]-7-undecene or 1,5-diazabicyclo[4.3.0]-5-nonene.

The above alkaline aqueous solution may contain suitable amounts of a water-soluble organic solvent such as 25 methanol or ethanol and a surfactant.

Development is preferably carried out at normal temperature for 30 to 180 seconds.

The development may be puddle development, dipping or spraying.

30 After development, rinsing with running water is carried out for 30 to 90 seconds, and compressed air or compressed nitrogen is sprayed to remove water in order to obtain a film having a predetermined pattern.

Thereafter, the film is heated with a heater such as

a hot plate or oven at 150 to 250°C, for example, on a hot plate for 5 to 30 minutes and in an oven for 30 to 90 minutes to be cured, thereby obtaining a spacer having a predetermined shape.

5

Examples

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

10

Synthetic Example 1

4 parts by weight of 2,2'-azobisisobutyronitrile (AIBN) and 200 parts by weight of diethylene glycol ethyl methyl ether were injected into a flask equipped with a stirrer, 5 parts by weight of 1,3-butadiene, 18 parts by weight of methacrylic acid, 40 parts by weight of benzyl methacrylate and 37 parts by weight of n-butyl methacrylate were further injected into the flask, the inside of the flask was substituted with nitrogen, these substances were stirred gently, and the temperature of the reaction solution was raised to 80°C, maintained at that point for 5 hours and then further to 100°C to continue the reaction for another 1 hour. Then, the temperature of the reaction solution was reduced to room temperature to obtain a polymer solution containing a copolymer [A] (solid content = 30.0 wt%). Mw of this copolymer was 27,000. This copolymer is designated as copolymer (A-1).

Synthetic Example 2

4 parts by weight of 2,2'-azobisisobutyronitrile (AIBN) and 200 parts by weight of diethylene glycol ethyl methyl ether were injected into a flask equipped with a stirrer, 5 parts by weight of 1,3-butadiene, 5 parts by weight of styrene, 18 parts by weight of methacrylic acid, 40 parts

by weight of glycidyl methacrylate and 32 parts by weight of tricyclo[5.2.1.0^{2,6}]decan-8-yl methacrylate were further injected into the flask, the inside of the flask was substituted with nitrogen, these substances were stirred
5 gently, and the temperature of the reaction solution was raised to 80°C, maintained at that point for 5 hours and then further to 100°C to continue the reaction for another 1 hour. Then, the temperature of the reaction solution was reduced to room temperature to obtain a polymer solution containing
10 a copolymer [A] (solid content = 29.8 wt%). Mw of this copolymer was 26,000. This copolymer is designated as copolymer (A-2).

Example 1

15 (1) preparation of composition solution

100 parts by weight (solid content) of the copolymer (A-1) as the component [A], 80 parts by weight of KAYARAD DPHA (of Nippon Kayaku Co., Ltd.) and 20 parts by weight of R-1302 (of Dai-ichi Kogyo Seiyaku Co., Ltd.) as the components
20 [B] and 25 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (Irgacure 369 of Ciba Specialty Chemicals Co., Ltd.) as the component [C] were dissolved in propylene glycol monomethyl ether acetate to a solid content of 35 wt% and
25 the obtained solution was filtered with a millipore filter having an opening diameter of 0.2 μm to prepare a composition solution.

(2) formation of spacer pattern

30 The above composition solution was applied to a glass substrate with a spinner and prebaked on a hot plate at 80°C for 3 minutes to form a coating film.

The coating film was then exposed in the air to ultraviolet radiation having an intensity of 100 W/m² at a

wavelength of 365 nm through a mask having a predetermined pattern (10 μm x 10 μm) for 30 seconds. Thereafter, the coating film was developed with a 0.2 wt% aqueous solution of tetramethylammonium hydroxide at 25°C for 1 minute and
 5 rinsed with pure water for 1 minute to remove unnecessary portions so as to obtain a spacer pattern (residue). This spacer pattern was heated in an oven at 220°C for 60 minutes to be cured so as to obtain a spacer pattern having a height of 5 μm .

10

(3) measurement of linear thermal expansion coefficient

The above composition solution was applied to a glass substrate with a spinner and prebaked on a hot plate at 80°C for 3 minutes to form a coating film.

15

This coating film was then exposed in the air to ultraviolet radiation having an intensity of 100 W/m² at a wavelength of 365 nm for 30 seconds, developed with a 0.2 wt% aqueous solution of tetramethylammonium hydroxide at 25°C for 1 minute, rinsed with pure water for 1 minute and
 20 heated in an oven at 220°C for 60 minutes to be cured so as to obtain a film for measurement.

The change of the thickness of this film at each measurement temperature was measured by an ellipsometer (DVA-36LH of Mizojiri Kogaku Kogyosho Co., Ltd.) equipped
 25 with a temperature changer at a temperature elevation rate of 2.5°C/min and a measurement temperature range of 20 to 180°C and plotted with respect to temperature to obtain an inclination ε from its linear approximation so as to obtain a linear thermal expansion coefficient α from the following
 30 expression. T represents the initial thickness of the film.

$$\alpha = \varepsilon/T$$

The linear thermal expansion coefficient of a conventional spacer material is $2.0 \times 10^{-4}/^{\circ}\text{C}$ or lower. It can be said that a linear thermal expansion coefficient higher

than this value is high. The measurement results are shown in Table 1.

(4) evaluation of spacer strength

5 The strength of the spacer pattern obtained in (2) above was evaluated by a micro-compression tester (MCTM-200 of Shimadzu Corporation) at a measurement temperature of 25°C. A load was applied to the spacer by a flat indenter having a diameter of 50 μm at a fixed rate (2.65 mN/sec) to measure
10 breaking load and breaking distortion (a value obtained by dividing compression displacement at the time of breaking by the height of the spacer and expressed in %) when the spacer was cracked or broken. The evaluation results are shown in Table 1.

15

(5) evaluation of thermal compression resistance

 The thermal compression resistance of the spacer pattern obtained in (2) above was evaluated by a micro-compression tester (MCTM-200 of Shimadzu Corporation).
20 A load was applied to the spacer heated at 160°C by a flat indenter having a diameter of 50 μm at a fixed rate (0.28 mN/sec) and removed when the spacer was compressed by 0.75 μm to obtain its recovery factor from the following expression.

25 Recovery factor (%) = $(0.75 - \text{residual distortion}) \times 100 / 0.75$

 It can be said that thermal compression resistance is satisfactory when the recovery factor is 90 % or more. The evaluation results are shown in Table 1.

30 (6) evaluation of thermal dimensional stability

 The spacer pattern obtained in (2) above was heated in an oven at 250°C for 60 minutes to measure the dimensional change rate of its film thickness before and after heating. It can be said that thermal dimensional stability is

satisfactory when this value is 5 % or less. The evaluation results are shown in Table 1.

Example 2

5 A composition solution was prepared and evaluated in the same manner as in Example 1 except that 70 parts by weight of KAYARAD DPHA (of Nippon Kayaku Co., Ltd.) and 30 parts by weight of R-1302 (of Dai-ichi Kogyo Seiyaku Co., Ltd.) were used as the components [B]. The evaluation results are
10 shown in Table 1.

Example 3

 A composition solution was prepared and evaluated in the same manner as in Example 1 except that the copolymer
15 (A-2) was used as the component [A]. The evaluation results are shown in Table 1.

Comparative Example 1

 A composition solution was prepared and evaluated in
20 the same manner as in Example 1 except that the copolymer (A-2) was used as the component [A] and 100 parts by weight of KAYARAD DPHA (of Nippon Kayaku Co., Ltd.) was used as the component [B]. The evaluation results are shown in Table 1.

Table 1

	Linear thermal expansion coefficient/spacer ($\times 10^{-4}/^{\circ}\text{C}$)	Spacer strength		Thermal Compression Resistance (%)	Thermal Dimensional Stability (%)
		Breaking Strength (mN)	Breaking Distortion (%)		
Example 1	4.9	185	56	91	3
Example 2	5.8	180	58	90	4
Example 3	2.6	189	55	91	3
Comparative Example 1	1.9	190	54	93	3

As described above, according to the present invention, there is provided a spacer for display panels which can keep the gap width between substrates constant at normal temperature and high temperatures, can always ensure
5 excellent display quality without being affected by temperature variations and has no restrictions on its shape and position and on the design freedom of a panel. The radiation sensitive resin composition of the present invention has the above characteristic properties and is
10 capable of forming a spacer for display panels having excellent physical properties such as strength, thermal compression resistance and thermal dimensional stability.

What is claimed is:

1. A spacer for display panels which has a linear thermal expansion coefficient of higher than $2.0 \times 10^{-4}/^{\circ}\text{C}$ and $8.0 \times 10^{-4}/^{\circ}\text{C}$ or lower.

5

2. A radiation sensitive resin composition comprising [A] a copolymer of (a1) an unsaturated carboxylic acid and/or an unsaturated carboxylic anhydride and (a2) an unsaturated compound other than the component (a1), [B] a polyfunctional
10 unsaturated monomer and [C] a radiation sensitive polymerization initiator, wherein a cured film of the radiation sensitive resin composition has a linear thermal expansion coefficient of higher than $2.0 \times 10^{-4}/^{\circ}\text{C}$ and $8.0 \times 10^{-4}/^{\circ}\text{C}$ or lower and the radiation sensitive resin
15 composition is used to form the spacer for display panels of claim 1.

3. The radiation sensitive resin composition of claim 2, wherein the content of the component [B] is 10 to 150 parts
20 by weight based on 100 parts by weight of the component [A] and the component [B] contains a polyfunctional (meth)acrylic ester having a urethane bond in an amount of 10 to 50 wt% based on the total amount of the compound [B].

25 4. A liquid crystal display device comprising the spacer for display panels of claim 1.