

FORMATION OF PROJECTIONS AND SPACERS AND RADIATION SENSITIVE
RESIN COMPOSITION FOR THE SAME

Field of the Invention

5 The present invention relates to a radiation sensitive resin composition used for the formation of projections and/or spacers for vertically aligned liquid crystal display devices, projections and spacers for vertically aligned liquid crystal display devices made of the radiation
10 sensitive resin composition, a vertically aligned liquid crystal display device comprising the projections and/or the spacers, and a method of forming the projections and/or the spacers.

15 Description of the Prior Art

 A liquid crystal display device is most widely used in flat panel displays. Along with the spread of OA equipment such as personal computers and word processors as well as liquid crystal TV's in recent years, requirements for the
20 display quality of TFT (thin film transistor) liquid crystal displays (TFT-LCD's) are becoming more and more severe.

 Out of the TFT-LCD's, TN (Twisted Nematic) LCD is now the most popular. This LCD is manufactured by forming two polarizing films whose aligning directions differ from each
25 other by 90° on the outer sides of two substrates having transparent electrodes (to be referred to as "transparent electrode substrates" hereinafter) and an alignment film on the inner sides of the two transparent electrode substrates, interposing a nematic liquid crystal between the alignment
30 films and twisting the aligning direction of the liquid crystal at 90° from one electrode side to the other electrode side.

 When non-polarized light is incident upon the TN LCD, linearly polarized light which has passed through one of the

polarizers passes through the liquid crystal while its polarization direction is shifted, whereby it can pass through the other polarizer, resulting in a bright state. When voltage is applied to the both transparent electrodes to make liquid crystal molecules upright, linearly polarized light reaching the liquid crystal passes through the liquid crystal without shifting its polarization direction, whereby it cannot pass through the other polarizer, resulting in a dark state. Thereafter, when the application of voltage is stopped, the LCD returns to the bright state.

Although the above TN LCD becomes equal or superior to a cathode-ray tube(CRT) in terms of contrast and color reproducibility on the front side due to technical improvements in recent years, it has a big problem to be solved, that is, a narrow viewing angle.

As one of the solutions to this problem, an MVA (Multi-domain Vertically Aligned) LCD has been developed.

This vertically aligned liquid crystal display device makes use of a birefringence mode in which a negative liquid crystal having negative anisotropy in dielectric constant and a vertical alignment film are combined together and not an optical rotatory mode as in TN LCD as disclosed in "Liquid Crystals", Vol. 3, No. 2, p. 117 (1999) and JP-A 11-258605 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). Even when no voltage is applied, as the aligning direction of the liquid crystal near the alignment film is kept almost vertical, the MVA LCD has excellent contrast and viewing angle and does not need rubbing for aligning the liquid crystal. Therefore, the MVA LCD is also excellent in terms of production process.

In the vertically aligned liquid crystal display device, a transparent electrode on the display side has a slit in one pixel area and a projection having a slope at a position different from the slit of the transparent

electrode, such as a projection shaped like a triangular cone or semi-convex lens, is formed in the same pixel area on the transparent electrode substrate on the light incident side as domain restricting means for enabling the liquid crystal
5 in one pixel area to take a plurality of aligning directions.

In general, in the liquid crystal display of the prior art, in order to keep the interval between the two transparent electrode substrates, that is, the cell gap constant, spherical or rod-like spacers made of a resin or ceramic are
10 used. The spacers are scattered over one of the substrates, when the two substrates are laminated, and the cell gap is determined by the diameter of the spacers.

Since a certain measure of difference in diameter among the projections and spacers cannot be eliminated, as means
15 of avoiding a problem such as nonuniformity in the cell gap caused by the above difference, JP-A 2001-201750 proposes a method of forming projections and spacers by using a photoresist. Although this method has advantages that fine patterning is possible and that shape control is easy, the
20 above publication fails to disclose the composition of the photoresist and the performance of the formed projections and spacers.

The requirements for the photoresist used for the formation of projections and spacers for vertically aligned
25 liquid crystal display devices are given below.

That is, the photoresist should have high film hardness, provide projections and spacers having excellent surface smoothness and hardly produce the development residue or stain on the substrate of a portion not exposed to radiation.
30 The obtained vertically aligned liquid crystal display device should be free from sticking and display nonuniformity.

The applicant of the present invention has already proposed a radiation sensitive resin composition for forming

projections and spacers at the same time, which comprises [A] a copolymer of (a1) an unsaturated carboxylic acid and/or an unsaturated carboxylic anhydride, (a2) an epoxy group-containing unsaturated compound and (a3) an
5 unsaturated compound other than these, [B] an unsaturated polymerizable compound and [C] a radiation sensitive polymerization initiator, projections and spacers made of the radiation sensitive resin composition, and a liquid crystal display device comprising the projections and the
10 spacers (JP-A 2003-29405).

However, the development of a radiation sensitive resin composition useful for the formation of projections and spacers for vertically aligned liquid crystal display devices has just begun. The development of a new radiation
15 sensitive resin composition capable of forming projections and spacers having excellent performance is now technically very important to cope with the fast spread of TFT-LCD and the requirements for TFT-LCD which are becoming more and more severe.

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Summary of the Invention

It is an object of the present invention which has been made in view of the above situation to provide a radiation sensitive resin composition used for the formation of
25 projections and/or spacers for vertically aligned liquid crystal display devices, more specifically a radiation sensitive resin composition which can provide projections and spacers having excellent surface smoothness, hardly produces the development residue on the substrate of an
30 unexposed portion, hardly causes the separation of the projections and spacers, and can provide a vertically aligned liquid crystal display device having excellent vertically alignability for liquid crystals, high voltage retainability and a short after-image erase time and almost free from

sticking and display nonuniformity, and a method of forming the projections and/or the spacers.

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

5 According to the present invention, firstly, the above objects and advantages of the present invention are attained by a radiation sensitive resin composition which comprises (A) at least one alkali-soluble resin selected from the group consisting of a novolak resin having a weight average
10 molecular weigh in terms of polystyrene measured by gel permeation chromatography of 2,000 to 20,000 and a hydroxystyrene resin having a weight average molecular weight in terms of polystyrene measured by gel permeation chromatography of 10,000 to 100,000, (B) a polyfunctional
15 monomer or a combination of a polyfunctional monomer and a monofunctional monomer and (C) a photopolymerization initiator, and which is used to form projections and/or spacers in a vertically aligned liquid crystal display device having an after-image erase time of 100 sec or less.

20 According to the present invention, secondly, the above objects and advantages of the present invention are attained by projections for vertically aligned liquid crystal display devices which are made of the above radiation sensitive resin composition.

25 According to the present invention, thirdly, the above objects and advantages of the present invention are attained by spacers for vertically aligned liquid crystal display devices which are made of the above radiation sensitive resin composition.

30 According to the present invention, in the fourth place, the above objects and advantages of the present invention are attained by a method of forming projections and/or spacers for vertically aligned liquid crystal display devices, comprising the steps of:

- (a) forming a coating film of the above radiation sensitive resin composition on a substrate;
- (b) exposing part of the coating film to radiation;
- (c) developing the coating film after exposure to form a pattern; and
- (d) heating the coating film after development.

According to the present invention, in the fifth place, the above objects and advantages of the present invention are attained by a vertically aligned liquid crystal display device comprising the above projections and/or the above spacers and having an after-image erase time of 100 sec or less.

The present invention will be described in detail hereinafter.

15 Radiation sensitive resin composition

The components of the radiation sensitive resin composition used for the formation of projections and/or spacers for vertically aligned liquid crystal display devices of the present invention (to be simply referred to as "radiation sensitive resin composition" hereinafter) will be described hereinafter.

(A) alkali-soluble resin

The alkali-soluble resin used in the present invention is a novolak resin and/or a hydroxystyrene resin.

25 The above novolak resin is obtained by polycondensing a phenol and an aldehyde in the presence of an acid catalyst.

Examples of the phenol used for the preparation of the novolak resin include phenol, o-cresol, m-cresol, p-cresol, 2,3-dimethylphenol, 2,4-dimethylphenol, 2,5-dimethylphenol, 2,6-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol, 2,3,5-trimethylphenol, 3,4,5-trimethylphenol, resorcinol, 2-methylresorcinol, 4-ethylresorcinol, hydroquinone, methylhydroquinone, catechol, 4-methylcatechol,

pyrrogallol, phloroglucinol, thymol and isothymol.

Out of these phenols, preferred are phenol, m-cresol, p-cresol, 2,3-dimethylphenol, 2,4-dimethylphenol, 2,5-dimethylphenol, 3,4-dimethylphenol, 3,5-dimethylphenol
5 and 2,3,5-trimethylphenol.

The above phenols may be used alone or in combination of two or more. When two or more of the above phenols are used in combination, preferred combinations include a combination of m-cresol and p-cresol, combination of
10 m-cresol and 2,3-dimethylphenol, combination of m-cresol and 2,4-dimethylphenol, combination of m-cresol and 2,5-dimethylphenol, combination of m-cresol and 2,3,5-trimethylphenol, combination of phenol, 2,3-dimethylphenol and 3,4-dimethylphenol, combination of
15 m-cresol, 2,3-dimethylphenol and 2,4-dimethylphenol, combination of m-cresol, 2,3-dimethylphenol and 3,4-dimethylphenol, combination of m-cresol, 2,4-dimethylphenol and 2,5-dimethylphenol, combination of m-cresol, 2,5-dimethylphenol and 3,4-dimethylphenol,
20 combination of m-cresol, 2,3-dimethylphenol and 2,3,5-trimethylphenol, combination of m-cresol, p-cresol and 2,3-dimethylphenol, combination of m-cresol, p-cresol and 2,4-dimethylphenol, combination of m-cresol, p-cresol and 2,5-dimethylphenol, and combination of m-cresol,
25 p-cresol and 2,3,5-trimethylphenol.

Examples of the aldehyde to be polycondensed with the phenol include formaldehyde, trioxan, paraformaldehyde, benzaldehyde, acetaldehyde, propylaldehyde, phenylacetaldehyde, α -phenylpropylaldehyde,
30 β -phenylpropylaldehyde, o-hydroxybenzaldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, o-methylbenzaldehyde, m-methylbenzaldehyde, p-methylbenzaldehyde, furfural, glyoxal, glutaraldehyde, terephthalaldehyde and isophthalaldehyde. Out of these

aldehydes, formaldehyde and o-hydroxybenzaldehyde are preferred.

The above aldehydes may be used alone or in combination of two or more.

5 The amount of the aldehyde is preferably 0.4 to 2.0 mol, more preferably 0.6 to 1.5 mol based on 1 mol of the phenol.

10 The novolak resin in the present invention is particularly preferably a polycondensate of m-cresol and formaldehyde, polycondensate of m-cresol, p-cresol and formaldehyde, polycondensate of m-cresol, 2,3-xyleneol and formaldehyde, polycondensate of m-cresol, 2,4-xyleneol and formaldehyde or polycondensate of m-cresol, 2,5-xyleneol and formaldehyde.

15 Examples of the acid catalyst used for the polycondensation of the phenol and the aldehyde include hydrochloric acid, nitric acid, sulfuric acid, formic acid, oxalic acid, acetic acid, methanesulfonic acid and p-toluenesulfonic acid.

20 These acid catalysts may be used alone or in combination of two or more.

The amount of the acid catalyst is generally 1×10^{-5} to 5×10^{-1} mol based on 1 mol of the phenol.

25 The polycondensation reaction between the phenol and the aldehyde is carried out in the absence or presence of a solvent.

30 Examples of the solvent include alcohols such as methanol, ethanol, n-propanol, i-propanol and n-butanol; ethers such as tetrahydrofuran, dioxane and propylene glycol monomethyl ether; and ketones such as ethyl methyl ketone, methyl isobutyl ketone and 2-heptanone.

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

The amount of the solvent when the polycondensation

reaction is carried out in the solvent is generally 20 to 1,000 parts by weight, preferably 50 to 800 parts by weight based on 100 parts by weight of the total of the reaction raw materials.

5 The temperature of the polycondensation reaction which can be suitably adjusted according to the reactivities of the reaction raw materials is generally 10 to 200°C.

 To carry out the polycondensation reaction, (i) a phenol, an aldehyde and an acid catalyst are fed to a reactor
10 at the same time, or (ii) an acid catalyst is fed to a reactor and then a phenol and an aldehyde are added along with the proceeding of a reaction in the presence of the acid catalyst.

 To collect a novolak resin after the end of the polycondensation reaction, (iii) the inside temperature of
15 a reaction system is raised to 130 to 230°C and volatile matter is removed under reduced pressure to collect the novolak resin, or (iv) a novolak resin obtained by polycondensation in the absence of a solvent or the novolak resin collected by the above method (iii) is dissolved in a good solvent such
20 as ethylene glycol methyl ether acetate, diethylene glycol ethyl methyl ether, methyl 3-methoxypropionate, ethyl lactate, propylene glycol monomethyl ether, methyl isobutyl ketone, 2-heptanone, dioxane, methanol or ethyl acetate, the resulting solution is mixed with water or a poor solvent such
25 as n-hexane or n-heptane to precipitate a resin, and the precipitated resin is separated to collect a polymer fraction of the novolak resin.

 The weight average molecular weight in terms of polystyrene measured by gel permeation chromatography (GPC)
30 (to be referred to as "Mw" hereinafter) of the novolak resin is 2,000 to 20,000, preferably 3,000 to 15,000. A radiation sensitive resin composition having excellent coatability, developability, sensitivity and heat resistance can be obtained by using the novolak resin having the above Mw.

In the present invention, the above novolak resins may be used alone or in combination of two or more.

The above hydroxystyrene resin is a polymer of alone or in combination of two or more of hydroxystyrenes such as
 5 o-hydroxystyrene, m-hydroxystyrene, p-hydroxystyrene, o-hydroxy- α -methylstyrene, m-hydroxy- α -methylstyrene and p-hydroxy- α -methylstyrene or a copolymer of at least one hydroxystyrene and at least other polymerizable monomer.

Examples of the other polymerizable monomer include
 10 styrene, α -alkylstyrenes (alkyl group is a linear or branched alkyl group having 1 to 10 carbon atoms, the same shall apply hereinafter) and styrene derivatives obtained by substituting the benzene ring of styrene by at least one substituent such as alkyl group, haloalkyl group, linear or
 15 branched alkoxy group having 1 to 10 carbon atoms, halogen atom, nitro group, cyano group, amido group or ester group; diolefins such as 1,3-butadiene, isoprene and chloroprene; (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl
 20 (meth)acrylate, n-butyl (meth)acrylate, sec-butyl (meth)acrylate, t-butyl (meth)acrylate, n-pentyl (meth)acrylate, neopentyl (meth)acrylate, cyclohexyl (meth)acrylate, 4-i-amylcyclohexyl (meth)acrylate, allyl (meth)acrylate, propargyl (meth)acrylate, phenyl
 25 (meth)acrylate, benzyl (meth)acrylate, phenethyl (meth)acrylate, 1-naphthyl (meth)acrylate, 9-anthracenyl (meth)acrylate, cumyl (meth)acrylate, adamantyl (meth)acrylate, tricyclo[5.2.1.0^{2,6}]decan-8-yl (meth)acrylate, anthraquinonyl (meth)acrylate, piperonyl
 30 (meth)acrylate, salicyl (meth)acrylate, cresyl (meth)acrylate, glycidyl (meth)acrylate, 1,1,1-trifluoroethyl (meth)acrylate, pentafluoroethyl (meth)acrylate, heptafluoro-n-propyl (meth)acrylate, heptafluoro-i-propyl (meth)acrylate, triphenyl methyl

(meth)acrylate, 2-(N,N-dimethylamino)ethyl (meth)acrylate, 3-(N,N-dimethylamino)propyl (meth)acrylate, furyl (meth)acrylate and furfuryl (meth)acrylate; and (meth)acrylamide, N,N-dimethyl (meth)acrylamide, 5 N,N,-diethyl (meth)acrylamide, N,N-di-n-propyl (meth)acrylamide, N,N-di-i-propyl (meth)acrylamide, N-phenyl (meth)acrylamide, N-anthracenyl (meth)acrylamide amide, (meth)acrylonitrile, acrolein, vinyl fluoride, vinylidene fluoride, vinyl chloride, vinylidene chloride, 10 N-vinylpyrrolidone, 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, vinyl acetate, N-phenylmaleimide, N-(4-hydroxyphenyl)maleimide, N-cyclohexylmaleimide and N-(meth)acryloylphthalimide.

The content of the other polymerizable monomer in the 15 copolymer of the hydroxystyrene and the other polymerizable monomer is preferably 30 wt% or less, more preferably 20 wt% or less based on the total of the monomers. When the content of the other polymerizable monomer is higher than 30 wt%, the alkali solubility of the obtained copolymer may be 20 unsatisfactory.

The hydroxystyrene resin particularly preferred in the present invention is, for example, poly(p-hydroxystyrene), copolymer of p-hydroxystyrene and o-methyl-p-hydroxystyrene or copolymer of p-hydroxystyrene 25 and styrene.

The hydroxystyrene resin can be prepared by polymerizing a hydroxystyrene and optionally other polymerizable monomer with a polymerization initiator in the presence of a solvent.

30 Examples of the solvent used for the preparation of the hydroxystyrene resin include alcohols such as methanol, ethanol and diacetone alcohol; ethers such as tetrahydrofuran, tetrahydropyran and dioxane; ethylene glycol ethers such as ethylene glycol monomethyl ether and

ethylene glycol monoethyl ether; ethylene glycol alkyl ether acetates such as ethylene glycol methyl ether acetate and ethylene glycol ethyl ether acetate; diethylene glycol ethers such as diethylene glycol monomethyl ether,

5 diethylene glycol monoethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether and diethylene glycol ethyl methyl ether; propylene glycol ethers such as propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-n-propyl ether

10 and propylene glycol mono-n-butyl ether; propylene glycol alkyl ether acetates such as propylene glycol methyl ether acetate, propylene glycol ethyl ether acetate, propylene, propylene glycol n-propyl ether acetate and propylene glycol n-butyl ether acetate; propylene glycol alkyl ether

15 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

20 and 4-hydroxy-4-methyl-2-pentanone; and other esters such as methyl acetate, ethyl acetate, n-propyl acetate, n-butyl acetate, methyl 2-hydroxy-2-methylpropionate, ethyl 2-hydroxy-2-methylpropionate, methyl hydroxyacetate, ethyl hydroxyacetate, n-butyl hydroxyacetate, methyl lactate,

25 ethyl lactate, n-propyl lactate, n-butyl lactate, methyl 3-hydroxypropionate, ethyl 3-hydroxypropionate, n-propyl 3-hydroxypropionate, n-butyl 3-hydroxypropionate, methyl 2-hydroxy-3-methylbutanoate, methyl methoxyacetate, ethyl methoxyacetate, n-propyl methoxyacetate, n-butyl

30 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
 2-methoxypropionate, ethyl 2-methoxypropionate, n-propyl
 2-methoxypropionate, n-butyl 2-methoxypropionate, methyl
 2-ethoxypropionate, ethyl 2-ethoxypropionate, n-propyl
 5 2-ethoxypropionate, n-butyl 2-ethoxypropionate, 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
 10 3-ethoxypropionate, ethyl 3-ethoxypropionate, n-propyl
 3-ethoxypropionate, 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
 15 3-n-butoxypropionate, n-propyl 3-n-butoxypropionate and
 n-butyl 3-n-butoxypropionate.

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

The amount of the solvent in the polymerization
 20 reaction is preferably 20 to 1,000 parts by weight, more preferably 100 to 500 parts by weight based on 100 parts by weight of the total of the reaction raw materials.

The polymerization initiator used for the preparation of the hydroxystyrene resin is generally a known radical
 25 polymerization initiator. Examples of the known radical polymerization initiator include azo compounds such as 2,2'-azobisisobutyronitrile,
 2,2'-azobis-(2,4-dimethylvaleronitrile) and 2,2'-azobis-(4-methoxy-2,4-dimethylvaleronitrile);
 30 organic peroxides such as benzoyl peroxide, lauroyl peroxide, t-butyl peroxyphthalate and 1,1'-bis-(t-butylperoxy)cyclohexane; and hydrogen peroxide. When a peroxide is used as the radical polymerization initiator, a reducing agent may be used in combination with

the radical polymerization initiator as a redox initiator.

As an alternative method of preparing the hydroxystyrene resin, one or more than one monomer prepared by protecting the phenolic hydroxyl group of the above
5 hydroxystyrene with a protection group such as an alkyl group, acetyl group or phenacyl group and optionally the above other polymerizable monomer are polymerized and hydrolyzed to eliminate the protection group.

In the present invention, the transparency and
10 softening point of the hydroxystyrene resin may be improved by hydrogenation or the like before use.

Mw of the hydroxystyrene resin is 10,000 to 100,000, preferably 15,000 to 50,000. By using the hydroxystyrene resin having the above Mw, a radiation sensitive resin
15 composition having a pattern shape, resolution, developability and heat resistance and good balance between developability and sensitivity can be obtained.

Commercially available products of the hydroxystyrene resin include Malkarincar M and Malkarincar PHM-C (of Maruzen
20 Petrochemical Co., Ltd.) and VP-15000 (of Nippon Soda Co., Ltd.) which are homopolymers and copolymers of a hydroxystyrene and partially hydrogenated products thereof.

In the present invention, the above hydroxystyrene resins may be used alone or in combination of two or more
25 and may be mixed with the above novolak resin.

(B) polyfunctional monomer or a combination of a polyfunctional monomer and a monofunctional monomer

Examples of the polyfunctional monomer in the present
30 invention include di(meth)acrylates of an alkylene glycol such as ethylene glycol or propylene glycol; di(meth)acrylates of a polyalkylene glycol such as polyethylene glycol or polypropylene glycol; poly(meth)acrylates of a polyhydric alcohol having 3 or more

hydroxyl groups such as glycerin, trimethylolpropane, pentaerythritol or dipentaerythritol and dicarboxylic acid modified products thereof; oligo(meth)acrylates such as polyester, epoxy resin, urethane resin, alkyd resin, 5 silicone resin and spiran resin; di(meth)acrylates of a polymer having a hydroxyl group at both terminals such as poly-1,3-butadiene having a hydroxyl group at both terminals, polyisoprene having a hydroxyl group at both terminals or polycaprolactone having a hydroxyl group at both terminals; 10 and tris[2-(meth)acryloyloxyethyl]phosphate.

Out of these polyfunctional monomers, poly(meth)acrylates of a polyhydric alcohol having 3 or more hydroxyl groups and dicarboxylic acid modified products thereof are preferred. Specifically, trimethylolpropane 15 triacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, succinic acid modified product of pentaerythritol triacrylate, succinic acid modified product of pentaerythritol trimethacrylate, pentaerythritol 20 tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol tetraacrylate, dipentaerythritol tetramethacrylate, dipentaerythritol hexaacrylate and dipentaerythritol hexamethacrylate are preferred, and trimethylolpropane triacrylate, pentaerythritol 25 triacrylate and dipentaerythritol hexaacrylate are particularly preferred because the obtained projections and spacers have high strength and excellent surface smoothness and a stain and the film residue are hardly produced in an area other than a portion where projections and/or spacers 30 are formed.

The above polyfunctional monomers may be used alone or in combination of two or more.

The amount of the polyfunctional monomer in the present invention is preferably 5 to 1,000 parts by weight, more

preferably 20 to 500 parts by weight based on 100 parts by weight of the alkali-soluble resin (A).

When the amount of the polyfunctional monomer is smaller than 5 parts by weight, the strength and surface smoothness of the obtained projections and spacers may become unsatisfactory. When the amount is larger than 1,000 parts by weight, alkali developability may deteriorate, or a stain and the film residue may be produced in an area other than a portion where projections and/or spacers are formed.

10 In the present invention, part of the polyfunctional monomer may be substituted by a monofunctional monomer.

Examples of the above monofunctional monomer include the same monomers as the compounds enumerated for the hydroxystyrene and the other polymerizable monomer of the above hydroxystyrene resin; unsaturated monocarboxylic acids such as (meth)acrylic acid, crotonic acid, α -chloroacrylic acid and cinnamic acid; unsaturated dicarboxylic acids and anhydrides thereof such as maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride and mesaconic acid; unsaturated polycarboxylic acids having three or more carboxyl groups and anhydrides thereof; mono[(meth)acryloyloxyalkyl]esters of a polycarboxylic acid having two or more carboxyl groups such as

20 mono[2-(meth)acryloyloxyethyl]succinate and mono[2-(meth)acryloyloxyethyl]phthalate; unsaturated carboxylic acids such as mono(meth)acrylates of a polymer having a carboxyl group and a hydroxyl group at both terminals exemplified by ω -carboxypolycaprolactone

25 mono(meth)acrylate; and other unsaturated carboxylates such as methoxydiethylene glycol (meth)acrylate, methoxytriethylene glycol (meth)acrylate, methoxypropylene glycol (meth)acrylate, methoxydipropylene glycol (meth)acrylate and 2-hydroxy-3-phenoxypropyl

30

(meth)acrylate.

Out of these monofunctional monomers, preferred are mono(2-acryloyloxyethyl)succinate (trade name: M-5300, manufactured by Toagosei Chemical Industry Co., Ltd.),

5 mono(2-methacryloyloxyethyl)succinate,
 ω -carboxypolycaprolactone monoacrylate,
 ω -carboxypolycaprolactone monomethacrylate,
methoxytriethylene glycol acrylate, methoxytriethylene
glycol methacrylate, methoxydipropylene glycol acrylate,
10 methoxydipropylene glycol methacrylate,
2-hydroxy-3-phenoxypropyl acrylate and
2-hydroxy-3-phenoxypropyl methacrylate.

The above monofunctional monomers may be used alone or in combination of two or more.

15 The amount of the monofunctional monomer is preferably 90 wt% or less, more preferably 50 wt% or less based on the total of the polyfunctional monomer and the monofunctional monomer.

20 (C) photopolymerization initiator

The term "photopolymerization initiator" as used in the present invention means a compound which forms active species capable of initiating the polymerization of the above component (B), such as a radical, anion or cation, by causing

25 decomposition or the cleavage of a bond upon exposure to radiation (to be referred to as "exposure" hereinafter).

The photopolymerization initiator is, for example, a biimidazole compound, acetophenone compound, other optical radical generator or a compound having a trihalomethyl group.

30 Examples of the biimidazole compound include
2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole,
2,2'-bis(2-bromophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole,

2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,

2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,

5 2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetraphenyl-
1,2'-biimidazole,

2,2'-bis(2-bromophenyl)-4,4',5,5'-tetraphenyl-1,2'-
biimidazole,

2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-
10 biimidazole and

2,2'-bis(2,4,6-tribromophenyl)-4,4',5,5'-tetraphenyl-
1,2'-biimidazole.

The above biimidazole-based compounds have excellent
solubility in a solvent, do not produce foreign matter such
15 as an undissolved product and a precipitate, have high
sensitivity and contrast, can fully promote a curing reaction
by exposure with a small amount of energy and does not cause
a curing reaction in an unexposed portion. Therefore, the
coating film after exposure is clearly divided into a cured
20 portion insoluble in an alkali developer and an uncured
portion having high solubility in an alkali developer,
thereby making it possible to form projections and spacers
which are not missing, lost or undercut.

Examples of the above acetophenone compound include
25 1-phenyl-2-hydroxy-2-methylpropan-1-one,
1-(4-i-propylphenyl)-2-hydroxy-2-methylpropan-1-one,
4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone,
1-hydroxycyclohexylphenyl ketone,
2,2-dimethoxy-2-phenylacetophenone,
30 2,2-dimethoxy-1,2-diphenylethan-1-one,
1-[4-(methylthio)phenyl]-2-methyl-2-morpholinopropan-1-
one and
1-(4-morpholinophenyl)-2-benzyl-2-dimethylaminobutan-1-
one.

Examples of the above other optical radical generator include benzophenone, 3,3'-dimethyl-4-methoxybenzophenone, 2,4-diethylthioxanthone, 4-azidobenzaldehyde, 4-azidoacetophenone, 4-azidobenzalacetophenone, 5 azidopyrene, 4-diazodiphenylamine, 4-diazo-4'-methoxydiphenylamine, 4-diazo-3-methoxydiphenylamine, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, dibenzoyl, benzoin isobutyl ether, 10 N-phenylthioacridone and triphenylpyrylium perchlorate.

Examples of the above compound having a trihalomethyl group include 1,3,5-tris(trichloromethyl)-s-triazine, 1,3-bis(trichloromethyl)-5-(2-chlorophenyl)-s-triazine, 1,3-bis(trichloromethyl)-5-(4-chlorophenyl)-s-triazine, 15 1,3-bis(trichloromethyl)-5-(2-methoxyphenyl)-s-triazine and 1,3-bis(trichloromethyl)-5-(4-methoxyphenyl)-s-triazine.

Out of the above acetophenone compounds, other optical radical generators and compounds having a trihalomethyl 20 group, 1-phenyl-2-hydroxy-2-methylpropan-1-one, 1-[4-(methylthio)phenyl]-2-methyl-2-morpholinopropan-1-one and 1-(4-morpholinophenyl)-2-benzyl-2-dimethylaminobutan-1-one are preferred because they have high sensitivity, and 25 the formed projections and spacers hardly come off from the substrate during development and have high strength.

In the present invention, the above photopolymerization initiators may be used alone or in combination of two or more.

30 In the present invention, at least one selected from the group consisting of a sensitizer, a curing accelerator and an optical crosslinking agent or optical sensitizer composed of a polymer compound (to be referred to as "polymer optical crosslinking/sensitizing agent" hereinafter) may be

used in combination with the above photopolymerization initiator as required.

Examples of the above sensitizer include

- 4,4'-bis(dimethylamino)benzophenone,
- 5 4,4'-bis(diethylamino)benzophenone,
- 4-diethylaminoacetophenone, 4-dimethylaminopropiophenone,
- ethyl-4-dimethylaminobenzoate,
- 2-ethylhexyl-1,4-dimethylaminobenzoate,
- 2,5-bis(4-diethylaminobenzal)cyclohexanone,
- 10 7-diethylamino-3-(4-diethylaminobenzoyl)coumarin and
- 4-(diethylamino)chalcone.

Examples of the above curing accelerator include chain transfer agents such as 2-mercaptobenzoimidazole,

- 2-mercaptobenzothiazole, 2-mercaptobenzoxazole,
- 15 2,5-dimercapto-1,3,4-thiadiazole,
- 2-mercapto-4,6-dimethylaminopyridine,
- 1-phenyl-5-mercapto-1H-tetrazole and
- 3-mercapto-4-methyl-4H-1,2,4-triazole.

Further, the above polymer optical

- 20 crosslinking/sensitizing agent is a polymer compound having
- a functional group which can serve as an optical crosslinking
- agent and/or optical sensitizer in the main chain and/or side
- chain. Examples of the polymer compound include a condensate
- of 4-azidobenzaldehyde and polyvinyl alcohol, condensate of
- 25 4-azidobenzaldehyde and phenol novolak resin, homopolymer
- and copolymer of 4-acryloylphenylcinnamoyl ester,
- poly-1,4-butadiene and poly-1,2-butadiene.

Out of these sensitizers, curing accelerators and polymer optical crosslinking/sensitizing agents,

- 30 4,4'-bis(dimethylamino)benzophenone,
- 4,4'-bis(diethylamino)benzophenone and
- 2-mercaptobenzothiazole are preferred because they have high
- sensitivity and the formed projections and spacers hardly
- fall off from the substrate during development and have high

strength.

In the present invention, the photopolymerization initiator is preferably a combination of a biimidazole compound and at least one selected from the group consisting of acetophenone compound, benzophenone sensitizer and thiazole-based curing accelerator.

Preferred examples of the above combination include a combination of

2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole and 4,4'-bis(diethylamino)benzophenone, combination of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole, 4,4'-bis(diethylamino)benzophenone and 1-(4-morpholinophenyl)-2-benzyl-2-dimethylaminobutan-1-one, combination of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole, 4,4'-bis(diethylamino)benzophenone and 1-[4-(methylthio)phenyl]2-methyl-2-morpholinopropan-1-one, combination of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole, 4,4'-bis(dimethylamino)benzophenone, 1-[4-(methylthio)phenyl]2-methyl-2-morpholinopropan-1-one and 2-mercaptobenzothiazole, combination of 2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole and 4,4'-bis(diethylamino)benzophenone, combination of 2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-biimidazole, 4,4'-bis(diethylamino)benzophenone and 1-(4-morpholinophenyl)-2-benzyl-2-dimethylaminobutan-1-one, combination of 2,2'-bis(2,4-dibromophenyl)-4,4',5,5'-tetraphenyl-1,2'-

biimidazole, 4,4'-bis(diethylamino)benzophenone and
1-[4-(methylthio)phenyl]2-methyl-2-morpholinopropan-1-
one, and combination of
2,2'-bis(2,4,6-trichlorophenyl)-4,4',5,5'-tetraphenyl-
5 1,2'-biimidazole, 4,4'-bis(dimethylamino)benzophenone,
1-[4-(methylthio)phenyl]2-methyl-2-morpholinopropan-1-
one and 2-mercaptobenzothiazole.

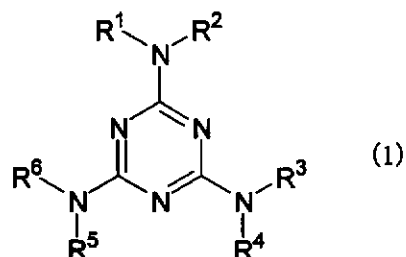
In the present invention, the total amount of the
acetophenone compound, the other optical radical generator
10 and the compound having a trihalomethyl group is preferably
80 wt% or less of the total of the photopolymerization
initiators, the total amount of the sensitizer and the curing
accelerator is preferably 80 wt% or less of the total of the
photopolymerization initiators, and further the amount of
15 the polymer optical crosslinking/sensitizing agent is
preferably 200 parts or less, more preferably 180 parts or
less by weight based on 100 parts by weight of the biimidazole
compound.

The amount of the photopolymerization initiator in the
20 present invention is preferably 0.01 to 500 parts by weight,
more preferably 1 to 300 parts by weight, particularly
preferably 10 to 200 parts by weight based on 100 parts by
weight of the component (B). When the amount of the
photopolymerization initiator is smaller than 0.01 part by
25 weight, some of the formed projections and spacers may be
missing, lost or undercut due to incomplete curing by
exposure and when the amount is larger than 500 parts by weight,
the formed projections and spacers may fall off from the
substrate during development, and a stain and the film
30 residue may be produced in an area other than a portion where
projections and/or spacers are formed.

(D) melamine compound

Preferably, the radiation sensitive resin composition

of the present invention further comprises a melamine compound represented by the following formula (1) (to be referred to as "melamine compound (D)" hereinafter):



5

wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are each independently a hydrogen atom or $-\text{CH}_2\text{OR}$, and R is a hydrogen atom or linear or branched alkyl group having 1 to 6 carbon atoms.

Examples of the melamine compound (D) include

- 10 melamine; alkylolmelamines such as N,N-dimethylolmelamine, N,N,N',N'-tetramethylolmelamine, hexamethylolmelamine and hexa-n-butyrolmelamine; and alkoxymethylmelamines such as N,N-di(methoxymethyl)melamine, N,N,N',N'-tetra(methoxymethyl)melamine,
 15 hexa(methoxymethyl)melamine and hexa(n-butoxymethyl)melamine.

Commercially available products of the melamine compound (D) include Simel 202, 238, 266, 267, 272, 300, 301, 303, 325, 327, 370, 701, 1141, 1156 and 1158 (of Mitsui
 20 Cyanamid Co., Ltd.), Nicalak Mx-31, -40, -45, -032, -706, -708 and -750, Nicalak Ms-11 and -001 and Nicalak Mw-22 and -30 (of Sanwa Chemical Co., Ltd.).

In the present invention, the above melamine compounds (D) may be used alone or in combination of two or more.

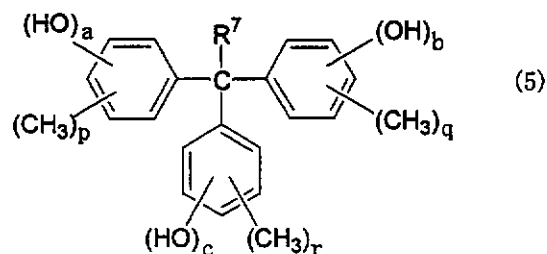
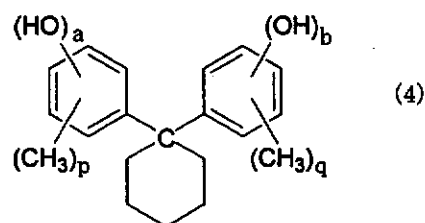
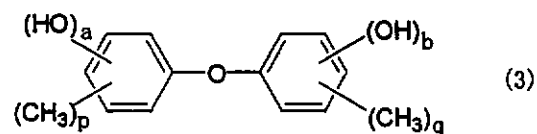
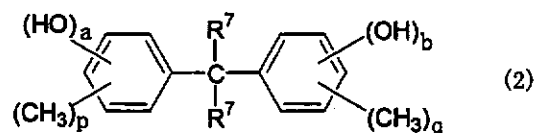
25 The amount of the melamine compound (D) in the present invention is preferably 1 to 500 parts by weight, more preferably 5 to 250 parts by weight based on 100 parts by weight of the alkali-soluble resin (A). By using the melamine compound (D) in this range, a composition showing
 30 suitable solubility in an alkali developer can be obtained,

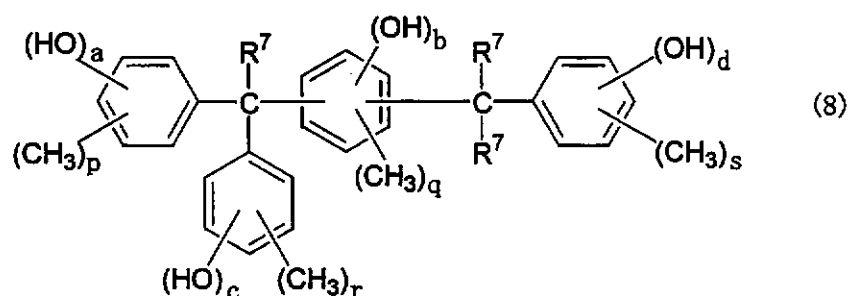
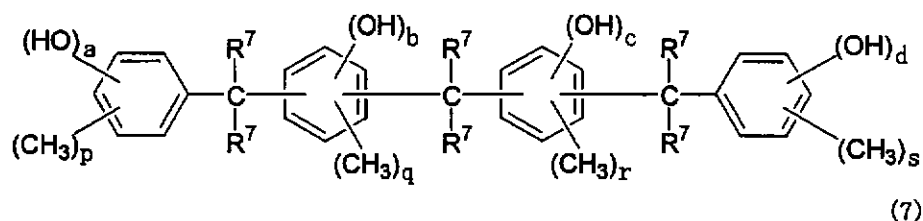
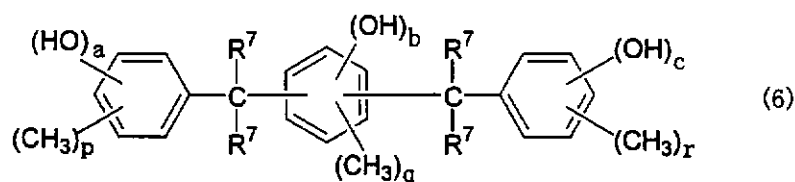
and projections and spacers having a good shape can be formed.

(E) phenolic compound

Preferably, the radiation sensitive resin composition of the present invention further comprises a phenolic compound having an Mw of less than 10,000 (to be referred to as "phenolic compound (E)" hereinafter).

Examples of the phenolic compound (E) include poly(vinylphenols) such as poly(o-vinylphenol), poly(m-vinylphenol), poly(p-vinylphenol), poly(p-isopropenylphenol) and poly(3-methyl-4-vinylphenol); and low molecular weight phenolic compounds represented by the following formulas (2) to (8):





wherein R^7 's are each independently a hydrogen atom or methyl group, and a, b, c, d, p, q, r and s are each an integer of 0 to 3 and satisfy $(a + b + c + d) \geq 2$.

Out of these phenolic compounds (E), poly(vinylphenols) are preferred. The poly(vinylphenols) can be synthesized by the cationic polymerization of a vinylphenol in the presence of boron trifluoride or hydrogen iodide as a polymerization initiator or the radical polymerization of a vinylphenol in the presence of azobisisobutyronitrile or benzoyl peroxide as a polymerization initiator.

Commercially available products of the poly(vinylphenols) include MARUKALYN CUR-M (of Maruzen Petrochemical Co., Ltd.).

Mw of the poly(vinylphenol) is preferably less than 10,000, more preferably 1,000 or more and less than 10,000. When Mw of the poly(vinylphenol) is 10,000 or more, the development residue may be produced in an area other than a portion where projections and/or spacers are formed.

Mw of a low molecular weight phenolic compound is preferably 1,000 or less. When Mw of the low molecular weight phenolic compound phenol is higher than 1,000, resolution may deteriorate.

5 In the present invention, the above phenolic compounds (E) may be used alone or in combination of two or more.

The amount of the phenolic compound (E) in the present invention is preferably 0.1 to 300 parts by weight, more preferably 1 to 150 parts by weight based on 100 parts by
10 weight of the alkali-soluble resin (A). By using the phenolic compound (E) in this range, sensitivity and resolution can be improved.

- other additives -

15 The radiation sensitive resin composition of the present invention may further comprise other additives as required.

The other additives include a dispersion aid such as blue pigment derivative or yellow pigment derivative as
20 exemplified by copper phthalocyanine derivatives; polymer compound such as polyvinyl alcohol, polyethylene glycol monoalkyl ether or poly(fluoroalkylacrylate); nonionic, cationic or anionic surfactant; adhesion accelerator such as vinyl trimethoxysilane, vinyl triethoxysilane, vinyl
25 tris(2-methoxyethoxy)silane,
N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane,
N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,
3-aminopropyltriethoxysilane,
3-glycidoxypropyltrimethoxysilane,
30 3-glycidoxypropylmethyldimethoxysilane,
2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
3-chloropropylmethyldimethoxysilane,
3-chloropropyltrimethoxysilane,
3-methacryloyloxypropyltrimethoxysilane or

3-mercaptopropyltrimethoxysilane; antioxidant such as 2,2-thiobis(4-methyl-6-t-butylphenol) or 2,6-di-t-butylphenol; ultraviolet light absorber such as 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazole or alkoxy benzophenone; and coagulation inhibitor such as sodium polyacrylate.

- solvent -

The radiation sensitive resin composition of the present invention is generally dissolved in a suitable solvent before use to be prepared as a composition solution.

A suitable solvent is selected and used as the solvent for the preparation of the above composition solution as far as it does not react with the components (A) to (E) and other additives and has suitable volatility.

Examples of the solvent include (poly)alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-n-butyl ether, tripropylene glycol monomethyl ether and tripropylene glycol monoethyl ether; (poly)alkylene glycol alkyl ether acetates such as ethylene glycol methyl ether acetate, ethylene glycol ethyl ether acetate, diethylene glycol methyl ether acetate, diethylene glycol ethyl ether acetate, propylene glycol methyl ether acetate and propylene glycol ethyl ether acetate; other ethers such as diethylene glycol dimethyl ether, diethylene glycol methyl ethyl ether, diethylene glycol diethyl ether

and tetrahydrofuran; ketones such as methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, 2-heptanone and 3-heptanone; alkyl lactates such as methyl lactate and ethyl lactate; other esters such as methyl

- 5 2-hydroxy-2-methylpropionate, ethyl 2-hydroxy-2-methylpropionate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, ethyl ethoxyacetate, ethyl hydroxyacetate, methyl 2-hydroxy-3-methylbutyrate,
- 10 3-methyl-3-methoxybutylacetate, 3-methyl-3-methoxybutylpropionate, ethyl acetate, n-propyl acetate, i-propyl acetate, n-butyl acetate, i-butyl acetate, n-amyl acetate, i-amyl acetate, n-butyl propionate, ethyl butyrate, n-propyl butyrate, i-propyl butyrate, n-butyl
- 15 butyrate, methyl pyruvate, ethyl pyruvate, n-propyl pyruvate, methyl acetoacetate, ethyl acetoacetate and ethyl 2-oxobutyrate; aromatic hydrocarbons such as toluene and xylene; and carboxylic acid amides such as N-methylpyrrolidone, N,N-dimethylformamide and
- 20 N,N-dimethylacetamide.

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

- Further, a high-boiling solvent such as benzyl ethyl ether, di-n-hexyl ether, acetonylacetone, isophorone,
- 25 caproic acid, caprylic acid, 1-octanol, 1-nonanol, benzyl alcohol, benzyl acetate, ethyl benzoate, diethyl oxalate, diethyl maleate, γ -butyrolactone, ethylene carbonate, propylene carbonate or ethylene glycol phenyl ether acetate may be used in combination with the solvent.

- 30 These high-boiling solvents may be used alone or in combination of two or more.

Out of the above solvents, propylene glycol monomethyl ether, ethylene glycol methyl ether acetate, propylene glycol methyl ether acetate, propylene glycol ethyl ether

acetate, diethylene glycol dimethyl ether, cyclohexanone, 2-heptanone, 3-heptanone, ethyl lactate, 3-methyl-3-methoxybutylpropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, n-butyl acetate, i-butyl acetate, n-amyl acetate, i-amyl acetate, n-butyl propionate, ethyl butyrate, i-propyl butyrate, n-butyl butyrate and ethyl pyruvate are preferred from the viewpoints of solubility and coatability. γ -butyrolactone is preferred as the high-boiling solvent.

The amount of the solvent is preferably 100 to 10,000 parts by weight, more preferably 500 to 5,000 parts by weight based on 100 parts by weight of the alkali-soluble resin (A).

The composition solution may be filtered with a Millipore filter having an opening diameter of about 0.5 μ m before use.

Method of forming projections and spacers

A description is subsequently given of the method of forming projections and/or spacers for vertically aligned liquid crystal display devices of the present invention.

In the present invention, only projections for vertically aligned liquid crystal display devices or the projections and spacers for vertically aligned liquid crystal display devices are preferably formed on a substrate.

The method of forming projections and/or spacers for vertically aligned liquid crystal display devices of the present invention comprises the steps of:

- (a) forming a coating film of the radiation sensitive resin composition of the present invention on a substrate;
- (b) exposing part of the coating film to radiation;
- (c) developing the coating film after exposure to form a pattern; and

(d) heating the coating film after development.

Each of the above steps will be described hereinunder.

In the step (a), the composition solution is applied to the substrate and prebaked to remove the solvent so as to form a coating film of the radiation sensitive resin composition.

The above substrate is made of glass such as float glass or soda glass, or transparent plastic such as polyethylene terephthalate, polybutylene terephthalate, polyether sulfone or polycarbonate. The substrate may be optionally subjected to a suitable pre-treatment such as chemical treatment with a silane coupling agent, plasma treatment, ion plating, sputtering, gas vapor reaction or vacuum deposition.

To apply the composition solution to the substrate, a suitable coating technique such as spray coating, roll coating or rotational coating may be employed.

The thickness of the coating film after prebaking is preferably 0.1 to 10 μm , more preferably 0.2 to 5.0 μm , particularly preferably 1.0 to 4.0 μm .

As for prebaking conditions which differ according to the type and amount of each component, the coating film is prebaked at 70 to 120°C for 1 to 15 minutes.

In the step (b), part of the coating film is exposed to ultraviolet radiation.

To expose part of the coating film, a photomask is preferably used. To form both projections and spacers on the substrate, (a) the coating film is exposed once by using a single photomask having both projection and spacer patterns, or (b) the coating film is exposed twice by using a photomask having a projection pattern and a photomask having a spacer pattern. A photomask having projection and spacer patterns which differ from each other in transmittance may be used as the photomask used in the method (a).

To form either projections or spacers on the substrate, (c) the coating film is exposed once by using either a photomask having a projection pattern or a photomask having a spacer pattern. In this case, the method of forming other
5 projections or spacers required for a vertically aligned liquid crystal display device is not particularly limited and a known method may be used.

The radiation used for exposure is visible radiation, ultraviolet radiation, far ultraviolet radiation, electron
10 beam or X-radiation but preferably ultraviolet radiation.

The dose of the radiation is preferably about 10 to 10,000 J/m².

In the step (c), the coating film is developed with an alkali developer to remove an unnecessary portion so as
15 to form a predetermined pattern.

The above alkali developer is preferably an aqueous solution of an inorganic alkali such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate or ammonia; primary amine such as
20 ethylamine or n-propylamine; secondary amine such as diethylamine or di-n-propylamine; tertiary amine such as trimethylamine, methyldiethylamine, dimethylethylamine or triethylamine; alkanol amine such as dimethylethanolamine, methyldiethanolamine or triethanolamine; alicyclic
25 tertiary amine such as pyrrole, piperidine, N-methylpiperidine, N-methylpyrrolidine, 1,8-diazabicyclo[5.4.0]-7-undecene or 1,5-diazabicyclo[4.3.0]-5-nonene; aromatic tertiary amine such as pyridine, collidine, lutidine or quinoline; or
30 quaternary ammonium salt such as tetramethylammonium hydroxide or tetraethylammonium hydroxide.

A water-soluble organic solvent such as methanol or ethanol and/or a surfactant may be added to the above alkali developer in a suitable amount.

Puddle development, dip development, shower development or the like may be employed, and the development time is preferably about 5 to 300 sec.

After alkali development, the coating film is rinsed
5 in running water for 30 to 90 sec and dried with compressed air or compressed nitrogen, for example.

In the subsequent step (d), the coating film after development is heated with a heater such as a hot plate or oven (to be referred to as "post-baking" hereinafter) to form
10 predetermined projections and/or spacers.

As for post-baking conditions, the temperature is preferably 150 to 250°C and the time is about 5 to 30 minutes on a hot plate and about 30 to 90 minutes in an oven.

The thus formed projections have a height of preferably
15 0.1 to 3.0 μm , more preferably 0.5 to 2.0 μm , particularly preferably 1.0 to 1.5 μm . They have a bottom size of preferably 1 to 50 μm , more preferably 2 to 30 μm , particularly preferably 3 to 10 μm .

The spacers have a height of preferably 1 to 10 μm ,
20 more preferably 2 to 8 μm , particularly preferably 3 to 5 μm . They have a bottom size of preferably 5 to 150 μm , more preferably 5 to 100 μm , particularly preferably 10 to 50 μm .

Vertically aligned liquid crystal display device

25 The vertically aligned liquid crystal display device of the present invention comprises projections made of the radiation sensitive resin composition of the present invention and/or spacers made of the radiation sensitive resin composition of the present invention and has an
30 after-image erase time of 100 sec or less, preferably 50 sec or less.

The vertically aligned liquid crystal display device can be manufactured by the following method (e) or (f).

(e) A transparent conductive film having a predetermined

pattern is formed on one side of the substrate, projections are formed on the conductive film by the above method, and a liquid crystal aligning agent is applied to the substrate by roll coating, spinner coating or printing and heated to
5 form a liquid crystal alignment film.

The above substrate is made of glass or transparent plastic as described in the method of forming projections and/or spacers.

A tin oxide (SnO_2) film or an ITO film made of indium oxide-tin oxide ($\text{In}_2\text{O}_3\text{-SnO}_2$) may be used as the transparent
10 conductive film.

To form the transparent conductive film pattern, photoetching or a method using a photomask may be used.

Prior to the application of the liquid crystal aligning
15 agent, in order to further improve adhesion between the surface of the substrate or the transparent conductive film and the liquid crystal alignment film, a functional silane compound or a functional titanium compound may be applied to the surface of the substrate having the transparent
20 conductive film.

The heating temperature after the application of the liquid crystal aligning agent is preferably 80 to 300°C, more preferably 120 to 250°C.

The thickness of the liquid crystal alignment film is
25 preferably 0.001 to 1 μm , more preferably 0.005 to 0.5 μm .

(f) Two of the substrates having a liquid crystal alignment film formed by the above method (e) are prepared, the liquid crystal alignment film formed surfaces of the substrates are
30 opposed to each other by keeping the cell gap therebetween, the outer edges of the substrates are joined together with an adhesive, a liquid crystal is filled into the cell gap defined by the surfaces of the substrates and the adhesive layer, and the filling hole is sealed up to construct a liquid

crystal cell. Thereafter, the outer surfaces of the liquid crystal cell, that is, the other surfaces of the substrates constituting the liquid crystal cell are joined to respective polarizers in order to obtain a liquid crystal display device.

The above adhesive is, for example, an epoxy resin containing a curing agent and aluminum oxide balls as spacers.

Examples of the above liquid crystal include nematic liquid crystal, smectic liquid crystal and ferroelectric liquid crystal such as p-n-decyloxybenzylidene-p-amino-2-methylbutylcinnamate, out of which nematic liquid crystal is particularly preferred.

Specific examples of the above nematic liquid crystal include Schiff's base liquid crystals, azoxy-based liquid crystals, biphenyl-based liquid crystals, phenylcyclohexane-based liquid crystals, ester-based liquid crystals, terphenyl-based liquid crystals, biphenylcyclohexane-based liquid crystals, pyrimidine-based liquid crystals, dioxane-based liquid crystals, bicyclooctane-based liquid crystals and cubane-based liquid crystals.

A cholesteric liquid crystal such as cholesteryl chloride, choleteryl nonanoate or cholesteryl carbonate and a chiral agent commercially available under the trade names of C-15 and CB-15 (of Merk Co., Ltd.) may be added to the above liquid crystal before use.

The polarizer to be joined to the outer surfaces of the liquid crystal cell is a polarizer composed of an H film which has absorbed iodine while a polyvinyl alcohol is stretched and aligned or a polarizer manufactured by sandwiching a polarizing film composed of the H film between cellulose acetate protective films.

The radiation sensitive resin composition of the present invention used for the formation of projections and/or spacers for vertically aligned liquid crystal display devices such as color display devices provides projections
5 and spacers having excellent surface smoothness, hardly produces the development residue on the substrate of an unexposed portion, hardly causes the peeling, lack or loss of the projections and spacers and can provide a vertically aligned liquid crystal display device having excellent
10 vertically alignability for liquid crystals, high voltage retainability and a short after-image erase time and almost free from sticking and display nonuniformity.

The method of forming projections and/or spacers for vertically aligned liquid color crystal display devices of
15 the present invention enables fine patterning, facilitates the control of shape and size (height and bottom size) and is capable of forming fine projections and spacers having the above excellent characteristic properties stably at a high yield.

20

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.

25

Synthetic Example 1

57 g of m-cresol, 38 g of p-cresol, 75.5 g of a 37 wt% formaldehyde aqueous solution, 0.63 g of oxalic acid dehydrate and 264 g of methyl isobutyl ketone were fed to
30 a flask equipped with a cooling tube, stirrer and thermometer, and the flask was immersed in an oil bath to carry out polycondensation for 4 hours under agitation while the solution was refluxed. Thereafter, the temperature of the oil bath was raised to 150°C and the inside pressure of the

flask was reduced to 30 to 50 mmHg in 3 hours to remove volatile matter, and then the molten resin was cooled to room temperature to be collected. This resin was then dissolved in ethyl acetate to a concentration of 30 wt% and methanol and water were added in amounts 1.3 times and 0.9 time the weight of this solution, respectively, stirred and left. Thereafter, the solution was separated into two layers, and the lower layer was taken out, concentrated and dried to obtain a novolak resin having an Mw of 8,000. This novolak resin is designated as resin (A-1).

Synthetic Example 2

After 176 g of p-t-butoxystyrene and 5.8 g of azobisbutyronitrile were fed to a flask equipped with a cooling tube, stirrer and thermometer and 250 ml of propylene glycol monomethyl ether was further added to dissolve these components, polymerization was carried out at 75°C for 4 hours. Thereafter, 50 g of a 5 wt% sulfuric acid aqueous solution was mixed with the obtained resin solution to carry out a hydrolytic reaction at 100°C for 3 hours. 500 ml of propylene glycol methyl ether acetate was then added to the reaction solution, the reaction solution was rinsed in 1,000 ml of deionized water three times, the organic layer was separated, the solvent was removed under reduced pressure, and the resulting reaction solution was dried under vacuum to obtain poly(p-hydroxystyrene) having an Mw of 24,000. This poly(p-hydroxystyrene) is designated as resin (A-2).

Synthetic Example 3

3 g of azobisisobutyronitrile and 300 g of propylene glycol monoethyl ether were fed to a flask equipped with a cooling tube, stirrer and thermometer, 25 g of methacrylic acid, 15 g of styrene and 60 g of benzyl methacrylate were further added, the inside of the flask was substituted by

nitrogen, and the temperature of the solution was raised to 70°C while it was stirred gently and maintained at that temperature for 5 hours to carry out polymerization. After the solvent was removed from the reaction solution under reduced pressure, the resulting reaction solution was dried under vacuum to obtain a copolymer of methacrylic acid, styrene and benzyl methacrylate having an Mw of 8,000 (weight ratio of 25/15/60). This copolymer is designated as resin (a-1).

10

Example 1

100 parts by weight of the resin (A-1) as the component (A), 40 parts by weight of dipentaerythritol hexaacrylate as the component (B), 10 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole, 10 parts by weight of 4,4'-bis(diethylamino)benzophenone and 20 parts by weight of 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one as the components (C), 20 parts by weight of Cymel 300 (trade name, manufactured by Mitsui Cyanamid Co., Ltd.) as the component (D), 10 parts by weight of poly(p-vinylphenol) (Mw = 8,000) as the component (E) and 1,500 parts by weight of ethyl 3-ethoxypropionate as the solvent were mixed and dissolved together and the obtained solution was filtered with a membrane filter having an opening diameter of 0.2 μ m to prepare a solution of a radiation sensitive resin composition (to be referred to as "composition solution (S1)" hereinafter).

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- formation of projections -

The composition solution (S1) was applied to the surface of a soda lime glass substrate having a silica (SiO_2) film for preventing the elution of sodium ions formed on the

surface with a spin coater and prebaked at 90°C for 4 minutes to form a 1.3 μm -thick coating film.

Thereafter, the substrate was cooled to room temperature and the coating film was exposed to 2,000 J/m^2 of ultraviolet radiation having a wavelength of 365 nm with a high-pressure mercury lamp through a photomask to be cured. Thereafter, the substrate was immersed in a 0.04 wt% potassium hydroxide aqueous solution at 23°C for 1 minute to be developed, rinsed in super pure water and dried with air to form a pattern. Then, the coating film was post-baked at 250°C for 30 minutes to form projections having a predetermined shape on the substrate.

The development residue was not observed on the obtained substrate of an unexposed portion and the separation, lack or loss of the projections was not seen. When the surfaces of the projections were observed through an optical microscope, no roughened surface was seen and the projections had excellent surface smoothness.

20 - manufacture of a vertically aligned liquid crystal display device for evaluation -

The composition solution (S1) was applied to a transparent conductive film composed of an ITO film formed on one side of a 1 mm-thick glass substrate with a spin coater and prebaked at 90°C for 4 minutes to form a 1.3 μm -thick coating film. Thereafter, the substrate was cooled to room temperature and the entire surface of the coating film was exposed to 2,000 J/m^2 of ultraviolet radiation having a wavelength of 365 nm with a high-pressure mercury lamp to be cured. The substrate was then immersed in a 0.04 wt% potassium hydroxide aqueous solution at 23°C for 1 minute to be developed, rinsed in super pure water and dried with air. The substrate was then post-baked at 250°C for 30 minutes to form a coating film of the radiation sensitive

resin composition on the substrate.

Subsequently, a liquid crystal aligning agent (trade name of JALS2095-S2, manufactured by JSR Corporation) was applied to one side of a substrate having a coating film of the radiation sensitive resin composition formed thereon and one side of a substrate having no coating film with a spinner and heated at 80°C for 1 minute and then at 180°C for 1 hour to form a liquid crystal alignment film having a thickness of 600 Å on the substrates. An epoxy resin-based adhesive containing aluminum oxide balls were applied to the outer edges of the substrates by screen printing, the liquid crystal alignment film formed surfaces of the two substrates were opposed to each other by keeping the cell gap therebetween, the outer edges of the substrates were brought into contact with each other to be pressure bonded together, and the adhesive was cured. Then, a negative nematic liquid crystal (trade name of MLC6608, manufactured by Merk Co., Ltd.) was filled into the cell gap defined by the surfaces of the substrates and the adhesive layers of the outer edge portions, and the filling hole was sealed up with an epoxy-based adhesive to manufacture a vertically aligned liquid crystal display device for evaluation.

The obtained vertically aligned liquid crystal display device was evaluated as follows. The evaluation results are shown in Table 1.

- evaluation of vertical alignability -

The vertically aligned liquid crystal display device is observed under a crossed-nicol when voltage is off and a DC of 12 V (peak-peak) is applied. When an aligning failure is not observed in the liquid crystal, vertical alignability is evaluated as excellent.

- evaluation of voltage retainability -

After a voltage of 5 V is applied to the vertically aligned liquid crystal display device for 60 μ sec at a span of 167 msec, voltage retainability after 167 msec from the time when the application of voltage is stopped in the end is measured with the VHR-1 of Toyo Technica Co., Ltd.

- evaluation of after-image erase time -

After a rectangular wave having a frequency of 30 Hz and a voltage of 3.0 V obtained by superimposing a DC of 6.0 V (peak value) with an AC of 6.0 V (peak value) is applied to the vertically aligned liquid crystal display device at 70°C for 167 hours, the application is stopped and the time before an after-image is erased visually is measured.

Example 2

A radiation sensitive composition solution (to be referred to as "composition solution (S2)" hereinafter) was prepared in the same manner as in Example 1 except that the resin (A-2) was used in place of 100 parts by weight of the resin (A-1) as the component (A).

Thereafter, the formation of projections and the manufacture of a liquid crystal display device were carried out in the same manner as in Example 1 except that the composition solution (S2) was used in place of the composition solution (S1) to make evaluations. The evaluation results are shown in Table 1.

Comparative Example 1

100 parts by weight of the resin (a-1) as the alkali-soluble resin (A), 80 parts by weight of dipentaerythritol hexaacrylate as the component (B), 20 parts by weight of 2,2'-bis(2-chlorophenyl)-4,4',5,5'-tetrakis(4-ethoxycarbonylphenyl)-1,2'-biimidazole, 20 parts by weight

of 4,4'-bis(diethylamino)benzophenone and 40 parts by weight of

2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one as the components (C) and 1,500 parts by weight of ethyl
5 3-ethoxypropionate as the solvent were mixed and dissolved together and the resulting solution was filtered with a membrane filter having an opening diameter of 0.2 μm to prepare a radiation sensitive composition solution (to be referred to as "composition solution (s1)" hereinafter).

10 Thereafter, the formation of projections and the manufacture of a liquid crystal display device were carried out in the same manner as in Example 1 except that the composition solution (s1) was used in place of the composition solution (S1) to make evaluations. The
15 evaluation results are shown in Table 1.

Table 1

	Development residue	separation, lack and loss	surface smoothness	vertical alignability	voltage retainability (%)	after-image erase time (sec)
Ex. 1	None	None	Excellent	Excellent	99.0	10
Ex. 2	None	None	Excellent	Excellent	98.8	15
C. Ex. 1	None	None	Excellent	Excellent	98.5	200 or more

Ex.: Example

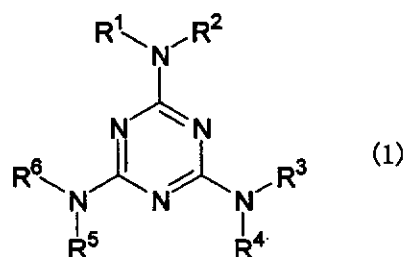
C.Ex. : Comparative Example

What is claimed is:

1. A radiation sensitive resin composition which comprises (A) at least one alkali-soluble resin selected from the group consisting of a novolak resin having a weight
 5 average molecular weigh in terms of polystyrene measured by gel permeation chromatography of 2,000 to 20,000 and a hydroxystyrene resin having a weight average molecular weight in terms of polystyrene measured by gel permeation chromatography of 10,000 to 100,000, (B) a polyfunctional
 10 monomer or a combination of a polyfunctional monomer and a monofunctional monomer and (C) a photopolymerization initiator, and which is used to form projections and/or spacers in a vertically aligned liquid crystal display device having an after-image erase time of 100 sec or less.

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2. The radiation sensitive resin composition according to claim 1 which further comprises a melamine compound represented by the following formula (1):



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wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are each independently a hydrogen atom or $-\text{CH}_2\text{OR}$, and R is a hydrogen atom or linear or branched alkyl group having 1 to 6 carbon atoms.

25 3. The radiation sensitive resin composition according to claim 1 which further comprises (E) a phenolic compound having a weight average molecular weight in terms of polystyrene measured by gel permeation chromatography of less than 10,000.

4. Projections for vertically aligned liquid crystal display devices which are made of the radiation sensitive resin composition of any one of claims 1 to 3.
- 5 5. Spacers for vertically aligned liquid crystal display devices which are made of the radiation sensitive resin composition of any one of claims 1 to 3.
6. A method of forming projections and/or spacers for
10 vertically aligned liquid crystal display devices,
comprising the steps of:
- (a) forming a coating film of the radiation sensitive resin composition of any one of claims 1 to 3 on a substrate;
 - 15 (b) exposing part of the coating film to radiation;
 - (c) developing the coating film after exposure to form a pattern; and
 - (d) heating the coating film after development.
- 20 7. A vertically aligned liquid crystal display device comprising the projections of claim 4 and/or the spacers of claim 5 and having an after-image erase time of 100 sec or less.