

TITLE

PHOTOSENSITIVE RESIN COMPOSITION

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a photosensitive resin composition and more particularly, to a photosensitive resin composition having excellent performances in transmission, insulation, flatness, chemistry resistance and so on, and further, securing reliable post-process by minimizing outgassing that may occur in interlayer dielectrics by virtue of high heat resistance property so that it is suitable for use in interlayer dielectrics during LCD manufacturing process.

Description of Related Art

TFT-type liquid crystal display elements or integrated circuit elements use interlayer dielectrics to insulate space between wirings arranged in interlayers.

To form such interlayer dielectrics, there are being used photosensitive substances with excellent flatness and small process number for obtaining interlayer dielectrics of necessary pattern configuration.

Further, according as the display quality of liquid crystal displays (LCD) is improved, the structure of TFT-type liquid crystal display elements changes and there is an increasing tendency that the flatness is increased by making the film thickness of interlayer dielectrics thick. Also, the interlayer dielectrics applied to LCD manufacturing process require excellent high heat resistance.

In prior arts, the interlayer dielectrics comprise PAC, binders, solvents, etc. and acryl resins have been mostly used as the binders. However, the acryl resins are difficult to exhibit high heat resistance that is required for interlayer dielectrics and therefore, they affected the reflectivity, adhesion and so on of dielectrics and caused damage on photo equipments due to outgassing.

Accordingly, studies about methods capable of minimizing outgassing by improving high heat resistance of the interlayer dielectrics applied to LCD manufacturing processes are required.

SUMMARY OF THE INVENTION

In order to solve the problems of the prior arts, it is an object of the present invention to provide a photosensitive resin composition having excellent performances in transmission, insulation, flatness, chemistry resistance and so on, and further, securing reliable post-process by minimizing outgassing that may occur in interlayer dielectrics by virtue of high heat resistance property so that it is suitable for use in interlayer dielectrics during LCD manufacturing process, an LCD substrate comprising a cured product of the photosensitive resin and a pattern formation method of an LCD substrate using the photosensitive resin composition.

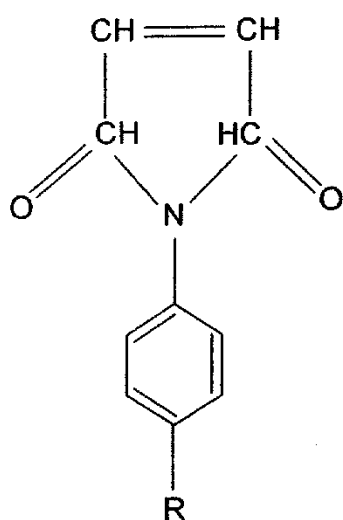
It is another object of the invention to provide a photosensitive resin composition having excellent high heat resistance so that it can improve the reflectivity and adhesion of interlayer dielectrics applied to LCD manufacturing process and cause no damage on photo equipments due to outgassing, an LCD substrate comprising a cured product of the

photosensitive resin and a pattern formation method of an LCD substrate using the photosensitive resin composition.

To achieve the aforementioned objects, the invention provides photosensitive resin composition comprising:

a) an acryl-based copolymer obtained by copolymerizing

i) a phenylmaleimide-based compound represented by formula 1:



wherein R is a hydroxy (OH-) or carboxy (CH₃COO⁻);

ii) an unsaturated carbonic acid, unsaturated carbonic anhydride or mixture thereof; and

iii) an epoxy group containing unsaturated compound;

b) a 1,2-quinonediazide compound; and

c) a solvent.

Preferably, the invention comprises

a) 100 parts by weight of the acryl-based copolymer obtained by copolymerizing

i) 5 to 60 parts by weight of the phenylmaleimide-based compound represented by formula 1 as described above;

ii) 5 to 40 parts by weight of the unsaturated carbonic acid, unsaturated carbonic anhydride or mixture thereof; and

iii) 10 to 70 parts by weight of the epoxy group containing unsaturated compound;

b) 5 to 100 parts by weight of the 1,2-quinonediazide compound; and

c) the solvent in such an amount that the content of the solids in the photosensitive resin composition is 10 to 50 % by weight.

Further, the invention provides an LCD comprising a cured product of the photosensitive resin.

Further, the invention provides a pattern formation method of an LCD substrate using the photosensitive resin composition.

DETAILED DESCRIPTION OF THE INVENTION

This invention is further described in detail.

The photosensitive resin composition of the invention is characterized by comprising a) an acryl-based copolymer obtained by copolymerizing i) a phenylmaleimide-based compound represented by formula 1 as defined above, ii) an unsaturated carbonic acid, unsaturated carbonic anhydride or mixture thereof, and iii) an epoxy group containing unsaturated compound; b) a 1,2-quinonediazide compound; and c) a solvent.

The acryl-based copolymer of a) used in the invention enables prescribed patterns which do not generate scum when developed to be readily formed.

The acryl-based copolymers of a) can be prepared by radical reaction using i) the phenylmaleimide-based compound represented by formula 1 above, ii) the unsaturated carbonic acid, unsaturated carbonic anhydride or mixture thereof, and iii) the epoxy group containing unsaturated compound as monomers in the presence of a solvent and polymerization initiator. The acryl-based copolymers can further comprise iv) an olefin-based unsaturated compound as a monomer.

The phenylmaleimide-based compound represented by formula 1 of a) i) used in the invention improves heat resistance and solubility with regard to alkaline aqueous solutions.

For the phenylmaleimide-based compound, 4-hydroxy phenylmaleimide or 4-carboxy phenylmaleimide can be employed.

The phenylmaleimide-based compound is contained preferably in an amount of 5 to 60 parts by weight with regard to 100 parts by weight of the total monomers and more preferably 5 to 40 parts by weight. When the amount is less than 5 parts by weight, heat resistance is decreased and when it exceeds 60 parts by weight, solubility with regard to alkaline aqueous solutions is decreased.

For the unsaturated carbonic acid, unsaturated carbonic anhydride or mixture thereof of a) ii) used in the invention, unsaturated monocarbonic acids such as acrylic acid, methacrylic acid; unsaturated dicarbonic acids such as maleic acid, fumaric acid, citraconic acid, methaconic acid and itaconic acid; or unsaturated dicarbonic anhydride thereof can be used alone or by mixture and in particular, it is more preferable to use acrylic acid, methacrylic acid or maleic anhydride in consideration of copolymerization

reactivity and solubility with regard to alkaline aqueous solution that is a development solution.

The unsaturated carbonic acid, unsaturated carbonic anhydride or mixture thereof is contained preferably in an amount of 5 to 40 parts by weight with regard to 100 parts by weight of the total monomers and more preferably 10 to 30 parts by weight. When the amount is less than 5 parts by weight, it is difficult to be dissolved in alkaline aqueous solutions and when it exceeds 40 parts by weight, solubility with regard to alkaline aqueous solutions becomes too high.

For the epoxy group containing unsaturated compound of a) iii) used in the invention, glycidyl acrylate, glycidyl methacrylate, glycidyl α -ethylacrylate, glycidyl α -n-propylacrylate, glycidyl α -n-butylacrylate, β -methylglycidyl acrylate, β -methylglycidyl methacrylate, β -ethylglycidyl acrylate, β -ethylglycidyl methacrylate, 3,4-epoxybutyl acrylate, 3,4-epoxybutyl methacrylate, 6,7-epoxyheptyl acrylate, 6,7-epoxyheptyl methacrylate, 6,7-epoxyheptyl α -ethylacrylate, o-vinylbenzylglycidylether, m-vinylbenzylglycidylether, or p-vinylbenzylglycidylether can be used alone or by mixture.

In particular, it is more preferable to use glycidyl methacrylate, β -methylglycidyl methacrylate, 6,7-epoxyheptyl methacrylate, o-vinylbenzylglycidylether, m-vinylbenzylglycidylether, or p-vinylbenzylglycidylether as the epoxy group containing unsaturated compounds for the improvement of copolymerization reactivity and heat resistance of patterns to be obtained.

The epoxy group containing unsaturated compound is contained preferably in an amount of 10 to 70 parts by weight with regard to 100 parts by weight of the total monomers and more preferably 20 to 60 parts by weight. When the amount is less than

10 parts by weight, the heat resistance of patterns to be obtained is decreased and when it exceeds 70 parts by weight, the preservation stability of the copolymers is decreased.

The acryl-based copolymers of the invention can further comprise a) iv) an olefin-based unsaturated compound as a monomer. For the olefin-based unsaturated compound of a) iv), methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, sec-butyl methacrylate, tert-butyl methacrylate, methyl acrylate, isopropyl acrylate, cyclohexyl methacrylate, 2-methylcyclohexyl methacrylate, dicyclopentenyl acrylate, dicyclopentanyl acrylate, dicyclopentenyl methacrylate, dicyclopentanyl methacrylate, dicyclopentanyloxyethyl methacrylate, isobornyl methacrylate, cyclohexyl acrylate, 2-methylcyclohexyl acrylate, dicyclopentanyloxyethyl acrylate, isobornyl acrylate, phenyl methacrylate, phenyl acrylate, benzyl acrylate, 2-hydroxyethyl methacrylate, styrene, α -methyl styrene, m-methyl styrene, p-methyl styrene, vinyl toluene, p-methoxy styrene, 1,3-butadiene, isoprene, or 2,3-dimethyl 1,3-butadiene can be used alone or by mixture.

In particular, it is more preferable to use styrene, dicyclopentanyl methacrylate, or p-methoxy styrene as the olefin-based unsaturated compounds in consideration of copolymerization reactivity and solubility with regard to alkaline aqueous solution that is a development solution.

The olefin-based unsaturated compound is contained preferably in an amount of 10 to 70 parts by weight with regard to 100 parts by weight of the total monomers and more preferably 20 to 50 parts by weight. With the above ranges, the problems that the preservation stability of acryl-based copolymers is decreased and the acryl-based copolymers are difficult to be dissolved in alkaline aqueous solutions which are development solutions can be solved at the same time.

For the solvent used to polymerize the above monomers into acryl-based copolymers, methanol, ethers such as tetrahydrofuran, ethyleneglycol monomethylether, ethyleneglycol monoethylether, methylcellosolveacetate, ethylcellosolveacetate, diethyleneglycol monomethylether, diethyleneglycol monoethylether, ethyleneglycol dimethylether, ethyleneglycol diethylether, ethyleneglycol methylethylether, propyleneglycol monomethylether, propyleneglycol monoethylether, propyleneglycol propylether, propyleneglycol butylether, propyleneglycol methyletheracetate, propyleneglycol ethyletheracetate, propyleneglycol propyletheracetate, propyleneglycol butyletheracetate, propyleneglycol methyletherpropionate, propyleneglycol ethyletherpropionate, propyleneglycol propyletherpropionate, propyleneglycol butyletherpropionate, toluene, xylene, methylethylketone, cyclohexanone, 4-hydroxy 4-methyl 2-pentanone, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, 2-hydroxy ethyl propionate, 2-hydroxy 2-methyl methyl propionate, 2-hydroxy 2-methyl ethyl propionate, hydroxyl methyl acetate, hydroxyl ethyl acetate, hydroxyl butyl acetate, methyl lactate, ethyl lactate, propyl lactate, butyl lactate, 3-hydroxy methyl propionate, 3-hydroxy ethyl propionate, 3-hydroxy propyl propionate, 3-hydroxy butyl propionate, 2-hydroxy 3-methyl methyl butyric acid, methoxy methyl acetate, methoxy ethyl acetate, methoxy propyl acetate, methoxy butyl acetate, ethoxy methyl acetate, ethoxy ethyl acetate, ethoxy propyl acetate, ethoxy butyl acetate, propoxy methyl acetate, propoxy ethyl acetate, propoxy propyl acetate, propoxy butyl acetate, butoxy methyl acetate, butoxy ethyl acetate, butoxy propyl acetate, butoxy butyl acetate, 2-methoxy methyl propionate, 2-methoxy ethyl propionate, 2-methoxy propyl propionate, 2-methoxy butyl propionate, 2-ethoxy methyl propionate, 2-ethoxy ethyl propionate, 2-ethoxy propyl

propionate, 2-ethoxy butyl propionate, 2-butoxy methyl propionate, 2-butoxy ethyl propionate, 2-butoxy propyl propionate, 2-butoxy butyl propionate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-methoxy propyl propionate, 3-methoxy butyl propionate, 3-ethoxy methyl propionate, 3-ethoxy ethyl propionate, 3-ethoxy propyl propionate, 3-ethoxy butyl propionate, 3-propoxy methyl propionate, 3-propoxy ethyl propionate, 3-propoxy propyl propionate, 3-propoxy butyl propionate, 3-butoxy methyl propionate, 3-butoxy ethyl propionate, 3-butoxy propyl propionate or 3-butoxy butyl propionate can be used alone or by mixture.

For the polymerization initiator used to polymerize the above monomers into the acryl-based copolymers, radical polymerization initiators can be used and in particular, there can be used 2,2-azobisisobutyronitrile, 2,2-azobis(2,4-dimethylvaleronitrile), 2,2-azobis(4-methoxy 2,4-dimethylvaleronitrile), 1,1-azobis(cyclohexane-1-carbonitrile), or dimethyl 2,2-azobisisobutylate.

The acryl-based copolymers prepared by the radical reaction of the above monomers in the presence of the solvents and polymerization initiators have preferably a weight average molecular weight (Mw) in terms of polystyrene of 5,000 to 30,000 and more preferably, 5,000 to 20,000. In case of the interlayer dielectrics having a weight average molecular weight in terms of polystyrene less than 5,000, their development properties, residual film rate and so on are decreased or pattern configuration, heat resistance, etc. are inferior and in case of the interlayer dielectrics exceeding 30,000, their sensitivity are decreased or pattern development is inferior.

The 1,2-quinonediazide compounds in the invention are used as a photosensitive compound.

For the 1,2-quinonediazide compounds, 1,2-quinonediazide-4-sulfonic ester, 1,2-quinonediazide-5-sulfonic ester, or 1,2-quinonediazide-6-sulfonic ester, etc. can be employed.

The quinonediazide compounds can be prepared by reacting naphtoquinonediazide sulfonic acid halogen compounds and phenol compounds under weak base.

For the phenol compounds, 2,3,4-trihydroxybenzophenone, 2,4,6-trihydroxybenzophenone, 2,2'-tetrahydroxybenzophenone, 4,4'-tetrahydroxybenzophenone, 2,3,4,3'-tetrahydroxybenzophenone, 2,3,4,4'-tetrahydroxybenzophenone, 2,3,4,2'-tetrahydroxy 4'-methylbenzophenone, 2,3,4,4'-tetrahydroxy 3'-methoxybenzophenone, 2,3,4,2'-pentahydroxybenzophenone, 2,3,4,6'-pentahydroxybenzophenone, 2,4,6,3'-hexahydroxybenzophenone, 2,4,6,4'-hexahydroxybenzophenone, 2,4,6,5'-hexahydroxybenzophenone, 3,4,5,3'-hexahydroxybenzophenone, 3,4,5,4'-hexahydroxybenzophenone, 3,4,5,5'-hexahydroxybenzophenone, bis(2,4-dihydroxyphenyl) methane, bis(p-hydroxyphenyl) methane, tri(p-hydroxyphenyl) methane, 1,1,1-tri(p-hydroxyphenyl) ethane, bis(2,3,4-trihydroxyphenyl) methane, 2,2-bis(2,3,4-trihydroxyphenyl) propane, 1,1,3-tris(2,5-dimethyl 4-hydroxyphenyl)-3-phenylpropane, 4,4'-[1-[4-[1-[4-hydroxyphenyl]-1-methylethyl]phenyl]ethylidene]bisphenol, or bis(2,5-dimethyl 4-hydroxyphenyl)-2-hydroxyphenylmethane can be used alone or by mixture.

When the quinonediazide compounds are synthesized with the above phenol compounds and naphtoquinonediazide sulfonic acid halogen compounds, their esterification rate is preferably 50 to 85 %. When the esterification rate is less than 50 %,

residual film rate can be deteriorated and when it exceeds 85 %, preservation stability is decreased.

The 1,2-quinonediazide compounds are contained preferably in an amount of 5 to 100 parts by weight with regard to 100 parts by weight of the acryl-based copolymers of a) and more preferably 10 to 50 parts by weight. If the amount is less than 5 parts by weight, solubility difference between exposed parts and unexposed parts is small so that pattern formation is difficult and if it exceeds 100 parts by weight, unreacted 1,2-quinonediazide compounds remain in large quantity when irradiated with light for short period so that solubility with regard to alkaline aqueous solution that is a development solution becomes too low and development is thus difficult.

The solvent of c) used in the invention does not generate coating stain and flatness of interlayer dielectrics and thus allows uniform pattern profile to be formed.

For the solvents, alcohols such as methanol and ethanol; ethers such as tetrahydrofuran; glycolethers such as ethyleneglycol monomethylether and ethyleneglycol monoethylether; ethyleneglycolalkylether acetates such as methylcellosolveacetate and ethylcellosolveacetate; diethylene glycols such as diethyleneglycol monomethylether, diethyleneglycol monoethylether and diethyleneglycol dimethylether; propyleneglycolmonoalkylethers such as propyleneglycol methylether, propyleneglycol ethylether, propyleneglycol propylether and propyleneglycol butylether; propyleneglycolalkyletheracetates such as propyleneglycol methyletheracetate, propyleneglycol ethyletheracetate, propyleneglycol propyletheracetate and propyleneglycol butyletheracetate; propyleneglycolalkyletherpropionates such as propyleneglycol methyletherpropionate,

propyleneglycol ethyletherpropionate, propyleneglycol propyletherpropionate and propyleneglycol butyletherpropionate; aromatic hydrocarbons such as toluene and xylene; ketones such as methylethylketone, cyclohexanone and 4-hydroxy 4-methyl 2-pentanone; or esters such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, 2-hydroxy ethyl propionate, 2-hydroxy 2-methyl methyl propionate, 2-hydroxy 2-methyl ethyl propionate, hydroxy methyl acetate, hydroxy ethyl acetate, hydroxy butyl acetate, methyl lactate, ethyl lactate, propyl lactate, butyl lactate, 3-hydroxy methyl propionate, 3-hydroxy ethyl propionate, 3-hydroxy propyl propionate, 3-hydroxy butyl propionate, 2-hydroxy 3-methyl methyl butyric acid, methoxy methyl acetate, methoxy ethyl acetate, methoxy propyl acetate, methoxy butyl acetate, ethoxy methyl acetate, ethoxy ethyl acetate, ethoxy propyl acetate, ethoxy butyl acetate, propoxy methyl acetate, propoxy ethyl acetate, propoxy propyl acetate, propoxy butyl acetate, butoxy methyl acetate, butoxy ethyl acetate, butoxy propyl acetate, butoxy butyl acetate, 2-methoxy methyl propionate, 2-methoxy ethyl propionate, 2-methoxy propyl propionate, 2-methoxy butyl propionate, 2-ethoxy methyl propionate, 2-ethoxy ethyl propionate, 2-ethoxy propyl propionate, 2-ethoxy butyl propionate, 2-butoxy methyl propionate, 2-butoxy ethyl propionate, 2-butoxy propyl propionate, 2-butoxy butyl propionate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, 3-methoxy propyl propionate, 3-ethoxy methyl propionate, 3-ethoxy ethyl propionate, 3-ethoxy propyl propionate, 3-ethoxy butyl propionate, 3-propoxy methyl propionate, 3-propoxy ethyl propionate, 3-propoxy propyl propionate, 3-propoxy butyl propionate, 3-butoxy methyl propionate, 3-butoxy ethyl propionate, 3-butoxy propyl propionate and 3-butoxy butyl propionate can be used. In particular, it is preferable to use one or more species selected from the group consisting

of glycolethers, ethylenealkyletheracetates and diethyleneglycols that are easy for coating film formation, reactivity with each component and solubility.

The solvents are contained preferably in such an amount that the amount of the solids of the total photosensitive resin compositions becomes 10 to 50 % by weight, and the compositions having the solids of the above ranges are used preferably after filtration with a millipore filter of $0.1 \sim 0.2 \mu\text{m}$. More preferably, they are contained in such an amount that the solids are 15 to 40 % by weight. If the amount of the solids of the total composition is less than 10 % by weight, the thickness of coating becomes thin and coating flatness is decreased, and if it exceeds 50 % by weight, the thickness of coating becomes thick and it may affect coating machines during coating.

The photosensitive resin compositions comprising the above components may further comprise d) epoxy resins, e) adhesives, f) acryl compounds, or g) surfactants, if necessary.

The epoxy resins of d) improve the heat resistance and sensitivity of patterns obtained from the photosensitive resin compositions

For the epoxy resins, bisphenol A epoxy resins, phenol novolac epoxy resins, cresol novolac epoxy resins, aliphatic epoxy resins, alicyclic epoxy resins, glycidyl ester epoxy resins, glycidyl amine epoxy resins, epoxy resins, heterocyclic epoxy resins, or resins (co)polymerized with glycidyl methacrylates other than the acryl-based copolymers of a) can be used and in particular, it is preferable to use bisphenol A epoxy resins, cresol novolac epoxy resins, or glycidyl ester epoxy resins.

The epoxy resins are contained preferably in an amount of 0.1 to 30 parts by weight with regard to 100 parts by weight of the acryl-based copolymers of a), and if the

amount deviates from the above ranges, compatibility with acryl-based copolymers is reduced and thus, sufficient coating performance cannot be obtained.

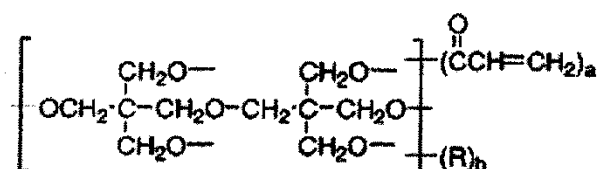
The adhesives of e) improve the adhesion to substrates.

For the adhesives, silane coupling agents having reactive substituents such as carboxyl group, methacryl group, isocyanate group or epoxy group can be used. In particular, γ -methacryloxypropyltrimethoxysilane, vinyltriacetoxysilane, vinyltrimethoxysilane, γ -isocyanatepropyltriethoxysilane, γ -glycidoxypropyltrimethoxysilane, or β -(3,4-epoxy cyclo hexyl)ethyltrimethoxysilane can be used.

The adhesives are contained preferably in amount of 0.1 to 20 parts by weight with regard to 100 parts by weight of the acryl-based copolymers of a).

The acryl compounds of f) improve transmission, heat resistance, sensitivity, etc. of the patterns obtained from the photosensitive resin compositions.

Preferably, the representative example of the acryl compounds is formula 2:



wherein R is a hydrogen atom, alkyl group having 1 ~ 5 carbon atoms, alkoxy group having 1 ~ 5 carbon atoms or alkanoyl group having 1 ~ 5 carbon atoms,

$$1 < a < 6, \text{ and } a + b = 6.$$

The acryl compounds are contained preferably in an amount of 0.1 to 30 parts by weight with regard to 100 parts by weight of the acryl-based copolymers and more

preferably 0.1 to 15 parts by weight. The amount within the above ranges is advisable for the improvement of the sensitivity, heat resistance and transmission of patterns.

The surfactants of g) improve the coating performance or development performance of photosensitive compositions.

For the surfactants, polyoxyethyleneoctylphenylether, polyoxyethylenononylphenylether, F171, F172, F173 (product names: Dainippon Ink & Chemicals Inc.), FC430, FC431 (product names: Sumitomo 3M Limited), or KP341 (product name: Shin-Etsu chemical Industry Co., Ltd.) can be used.

The surfactants are contained preferably in an amount of 0.0001 to 2 parts by weight with regard to 100 parts by weight of the acryl-based copolymers of a), and the amount within the above ranges is advisable for the improvement of the development or coating performances of the photosensitive compositions

Also, the invention provides LCD substrates comprising the cured products of the photosensitive resins and pattern formation methods of LCD substrates using the photosensitive resin compositions.

The pattern formation methods of the invention are characterized in that in methods of forming the pattern of LCD substrates by forming photosensitive resin compositions into organic insulating films, the photosensitive resin compositions are employed.

In particular, one embodiment of the methods of forming the pattern of LCD substrates using the photosensitive resin compositions is as follows.

First, the photosensitive resin compositions of the invention are coated onto the surface of substrates using a spray method, roll coater method, spin coating method, etc.,

and coating films are formed by the elimination of solvents by pre-bake. The pre-bake is preferably carried out at temperature of $70 \sim 110^{\circ}\text{C}$ for $1 \sim 15$ min.

Next, the above formed coating films are irradiated with visible rays, UV, deep UV, electron beams, X rays, etc. in accordance with the prepared patterns and developed with development solutions to remove unnecessary parts whereby prescribed patterns are formed.

For the development solutions, alkaline aqueous solutions are preferably employed and in particular, there can be used inorganic alkalines such as sodium hydroxide, potassium hydroxide and sodium carbonate; primary amines such as n-propylamine; secondary amines such as diethylamine and n-propylamine; tertiary amines such as trimethylamine, methyl diethyl amine, dimethyl ethyl amine and triethyl amine; alcohol amines such as dimethylethanolamine, methyldiethanolamine and triethanolamine; or aqueous solutions of quaternary ammonium salts such as tetramethyl ammonium hydroxide and tetraethyl ammonium hydroxide. The development solutions are used by dissolving alkaline compounds at a concentration of $0.1 \sim 10\%$ by weight, and aqueous organic solvents such as methanol and ethanol and surfactants can be added thereto in a suitable amount.

Also, after development with the above development solutions, unnecessary parts are eliminated by wash with ultra pure water and patterns are formed after dry. After the formed patterns are irradiated with lights such as UV, the patterns are heated in heating machines such as an oven at a temperature of $150 \sim 250^{\circ}\text{C}$ for $30 \sim 90$ min. Thus, final patterns can be obtained.

The photosensitive resin compositions in accordance with the invention have excellent performances such as transmission, insulation, flatness and chemistry resistance and in particular, they secure reliable post-process by minimizing outgassing that may occur in interlayer dielectrics by virtue of high heat resistance property so that they are suitable for use in interlayer dielectrics during LCD manufacturing process and further, they can improve the reflectivity and adhesion of interlayer dielectrics applied to LCD manufacturing process and cause no damage on photo equipments due to outgassing,

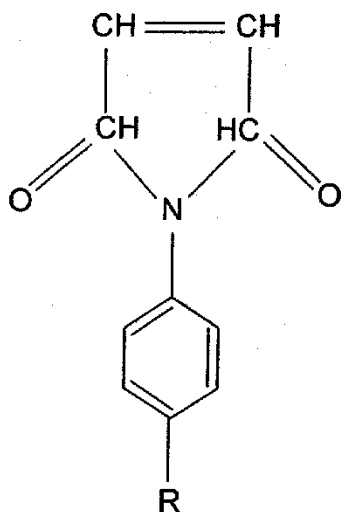
For better understanding of the present invention, preferred embodiments follow. The following examples are intended to merely illustrate the invention more fully without limiting the scope of the invention.

EXAMPLES

EXAMPLE 1

(Preparation of Acryl-Based Copolymer)

To a flask with a cooling tube and stirrer, 10 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile), 200 parts by weight of propyleneglycol monomethyletheracetate, 30 parts by weight of methacrylic acid, 30 parts by weight of glycidyl methacrylate, 10 parts by weight of 4-hydroxy phenylmaleimide having formula 1a:



wherein R is OH and 30 parts by weight of styrene were added and gently stirred after nitrogen substitution. The reaction solution was heated to 62 °C, which was maintained for 5 hours to prepare a polymer solution containing acryl-based copolymers.

The concentration of the solid of the polymer solution containing acryl-based copolymers was 45 % by weight and the weight average molecular weight of the polymer was 8,5000. The weight average molecular weight is an average molecular weight in terms of polystyrene measured using GPC.

(Preparation of 1,2-Quinonediazide)

1 mol of 4,4'-[1-[4-[1-[4-hydroxyphenyl]-1-methylethyl]phenyl]ethylidene]bisphenol and 2 mols of 1,2-naphtoquinonediazide-5-sulfonic acid[chloride] were condensation-reacted and 4,4'-[1-[4-[1-[4-hydroxyphenyl]-1-methylethyl]phenyl]ethyliden]bisphenol 1,2-naphtoquinonediazide-5-sulfonic ester was thus prepared.

(Preparation of Photosensitive Resin Composition)

100 parts by weight of the above prepared polymer solution containing acryl-based copolymers and 25 parts by weight of the prepared 4,4'-[1-[4-[1-[4-hydroxyphenyl]-1-methylethyl]phenyl]ethyliden]bisphenol 1,2-naphtoquinonediazide-5-sulfonic ester were mixed. The mixture was dissolved in diethyleneglycol dimethylether so that the concentration of the solid of the mixture became 35 % by weight and then filtered using a millipore filter of 0.2 μ m whereby a photosensitive resin composition was prepared.

EXAMPLE 2

With the exception that when acryl-based copolymers were prepared in Example 1, 4-hydroxy phenylmaleimide of formula 1a was used in an amount of 20 parts by weight and styrene was used in an amount of 20 parts by weight whereby acryl-based copolymers where the concentration of the solid was 45 % by weight and their weight average molecular weight was 8,400 were prepared, a photosensitive resin composition was prepared by carrying out the same method as used in Example 1.

EXAMPLE 3

With the exception that when acryl-based copolymers were prepared in Example 1, methacrylic acid was used in an amount of 35 parts by weight, 4-hydroxy phenylmaleimide of formula 1a was used in an amount of 30 parts by weight and styrene was used in an amount of 5 parts by weight whereby acryl-based copolymers where the concentration of the solid was 45 % by weight and their weight average molecular weight

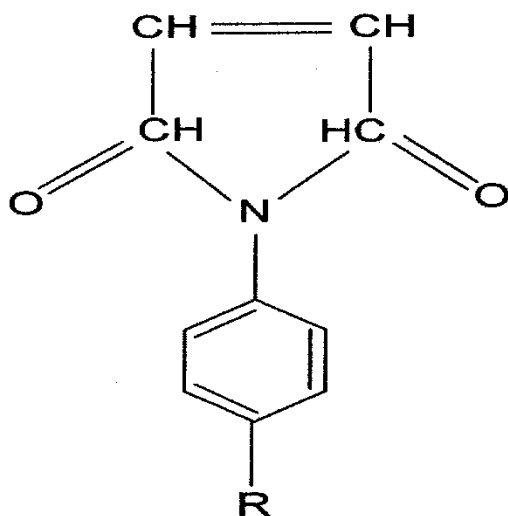
was 8,800 were prepared, a photosensitive resin composition was prepared by carrying out the same method as used in Example 1.

EXAMPLE 4

With the exception that when acryl-based copolymers were prepared in Example 1, methacrylic acid was used in an amount of 40 parts by weight, glycidyl methacrylate was used in an amount of 20 parts by weight, 4-hydroxy phenylmaleimide of formula 1a was used in an amount of 40 parts by weight and no styrene was used whereby acryl-based copolymers where the concentration of the solid was 45 % by weight and their weight average molecular weight was 9,100 were prepared, a photosensitive resin composition was prepared by carrying out the same method as used in Example 1.

EXAMPLE 5

With the exception that when acryl-based copolymers were prepared in Example 1, 10 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile), 200 parts by weight of propyleneglycol monomethyletheracetate, 30 parts by weight of methacrylic acid, 30 parts by weight of glycidyl methacrylate, 10 parts by weight of 4-carboxy phenylmaleimide of formula 1b:



wherein R is CH_3COO , and 30 parts by weight of styrene were used

whereby acryl-based copolymers where the concentration of the solid was 45 % by weight and their weight average molecular weight was 8,400 were prepared, a photosensitive resin composition was prepared by carrying out the same method as used in Example 1.

EXAMPLE 6

With the exception that when acryl-based copolymers were prepared in Example 1, 4-carboxy phenylmaleimide of formula 1b was used in an amount of 20 parts by weight and styrene was used in an amount of 20 parts by weight whereby acryl-based copolymers where the concentration of the solid was 45 % by weight and their weight average molecular weight was 8,600 were prepared, a photosensitive resin composition was prepared by carrying out the same method as used in Example 1.

EXAMPLE 7

With the exception that when acryl-based copolymers were prepared in Example 1, methacrylic acid was used in an amount of 35 parts by weight, 4-carboxy phenylmaleimide of formula 1b was used in an amount of 30 parts by weight and styrene was used in an amount of 5 parts by weight whereby acryl-based copolymers where the concentration of the solid was 45 % by weight and their weight average molecular weight was 9,100 were prepared, a photosensitive resin composition was prepared by carrying out the same method as used in Example 1.

EXAMPLE 8

With the exception that when acryl-based copolymers were prepared in Example 1, methacrylic acid was used in an amount of 40 parts by weight, glycidyl methacrylate was used in an amount of 20 parts by weight, 4-carboxy phenylmaleimide of formula 1b was used in an amount of 40 parts by weight and no styrene was used whereby acryl-based copolymers where the concentration of the solid was 45 % by weight and their weight average molecular weight was 9,300 were prepared, a photosensitive resin composition was prepared by carrying out the same method as used in Example 1.

COMPARATIVE EXAMPLE 1

With the exception that when acryl-based copolymers were prepared in Example 1, 4-hydroxy phenylmaleimide of formula 1a was not used and 10 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile, 200 parts by weight of propyleneglycol monomethyletheracetate, 40 parts by weight of methacrylic acid, 20 parts by weight of glycidyl methacrylate, and 40 parts by weight of methylmethacrylate were used whereby

acryl-based copolymers where the concentration of the solid was 45 % by weight and their weight average molecular weight was 9,300 were prepared, a photosensitive resin composition was prepared by carrying out the same method as used in Example 1.

The properties of the photosensitive resin compositions prepared in Examples 1 to 8 and Comparative Example 1 were evaluated by the following procedures and the results were summarized in Table 1 below.

a) Sensitivity-The photosensitive resin compositions prepared in Examples 1 to 8 and Comparative Example 1 were coated onto glass substrates using a spin coater and then pre-baked on hot plates at 90 °C for 2 min whereby films were formed.

The thus obtained films were irradiated with UV having an intensity of 15 mW/cm² at 365 nm for 15 seconds using predetermined pattern masks. Thereafter, they were developed with 0.38 wt.% aqueous solution of tetramethylammoniumhydroxide at 25 °C for 2 min. and then washed with ultra pure water for 1 min.

Thereafter, the above developed patterns were irradiated with UV an intensity of 15 mW/cm² at 365 nm for 34 seconds, mid-baked at 120 °C for 3 min. and then heated, cured in the oven of 220 °C for 60 min. whereby patterned films were obtained.

b) Heat Resistance-The width of top/bottom and left/right of the patterned films formed in above a) was measured. When the change rate of angles on the basis of before-midbake was 0 ~ 20 %, it was marked as "excellent," when it was 20 ~ 40 %, "not bad," and when it exceeds 40 %, "bad."

c) After-Image-In order to evaluate after-image, panels were fabricated using the photosensitive resin compositions prepared in Example 1 to 8 and Comparative Example

1 and after the panels were fixed into frames for certain period, whether stripes or image of previous frames remain when the next frame was turned was observed.

When there was no after-image, it was marked "very good," when after-image appeared for several minutes and then disappeared, "good," and when after-image still remained in the next frame, "bad."

Table 1

	Sensitivity (mJ/cm ²)	Heat Resistance	After-Image
Example 1	100	Not Bad	Good
Example 2	115	Excellent	Good
Example 3	130	Excellent	Good
Example 4	150	Excellent	Very Good
Example 5	110	Not Bad	Good
Example 6	125	Excellent	Good
Example 7	145	Excellent	Good
Example 8	155	Excellent	Very Good
Co. Example 1	90	Bad	Bad

From Table 1 above, Examples 1 to 8 where there were used acryl-based copolymers prepared by comprising the phenylmaleimide compounds in accordance with the invention had an excellent sensitivity of 100 ~ 160 mJ/cm² and especially, they were very excellent in heat resistance and had thus little effect on the formation of after-image of liquid crystals. Therefore, the invention is applicable to interlayer dielectrics. In

contrast, Comparative Example 1 was not good in sensitivity, heat resistance and after-image and it is thus difficult to be applied to interlayer dielectrics.

The photosensitive resin compositions in accordance with the invention have excellent performances such as transmission, insulation, flatness and chemistry resistance and in particular, they secure reliable post-process by minimizing outgassing that may occur in interlayer dielectrics by virtue of high heat resistance property so that they are suitable for use in interlayer dielectrics during LCD manufacturing process and further, they can improve the reflectivity and adhesion of interlayer dielectrics applied to LCD manufacturing process and cause no damage on photo equipments due to outgassing,

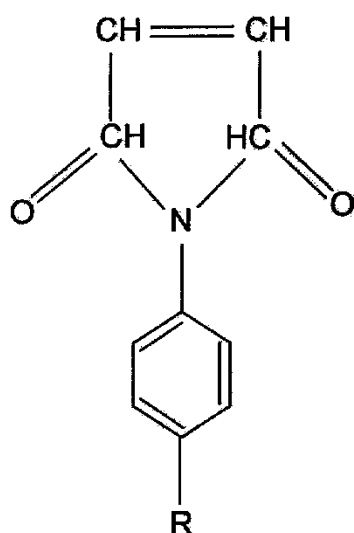
CLAIMS

What is claimed is:

1. A photosensitive resin composition comprising:

a) 100 parts by weight of the acryl-based copolymer, which has a weight average molecular weight (Mw) in terms of polystyrene of 5000 to 300000, obtained by copolymerizing

i) 5 to 60 parts by weight of the phenylmaleimide compound represented by formula 1:



wherein R is a hydroxy (OH-) or carboxy (CH₃COO⁻);

ii) 5 to 40 parts by weight of the unsaturated carbonic acid, unsaturated carbonic anhydride or mixture thereof; and

iii) 10 to 70 parts by weight of the epoxy group containing unsaturated compound;

b) 5 to 100 parts by weight of the 1,2-quinonediazide compound; and

c) the solvent in such an amount that the content of the solids in the photosensitive resin composition is 10 to 50% by weight.

2. The photosensitive resin composition according to claim 1 wherein the unsaturated carbonic acid, unsaturated carbonic anhydride or mixture thereof of a) ii) is selected from the group consisting of acrylic acid, methacrylic acid, maleic acid, fumaric acid, citraconic acid, methaconic acid, itaconic acid, unsaturated dicarbonic anhydride thereof and mixture thereof.

3. The photosensitive resin composition according to claim 1 wherein the epoxy group containing unsaturated compound of a) iii) is selected from the group consisting of glycidyl acrylate, glycidyl methacrylate, glycidyl α -ethylacrylate, glycidyl α -n-propylacrylate, glycidyl α -n-butylacrylate, β -methylglycidyl acrylate, β -methylglycidyl methacrylate, β -ethylglycidyl acrylate, β -ethylglycidyl methacrylate, 3,4-epoxybutyl acrylate, 3,4-epoxybutyl methacrylate, 6,7-epoxyheptyl acrylate, 6,7-epoxyheptyl methacrylate, 6,7-epoxyheptyl α -ethylacrylate, o-vinylbenzylglycidylether, m-vinylbenzylglycidylether, p-vinylbenzylglycidylether, mixture thereof.

4. The photosensitive resin composition according to claim 1 wherein when the acryl-based copolymer is prepared, it further comprises as a monomer iv) 10 to 70 parts by weight of an olefin-based unsaturated compound selected from the group consisting of methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, sec-butyl methacrylate, tert-butyl methacrylate, methyl acrylate, isopropyl acrylate, cyclohexyl methacrylate, 2-methylcyclohexyl methacrylate, dicyclopentenyl acrylate, dicyclopentanyl acrylate, dicyclopentenyl methacrylate, dicyclopentanyl methacrylate, dicyclopentanyloxyethyl methacrylate, isobornyl methacrylate, cyclohexyl acrylate, 2-methylcyclohexyl acrylate,

dicyclopentanyloxyethyl acrylate, isobornyl acrylate, phenyl methacrylate, phenyl acrylate, benzyl acrylate, 2-hydroxyethyl methacrylate, styrene, α -methyl styrene, m-methyl styrene, p-methyl styrene, vinyl toluene, p-methoxy styrene, 1,3-butadiene, isoprene, 2,3-dimethyl 1,3-butadiene, and mixture thereof.

5. The photosensitive resin composition according to claim 1 wherein the 1,2-quinonediazide compound of b) is selected from the group consisting of 1,2-quinonediazide-4-sulfonic ester, 1,2-quinonediazide-5-sulfonic ester, 1,2-quinonediazide-6-sulfonic ester, and mixture thereof.

6. The photosensitive resin composition according to claim 1 further comprising at least one additive selected from the group consisting of d) 0.1 to 30 parts by weight of an epoxy resin, e) 0.1 to 20 parts by weight of an adhesive, f) 0.1 to 30 parts by weight of an acryl compound, and g) 0.0001 to 2 parts by weight of a surfactant with regard to 100 parts by weight of the acryl-based copolymer of a).

7. An LCD substrate comprising a cured product of the photosensitive resin of any one of claims 1 to 6.

8. A pattern formation method of an LCD substrate using the photosensitive resin of any one of claims 1 to 6.