

DESCRIPTION

Silane Coupling Agent, Negative-Tone Photosensitive Resin Composition, Cured
Film, and Component for Touch Panel

TECHNICAL FIELD

5 [0001]

The present invention relates to a silane coupling agent suitable for a resin composition for forming a planarization film for a thin-film transistor (TFT) substrate in, for example, a liquid crystal display device or an organic EL display device, a protective film or an insulating film in, for example, a touch panel sensor device, and an interlayer insulating film for a semiconductor device. The present
10 invention also relates to a negative-tone photosensitive composition using the same, a cured film formed therefrom, and a component for a touch panel having the cured film.

BACKGROUND ART

15 [0002]

Currently, hard coating materials find use in various applications. For example, they are used to improve surface hardness, for example, of automotive parts, containers for cosmetics and the like, sheets, films, optical disks, and flat displays. Examples of the properties required for hard coating materials include heat resistance,
20 weatherability, and adhesion as well as hardness and abrasion resistance. Representative examples of hard coating materials include radical polymerizable and UV-curable hard coating materials (see, for example, Non-patent Document 1). The constituents of the hard coating materials are a polymerizable group-containing oligomer, a monomer, a photopolymerization initiator, and other additives.

25 [0003]

An oligomer and a monomer are radically polymerized by UV irradiation and thus cross-linked to obtain a film with high hardness. This hard coating

material requires little time for curing, and therefore the use thereof improves productivity. In addition, a negative-tone photosensitive material based on a common radical polymerization mechanism can be used, and therefore it has an advantage of reduced production cost.

5 [0004]

A capacitive-type touch panel, which has been receiving attention in recent years, is one application of hard coating materials. The capacitive-type touch panel has a pattern formed from an ITO (Indium Tin Oxide) film on a glass. To protect this ITO, films having high hardness are demanded. However, it is difficult to
10 simultaneously achieve high hardness and good adhesion to ITO, and hard coating materials that overcome this problem have been demanded.

[0005]

As a method of improving adhesion, the method of adding a silane coupling agent is well known. For example, the silane coupling agent having an imide group
15 (see Patent Document 1 and Patent Document 2) has been proposed as a silane coupling agent. In these Documents, it is recommended to use a compound that has not an amic acid structure but an imide group in order to improve adherence while having good planarization properties. As a silane coupling agent suitable for heat-resistant resin precursor compositions, a compound having a carboxyl group and
20 an ester group or a carboxyl group and an amide group (see Patent Document 3) has been proposed.

[0006]

However, none of the silane coupling agents had sufficient adhesion-improving effect when used as a hard coating agent for a touch panel.

25 [0007]

Further, the addition of an organic silicon compound having an amide acid structure to a polyimide resin composition (Patent Document 4) has also been

proposed. However, this organic silicon compound has a structure in which an amino group-containing silane coupling agent is added to an aromatic ring-nonhydrate. This organic silicon compound is not suitable for touch panel application because of its high colorability and also provides insufficient adhesion-improving effect.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0008]

Patent Document 1: WO 2008-065944 A

Patent Document 2: WO 2009-096050 A

Patent Document 3: JP 2006-316032 A

Patent Document 4: JP 09-222729 A

NON-PATENT DOCUMENTS

[0009]

Non-patent Document 1: "Material design, coating technique, and hardness improvement in hard coating film on plastic substrate", Ohara Noboru et al., TECHNICAL INFORMATION INSTITUTE CO., LTD., Apr. 28, 2005, p 301.

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0010]

An object of the present invention is to provide a cured film having excellent adhesion to a substrate surface made of metal or inorganic matter, high hardness, and excellent resolution. Further, another object of the present invention is to provide a cured film having low cure shrinkage and good planarization properties.

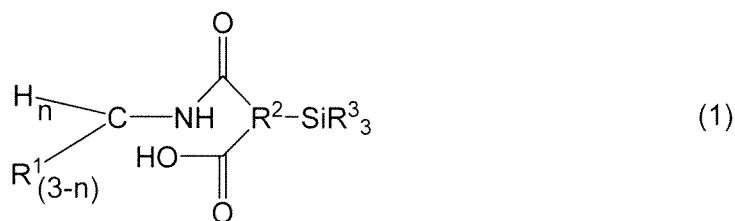
MEANS FOR SOLVING THE PROBLEMS

[0011]

To achieve the objects described above, the present invention has a constitution below.

Thus the present invention is a silane coupling agent represented by Formula (1) below.

[0012]



[0013]

(Each R^1 may be the same or different from each other and represents $\text{C}_1\text{-C}_6$ alkyl; the alkyl may further have a substituent(s); n represents 0 or 1; R^2 represents a $\text{C}_3\text{-C}_{30}$ trivalent organic group; and R^3 may be the same or different from each other and represents $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ alkoxy, phenyl, hydroxyl, and phenoxy, among which groups for R^3 groups other than hydroxyl may further have a substituent(s)).

EFFECTS OF THE INVENTION

[0014]

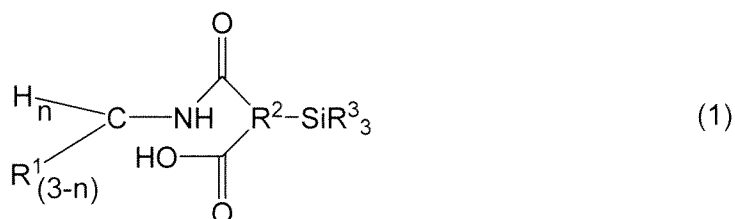
A cured film containing the silane coupling agent of the present invention has the effect of having superiority in improving adhesion to a substrate surface made of metal or inorganic matter, high hardness, and excellent resolution. Moreover, the cured film containing the silane coupling agent of the present invention also has the effect of having low cure shrinkage and good planarization properties.

BEST MODE FOR CARRYING OUT THE INVENTION

[0015]

The silane coupling agent of the present invention has a structure represented by Formula (1) below.

[0016]



[0017]

(Each R^1 may be the same or different from each other and represents $\text{C}_1\text{-C}_6$ alkyl; the alkyl may further have a substituent(s); n represents 0 or 1; R^2 represents a $\text{C}_3\text{-C}_{30}$ trivalent organic group; and R^3 may be the same or different from each other and represents $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ alkoxy, phenyl, hydroxyl, and phenoxy, among which groups for R^3 groups other than hydroxyl may further have a substituent(s)).

R^1 is preferably methyl, ethyl, and butyl, and, in particular, methyl and ethyl are preferred in terms of raw material availability. R^1 may have a substituent(s) such as alkoxy, aryl, phenoxy, or halogen. R^2 is preferably a $\text{C}_3\text{-C}_{30}$ trivalent organic group and more preferably a $\text{C}_3\text{-C}_{10}$ trivalent organic group in terms of solubility in an organic solvent.

[0018]

Examples of the silane coupling agent of the present invention represented by Formula (1) include 3-(tert-butylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(tert-butylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(isopropylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(isopropylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(isobutylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(isobutylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(tert-pentylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid, 2-(2-(tert-pentylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid, 3-(tert-butylcarbamoyl)-6-(triethoxysilyl) hexanoic acid,

2-(2-(tert-butylamino)-2-oxoethyl)-5-(triethoxysilyl) pentane acid,
 6-(dimethoxy(methyl)silyl)-3-(tert-butylcarbamoyl) hexanoic acid,
 5-(dimethoxy(methyl)silyl)-2-(2-(tert-butylamino)-2-oxoethyl) pentane acid,
 3-(tert-butylcarbamoyl)-6-(trimethoxysilyl) pentane acid,
 5 2-(2-(tert-butylamino)-2-oxoethyl)-5-(trimethoxysilyl) butanoic acid,
 2-(tert-butylcarbamoyl)-4-(2-(trimethoxysilyl)ethyl)cyclohexane carboxylic acid,
 2-(tert-butylcarbamoyl)-5-(2-(trimethoxysilyl)ethyl)cyclohexane carboxylic acid, and
 the like.

[0019]

10 Above all, the compound of Formula (1) above wherein $n = 0$ are preferred
 because it increases the effect of improving adhesion to ITO.

[0020]

Specifically, 3-(tert-butylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid,
 2-(2-(tert-butylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid,
 15 3-(isopropylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid,
 3-(tert-pentylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid,
 2-(2-(tert-pentylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid,
 3-(tert-butylcarbamoyl)-6-(triethoxysilyl) hexanoic acid,
 2-(2-(tert-butylamino)-2-oxoethyl)-5-(triethoxysilyl) pentane acid,
 20 6-(dimethoxy(methyl)silyl)-3-(tert-butylcarbamoyl) hexanoic acid,
 5-(dimethoxy(methyl)silyl)-2-(2-(tert-butylamino)-2-oxoethyl) pentane acid,
 3-(tert-butylcarbamoyl)-6-(trimethoxysilyl) pentane acid,
 2-(2-(tert-butylamino)-2-oxoethyl)-5-(trimethoxysilyl) butanoic acid,
 2-(tert-butylcarbamoyl)-4-(2-(trimethoxysilyl)ethyl)cyclohexane carboxylic acid, and
 25 2-(tert-butylcarbamoyl)-5-(2-(trimethoxysilyl)ethyl)cyclohexane carboxylic acid fall
 thereunder.

[0021]

These silane coupling agents may be used alone or as a mixture when added to a negative-tone photosensitive resin.

[0022]

As a method of preparing these silane coupling agents, a preparation method by the reaction of a silane coupling agent containing acid anhydride and alkyl amine is preferred in terms of ease of preparation. In this case, depending on the structure of the silane coupling agent containing acid anhydride, two types of silane coupling agent of the present invention will generate at the same time. However, they can be used as a mixture without particular separation or purification. Further, although this synthesis method can possibly cause replication of, for example, a small amount of oligomers, this does not significantly affect the adherence-improving effect and need not be considered.

[0023]

The amount of addition is preferably 1 to 15% by mass and more preferably 3 to 10% by mass, based on the resin component in a negative-tone photosensitive resin composition, i.e., the total amount of (B) an alkali-soluble resin and (C) a polyfunctional acryl monomer. When the amount is less than 1% by mass, the adhesion-improving effect is not sufficient, and when more than 15% by mass, fine patterns are absent in alkaline development, which leads to decreased resolution.

[0024]

The negative-tone photosensitive resin composition using the silane coupling agent of the present invention is characterized by containing at least (A) a silane coupling agent represented by Formula (1), (B) an alkali-soluble resin, (C) a polyfunctional acryl monomer, and (D) a photo-radical polymerization initiator.

[0025]

Each component of the negative-tone photosensitive resin composition using the silane coupling agent of the present invention will now be described.

[0026]

The negative-tone photosensitive composition of the present invention contains (B) the alkali-soluble resin. By having an alkali-soluble resin, the alkali solubility (developability) of the negative-tone photosensitive resin composition will be excellent, and residue after development can be reduced to form a good pattern. Further, by having an ethylenically unsaturated double bond group, the crosslink density can be enhanced, and the hardness of a cured film can be enhanced.

[0027]

Examples of (B) the alkali-soluble resin include polysiloxanes, acrylic resins, vinyl ether resins, polyhydroxystyrenes, novolac resins, polyimides, polyamides, and the like. In (B) the alkali-soluble resin, an ethylenically unsaturated double bond group is preferably introduced into at least a portion thereof in order to increase hardness of a cured film. Among these polymers, polysiloxanes and acrylic resins are more preferred in terms of ease of introduction of an ethylenically unsaturated double bond group. Further, two or more of these polymers may be contained. Preferred examples of (B) the alkali-soluble resin include the following, but are not limited thereto.

[0028]

As a polysiloxane, reaction products obtained by hydrolysis and condensation reaction of trifunctional alkoxysilane compounds are particularly preferred. Examples of trifunctional alkoxysilane compounds include the following.

[0029]

Specific examples thereof include methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, hexyltrimethoxysilane, octadecyltrimethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, naphthyltrimethoxysilane, anthracenyltrimethoxysilane,

- 3-aminopropyltriethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,
 3-(N,N-diglycidyl)aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane,
 glycidoxymethyltrimethoxysilane, glycidoxymethyltriethoxysilane,
 α -glycidoxyethyltrimethoxysilane, α -glycidoxyethyltriethoxysilane,
 5 β -glycidoxyethyltrimethoxysilane, β -glycidoxyethyltriethoxysilane,
 α -glycidoxypropyltrimethoxysilane, α -glycidoxypropyltriethoxysilane,
 β -glycidoxypropyltrimethoxysilane, β -glycidoxypropyltriethoxysilane,
 γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropyltriethoxysilane,
 γ -glycidoxypropyltripropoxysilane, γ -glycidoxypropyltriisopropoxysilane,
 10 γ -glycidoxypropyltributoxysilane, α -glycidoxybutyltrimethoxysilane,
 α -glycidoxybutyltriethoxysilane, β -glycidoxybutyltrimethoxysilane,
 β -glycidoxybutyltriethoxysilane, γ -glycidoxybutyltrimethoxysilane,
 γ -glycidoxybutyltriethoxysilane, δ -glycidoxybutyltrimethoxysilane,
 δ -glycidoxybutyltriethoxysilane, (3,4-epoxycyclohexyl)methyltrimethoxysilane,
 15 (3,4-epoxycyclohexyl)methyltriethoxysilane,
 (3,4-epoxycyclohexyl)methyltrimethoxysilane,
 (3,4-epoxycyclohexyl)methyltriethoxysilane,
 2-(3,4-epoxycyclohexyl)ethyltripropoxysilane,
 2-(3,4-epoxycyclohexyl)ethyltributoxysilane,
 20 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane,
 3-(3,4-epoxycyclohexyl)propyltrimethoxysilane,
 3-(3,4-epoxycyclohexyl)propyltriethoxysilane,
 4-(3,4-epoxycyclohexyl)butyltrimethoxysilane,
 25 4-(3,4-epoxycyclohexyl)butyltriethoxysilane, trifluoromethyltrimethoxysilane,
 trifluoromethyltriethoxysilane, trifluoropropyltrimethoxysilane,
 trifluoropropyltriethoxysilane, and the like.

[0030]

Further, by using a trifunctional alkoxysilane containing an ethylenically unsaturated double bond group, an ethylenically unsaturated double bond group can be readily introduced into a polysiloxane, and the hardness of a cured film can be increased, which is more preferred.

[0031]

Specific examples thereof include vinyltrimethoxysilane, vinyltriethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -acryloxypropyltrimethoxysilane, γ -acryloxypropyltriethoxysilane, and the like.

[0032]

As an acrylic resin, those obtained by radical polymerization of (meth)acrylic acid or (meth)acrylic acid ester are preferred. As a (meth)acrylic acid ester, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, cyclopropyl (meth)acrylate, cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate, cyclohexenyl (meth)acrylate, 4-methoxycyclohexyl (meth)acrylate, 2-cyclopropyloxycarbonylethyl (meth)acrylate, 2-cyclopentyloxycarbonylethyl (meth)acrylate, 2-cyclohexyloxycarbonylethyl (meth)acrylate, 2-cyclohexenyloxycarbonylethyl (meth)acrylate, 2-(4-methoxycyclohexyl)oxycarbonylethyl (meth)acrylate, norbornyl (meth)acrylate, isobornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, tetracyclodecanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, adamantyl (meth)acrylate, adamantylmethyl (meth)acrylate, 1-methyladamantyl (meth)acrylate, and the like are used. Aromatic vinyl compounds such as styrene, p-methylstyrene, o-methylstyrene, m-methylstyrene, and α -methylstyrene may be copolymerized with the (meth)acrylic acid or (meth)acrylic acid ester described above.

[0033]

An ethylenically unsaturated double bond group can also be introduced by

addition reaction of an epoxy compound having an ethylenically unsaturated double bond group with (meth)acrylic acid. Examples of the epoxy compound having an ethylenically unsaturated double bond group include the compounds below.

[0034]

5 Specific examples include glycidyl (meth)acrylate, α -ethyl glycidyl (meth)acrylate, α -n-propyl glycidyl (meth)acrylate, α -n-butyl glycidyl (meth)acrylate, 3,4-epoxybutyl (meth)acrylate, 3,4-epoxyheptyl (meth)acrylate, α -ethyl-6,7-epoxyheptyl (meth)acrylate, allyl glycidyl ether, vinyl glycidyl ether, o-vinylbenzyl glycidyl ether, m-vinylbenzyl glycidyl ether, p-vinylbenzyl glycidyl ether, α -methyl-o-vinylbenzyl glycidyl ether, α -methyl-m-vinylbenzyl glycidyl ether, α -methyl-p-vinylbenzyl glycidyl ether, 2,3-diglycidyl oxymethylstyrene, 2,4-diglycidyl oxymethylstyrene, 2,5-diglycidyl oxymethylstyrene, 2,6-diglycidyl oxymethylstyrene, 2,3,4-triglycidyl oxymethylstyrene, 2,3,5-triglycidyl oxymethylstyrene, 2,3,6-triglycidyl oxymethylstyrene, 3,4,5-triglycidyl oxymethylstyrene, 2,4,6-triglycidyl oxymethylstyrene, and the like.

[0035]

In the negative-tone photosensitive resin composition of the present invention, the content of (B) the alkali-soluble resin is not particularly restricted and can be arbitrarily selected depending on the desired film thickness and application.

20 (B) the alkali-soluble resin is preferably added in an amount of 10 to 60% by mass based on the solid content of the negative-tone photosensitive resin composition.

[0036]

25 The negative-tone photosensitive composition of the present invention contains (C) the polyfunctional monomer. Polyfunctional monomer refers to a compound having in its molecule at least two or more ethylenically unsaturated double bonds. In view of radical polymerizability, a polyfunctional monomer having an acrylic group is preferred.

[0037]

Specific examples include oligomers such as bisphenol A diglycidyl ether (meth)acrylate, poly(meth)acrylate carbamate, modified bisphenol A epoxy (meth)acrylate, adipic acid 1,6-hexanediol (meth)acrylic acid ester, phthalic anhydride propylene oxide (meth)acrylic acid ester, trimellitic acid diethylene glycol (meth)acrylic acid ester, rosin-modified epoxy di(meth)acrylate, and alkyd-modified (meth)acrylate, or tripropylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, bisphenol A diglycidyl ether di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, triacrylformal, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, tripentaerythritol hepta(meth)acrylate, tripentaerythritol octa(meth)acrylate, [9,9-bis[4-(2-acryloyloxyethoxy)phenyl]fluorene, and the like.

[0038]

The negative-tone photosensitive resin composition of the present invention contains (D) the photo-radical polymerization initiator. (D) the photo-radical polymerization initiator may be any initiator as long as it is decomposed and/or reacted by light (including ultraviolet light and electron beam) to generate radicals. To further increase hardness of a cured film, it is preferable to use α -aminoalkylphenone compounds, acylphosphine oxide compounds, oxime ester compounds, benzophenone compounds having an amino group, or benzoic acid ester compounds having an amino group. Further, two or more of these compounds may be contained.

[0039]

Specific examples of α -aminoalkylphenone compounds include 2-methyl-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, 2-dimethylamino-2-(4-methylbenzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, and the like.

[0040]

Specific examples of acylphosphine oxide compounds include

2,4,6-trimethylbenzoyl phenylphosphine oxide,

bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide,

5 bis(2,6-dimethoxybenzoyl)-(2,4,4-trimethylpentyl)-phosphine oxide, and the like.

[0041]

Specific examples of oxime ester compounds include

1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime,

1,2-octanedione, 1-[4-(phenylthio)-2-(O-benzoyloxime)],

10 1-phenyl-1,2-butadione-2-(o-methoxycarbonyl)oxime,

1,3-diphenylpropanetrione-2-(o-ethoxycarbonyl)oxime,

ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-, 1-(O-acetyloxime), and the like.

[0042]

15 Specific examples of benzophenone compounds having an amino group include 4,4-bis(dimethylamino)benzophenone, 4,4-bis(diethylamino)benzophenone, and the like.

[0043]

Specific examples of benzoic acid ester compounds having an amino group

20 include ethyl p-dimethylaminobenzoate, 2-ethylhexyl-p-dimethylaminobenzoate, ethyl p-diethylaminobenzoate, and the like.

[0044]

The content of (D) the photo-radical polymerization initiator is preferably

0.01% by mass or more and more preferably 0.1% by mass or more, and preferably

25 not more than 20% by mass and more preferably not more than 10% by mass, based on the solid content of the negative-tone photosensitive resin composition. When the content is within the above range, sufficient progress of radical curing can be

made, and the remaining radical polymerization initiator can be prevented from, for example, dissolving to thereby ensure solvent resistance.

[0045]

The negative-tone photosensitive resin composition of the present invention
5 may contain a polymerization inhibitor. By containing a polymerization inhibitor, storage stability of the composition is improved, and resolution after development is improved in applications that require pattern processing. Specific examples of polymerization inhibitors include phenol, catechol, resorcinol, hydroquinone, 4-t-butylcatechol, 2,6-di(t-butyl)-p-cresol, phenothiazine, 4-methoxyphenol, and the
10 like.

[0046]

The content of the polymerization inhibitor is preferably 0.01% by mass or more and more preferably 0.1% by mass or more, based on the solid content of the negative-tone photosensitive resin composition. On the other hand, from the
15 standpoint of maintaining the hardness of a cured film at a high level, the content is preferably not more than 5% by mass and more preferably not more than 1% by mass.

[0047]

The negative-tone photosensitive resin composition of the present invention
20 may contain a thermal acid generator. The thermal acid generator can further increase the adhesion-enhancing effect of a silane coupling agent. Specific examples of thermal acid generators that are preferably used include triphenylsulfonium, 4-hydroxyphenyldimethylsulfonium, benzyl-4-hydroxyphenylmethylsulfonium,
25 2-methylbenzyl-4-hydroxyphenylmethylsulfonium, 2-methylbenzyl-4-acetylphenylmethylsulfonium, 2-methylbenzyl-4-benzoyloxyphenylmethylsulfonium, their methanesulfonic acid

salts, trifluoromethanesulfonic acid salts, camphorsulfonic acid salts, p-toluenesulfonic acid salts, and the like.

[0048]

SI-60, SI-80, SI-100, SI-110, SI-145, SI-150, SI-200, SI-60L, SI-80L, SI-100L, SI-110L, SI-145L, SI-150L, SI-160L, and SI-180L (all of which are available from SANSIN CHEMICAL INDUSTRY CO., LTD.) are also preferably used. Two or more of them may be contained.

[0049]

The content of the thermal acid generator is preferably 0.1 to 3% by mass based on the resin component of the negative-tone photosensitive resin composition, i.e., the total amount of (B) the alkali-soluble resin and (C) the polyfunctional acryl monomer. When the content is less than 0.1% by mass, the adhesion-enhancing effect is small, and when more than 3% by mass, patterns become larger than mask patterns, which leads to decreased resolution.

[0050]

The siloxane resin composition of the present invention may contain an UV absorber. By containing an UV absorber, light resistance of a resulting cured film is improved, and resolution after development is improved in applications that require pattern processing. The UV absorber is not particularly limited, and a known absorber can be used.

[0051]

In terms of transparency and uncolorability, benzotriazole compounds, benzophenone compounds, and triazine compounds are preferably used.

[0052]

Examples of the UV absorber of a benzotriazole compound include 2-(2Hbenzotriazol-2-yl)phenol, 2-(2H-benzotriazol-2-yl)-4,6-t-pentylphenol, 2-(2Hbenzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol,

2(2H-benzotriazol-2-yl)-6-dodecyl-4-methylphenol,
2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole, and the like.

[0053]

Examples of the UV absorber of a benzophenone compound include

5 2-hydroxy-4-methoxybenzophenone and the like.

[0054]

Examples of the UV absorber of a triazine compound include

2-(4,6-diphenyl-1,3,5 triazin-2-yl)-5-[(hexyl)oxy]-phenol and the like.

[0055]

10 The negative-tone photosensitive resin composition of the present invention may contain solvents. Compounds having an alcoholic hydroxyl group or cyclic compounds having a carbonyl group are preferably used because they can dissolve each component uniformly and improve transparency of a resulting coated film. Two or more of them may be contained. Compounds having a boiling point of 110
15 to 250°C under atmospheric pressure are more preferred.

[0056]

When the boiling point is 110°C or higher, drying proceeds moderately during coating, and a good coated film without uneven coating is obtained. On the other hand, when the boiling point is 250°C or lower, the amount of residual solvents
20 in a film can be kept small, and film shrinkage upon heat curing can be reduced furthermore; therefore better planarization properties can be obtained.

[0057]

Specific examples of compounds having an alcoholic hydroxyl group and a boiling point of 110 to 250°C under atmospheric pressure include acetol,

25 3-hydroxy-3-methyl-2-butanone, 4-hydroxy-3-methyl-2-butanone,
5-hydroxy-2-pentanone, 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol), ethyl lactate, butyl lactate, propylene glycol monomethyl ether, propylene glycol

monoethyl ether, propylene glycol mono n-propyl ether, propylene glycol mono n-butyl ether, propylene glycol mono t-butyl ether, 3-methoxy-1-butanol, 3-methyl-3-methoxy-1-butanol, and the like. Among them, diacetone alcohol is preferred from the standpoint of storage stability, and propylene glycol mono t-butyl ether is preferred in terms of step coverage.

[0058]

Specific examples of cyclic compounds having a carbonyl group and a boiling point of 110 to at 250°C under atmospheric pressure include γ -butyrolactone, γ -valerolactone, δ -valerolactone, propylene carbonate, N-methylpyrrolidone, cyclohexanone, cycloheptanone, and the like. Among them, γ -butyrolactone is preferred.

[0059]

The negative-tone photosensitive resin composition of the present invention may also contain various solvents other than the above, such as acetates, ketones, and ethers.

[0060]

The content of solvents is not particularly restricted, and the solvents can be used in any amount depending, for example, on the coating method. For example, in the case where films are formed by spin coating, the solvent amount is generally 50 to 95% by mass based on the total negative-tone photosensitive resin composition.

[0061]

The negative-tone photosensitive resin composition of the present invention may contain various curing agents that promote or facilitate curing of the resin composition. The curing agent is not particularly limited, and a known curing agent can be used. Specific examples thereof include nitrogen-containing organic matter, silicone resin curing agents, various metal alcoholates, various metal chelate compounds, isocyanate compounds and polymers thereof, methylolated melamine

derivatives, methylolated urea derivatives, and the like. Two or more of them may be contained. Among them, metal chelate compounds, methylolated melamine derivatives, and methylolated urea derivatives are preferably used in terms, for example, of stability of a curing agent and processability of the coated film obtained.

5 [0062]

The negative-tone photosensitive resin composition of the present invention may contain various surfactants such as fluorine-based surfactants and silicone-based surfactants in order to improve flowability during coating. The type of surfactants is not particularly restricted, and, for example, fluorine-based surfactants,
10 silicone-based surfactants, polyalkylene oxide-based surfactants, poly(meth)acrylate-based surfactants, and the like can be used. Two or more of them may be used.

[0063]

Examples of commercially available products of fluorine-based surfactants
15 that are preferably used include "MEGAFACE" (registered trademark) F142D, F172, F173, F183, F445, F470, F475, and F477 (available from Dainippon Ink and Chemicals, Incorporated); and NBX-15 and FTX-218 (available from NEOS COMPANY LIMITED). Examples of commercially available products of silicone-based surfactants that are preferably used include BYK-333, BYK-301,
20 BYK-331, BYK-345, and BYK-307 (available from BYK-Chemie Japan).

[0064]

The representative method of preparing the negative-tone photosensitive resin composition of the present invention will be described. For example, (A) a silane coupling agent represented by Formula (1), (B) an alkali-soluble resin, (C) a
25 polyfunctional acryl monomer, (D) a photo-radical polymerization initiator, and other additives as required are added to any solvent and dissolved by stirring, and then the solution obtained is filtered to obtain a negative-tone photosensitive resin

composition.

[0065]

A method of forming a cured film using the negative-tone photosensitive resin composition of the present invention will be described by way of example.

5 The negative-tone photosensitive resin composition of the present invention is applied onto a base substrate by a known method such as microgravure coating, spin coating, dip coating, curtain flow coating, roll coating, spray coating, or slit coating, and pre-baked with a heating apparatus such as a hot plate or an oven. It is preferred that the pre-baking be carried out in the range of 50 to 150°C for 30
10 seconds to 30 minutes and that the film thickness after the pre-baking be 0.1 to 15 μm .

[0066]

After the pre-baking, exposure is performed using an exposure apparatus such as a stepper, a mirror projection mask aligner (MPA), or a parallel light mask
15 aligner (PLA). At an exposure intensity of about 10 to 4000 J/m^2 (in terms of exposure at a wavelength of 365 nm), the film is irradiated with this light through or not through a desired mask. The exposure light source is not limited, and UV rays such as i-ray, g-ray, and h-ray, KrF (wavelength: 248 nm) laser, ArF (wavelength: 193 nm) laser, and the like can be used.

20 [0067]

Next, the exposed portion is dissolved by development to obtain a negative-tone pattern. A preferred method for development is immersion in a developing solution for 5 seconds to 10 minutes by means of, for example, showering, dipping, or puddling. As a developing solution, a known alkaline
25 developing solution can be used. Specific examples include, for example, an aqueous solution containing one, or two or more of inorganic alkalis such as hydroxides, carbonates, phosphates, silicates, and borates of alkali metals; amines

such as 2-diethylaminoethanol, monoethanolamine, and diethanolamine; and quarternary ammonium salts such as tetramethylammonium hydroxide and choline. After the development, it is preferable to rinse with water, and then dry baking can also be carried out in the range of 50 to 150°C.

5 [0068]

Thereafter, this film is heated with a heating apparatus such as a hot plate or an oven in the range of 150 to 450°C for about 20 minutes to 1 hour.

[0069]

The cured film obtained by curing the negative-tone photosensitive resin
10 composition of the present invention is used as a touch panel protective film, a touch panel insulating film, various hard coating materials, an antireflection film, and an optical filter. Further, it is suitably used as a planarization film for a TFT in a liquid crystal display or an organic EL display, an insulating film, and an antireflection film, an overcoat for a color filter, a column material, and the like because it has
15 negative-tone photosensitivity. Among them, it can be suitably used particularly as a touch panel protective film and a touch panel insulating film that require adhesion to a substrate that does not have Si such as ITO and molybdenum after heat treatment and after chemical treatment. Examples of types of a touch panel include the resistive type, the optical type, the electromagnetic induction type, the capacitive
20 type, and the like. Since a capacitive-type touch panel requires particularly high hardness, the cured film of the present invention can be suitably used therefor.

[0070]

When the cured film of the present invention is used as a protective film for a touch panel, the film, when having a thickness of 1.5 μm , preferably has a hardness
25 of 4H or more, a transmittance of 95% or more, and a resolution of not more than 20 μm . The hardness and the transmittance can be controlled by selection of exposure amount and heat-curing temperature.

EXAMPLES

[0071]

The present invention will now be described more specifically by way of Examples. The present invention is not limited to these Examples. Among the compounds used in Synthesis Examples and Examples, those indicated by abbreviations are shown below.

[0072]

PGMEA: Propylene Glycol Monomethyl Ether Acetate

DAA: Diacetone Alcohol

[0073]

Synthesis Example 1: Synthesis of Mixed Silane Coupling Agent Solution (a-1)

To 200 g of PGMEA, 41.97 g (160 mmol) of 3-trimethoxysilylpropylsuccinic anhydride and 11.70 g (160 mmol) of t-butylamine were added, and the resulting mixture was stirred at room temperature for some time and then stirred at 40°C for 2 hours. Thereafter, the temperature was raised to 80°C, and the mixture was allowed to react for 6 hours. The solution obtained was diluted with PGMEA to a solid content of 20% to obtain a mixed solution (a-1) of 3-(tert-butylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid and 2-(2-(tert-butylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid.

[0074]

Synthesis Example 2: Synthesis of Mixed Silane Coupling Agent Solution (a-2)

To 200 g of PGMEA, 41.97 g (160 mmol) of 3-trimethoxysilylpropylsuccinic anhydride and t-pentyl amine 9.45 g (160 mmol) were added, and the resulting mixture was stirred at room temperature for some time and then stirred at 40°C for 2 hours. Thereafter, the temperature was raised to 80°C, and the mixture was allowed to react for 6 hours. The solution obtained was diluted with PGMEA to a solid content of 20% to obtain a mixed solution (a-2) of

2-(2-(t-pentylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid and
3-(tert-pentylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid.

[0075]

Synthesis Example 3: Synthesis of Mixed Silane Coupling Agent Solution (a-3)

5 To 200 g of PGMEA, 41.97 g (160 mmol) of
3-trimethoxysilylpropylsuccinic anhydride and 9.45 g (160 mmol) of isopropyl
amine were added, and the resulting mixture was stirred at room temperature for
some time and then stirred at 40°C for 2 hours. Thereafter, the temperature was
raised to 80°C, and the mixture was allowed to react for 6 hours. The solution
10 obtained was diluted with PGMEA to a solid content of 20% to obtain a mixed
solution (a-3) of 2-(2-(isopropylamino)-2-oxoethyl)-5-(trimethoxysilyl) pentane acid
and 3-(tert-isopropylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid.

[0076]

Synthesis Example 4: Synthesis of Mixed Silane Coupling Agent Solution (a-4)

15 To 200 g of PGMEA, 41.97 g (160 mmol) of
3-trimethoxysilylpropylsuccinic anhydride and 9.45 g (160 mmol) of n-propylamine
were added, and the resulting mixture was stirred at room temperature for some time
and then stirred at 40°C for 2 hours. Thereafter, the temperature was raised to 80°C,
and the mixture was allowed to react for 6 hours. The solution obtained was diluted
20 with PGMEA to a solid content of 20% to obtain a mixed solution (a-4) of
2-(2-oxo-2-(propylamino)ethyl)-5-(trimethoxysilyl) pentane acid and
3-(propylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid.

[0077]

Synthesis Example 5: Synthesis of Mixed Silane Coupling Agent Solution (a-5)

25 To 200 g of PGMEA, 41.97 g (160 mmol) of
3-trimethoxysilylpropylsuccinic anhydride and 14.90 g (160 mmol) of aniline were
added, and the resulting mixture was stirred at room temperature for some time and

then stirred at 40°C for 2 hours. Thereafter, the temperature was raised to 80°C, and the mixture was allowed to react for 6 hours. The solution obtained was diluted with PGMEA to a solid content of 20% to obtain a mixed solution (a-5) of 2-(2-oxo-2-(phenylamino)ethyl)-5-(trimethoxysilyl) pentane acid and 3-(phenylcarbamoyl)-6-(trimethoxysilyl) hexanoic acid.

[0078]

Synthesis Example 6: Synthesis of Mixed Silane Coupling Agent Solution (a-6)

To 200 g of PGMEA, 41.97 g (160 mmol) of 3-trimethoxysilylpropylsuccinic anhydride and 7.37 g (160 mmol) of ethanol were added, and the resulting mixture was stirred at room temperature for some time and then stirred at 40°C for 2 hours. Thereafter, the temperature was raised to 80°C, and the mixture was allowed to react for 6 hours. The solution obtained was diluted with PGMEA to a solid content of 20% to obtain a mixed solution (a-6) of 4-ethoxy-4-oxo-2-(trimethoxysilyl) butanoic acid and 4-ethoxy-4-oxo-3-(trimethoxysilyl) butanoic acid.

[0079]

Synthesis Example 7: Synthesis of Silane Coupling Agent Solution (a-7)

To 400 g of PGMEA, 41.97 g (160 mmol) of 3-trimethoxysilylpropylsuccinic anhydride and 11.70 g (160 mmol) of t-butylamine were added, and the resulting mixture was stirred at room temperature for some time and then stirred at 60°C for 2 hours. Thereafter, the temperature was raised to 140°C, and the mixture was allowed to react for 6 hours while azeotroping PGMEA and water. The solution obtained was diluted with PGMEA to a solid content of 20% to obtain a 1-(tert-butyl)-3-trimethoxysilyl pyrrolidine-2,5-dione solution (a-7).

[0080]

Synthesis Example 8: Synthesis of Siloxane Resin Solution (b-1)

Into a 500-ml three-necked flask, 13.62 g (0.1 mol) of

methyltrimethoxysilane, 118.98 g (0.6 mol) of phenyltrimethoxysilane, 39.39 g (0.15 mol) of 3-trimethoxysilylpropyl succinic acid, 35.16 g of γ -methacryloxypropyltrimethoxysilane, and 140.87 g of DAA were added.

Thereafter, while stirring the mixed solution at room temperature, an aqueous
5 phosphoric acid solution obtained by dissolving 0.106 g (0.05% by mass based on the monomer charged) of phosphoric acid in 59.4 g of water was added over 30 minutes. Thereafter, the flask was immersed in an oil bath at 40°C and stirred for 30 minutes, and then the temperature of the oil bath was raised to 115°C over 30 minutes. After 1 hour from the start of temperature rise, the inner temperature of
10 the solution reached 100°C, and the flask was heated under stirring for further 45 minutes (the inner temperature was 100 to 110°C). During the reaction, by-products, methanol and water, in a total amount of 89 g were distilled out. To the polysiloxane solution in DAA obtained, DAA was added to a polymer concentration of 40% by mass to obtain a siloxane resin solution (b-1). The weight
15 average molecular weight of the polymer obtained was 7500.

[0081]

Synthesis Example 9: Synthesis of Acrylic Resin Solution (b-2)

To a 500-ml flask, 3 g of 2,2'-azobis(isobutyronitrile) and 50 g of PGMEA (Propylene Glycol Methyl Ether Acetate) were charged. Thereafter, 30 g of
20 methacrylic acid, 22.48 g of styrene, and 25.13 g of cyclohexyl methacrylate were added. Thereafter, the mixed solution was stirred at room temperature for some time, and the flask was purged with nitrogen and then heated under stirring at 70°C for 5 hours. Next, 15 g of glycidyl methacrylate, 1 g of dimethylbenzylamine, 0.2 g of p-methoxyphenol, and 100 g of PGMEA were added to the solution obtained, and
25 the resulting mixture was heated under stirring at 90°C for 4 hours. PGMEA was added to obtain an acrylic resin solution (b-2) such that the acrylic resin solution obtained had a solid content of 40% by mass. The weight average molecular weight

of the acrylic resin was 13500, and the acid number was 100 mg KOH/g.

[0082]

Synthesis Example 10: Synthesis of Quinonediazide Compound (q-1)

Under a stream of dry nitrogen, 21.23 g (0.05 mol) of TrisP-PA (trade name,
5 available from HONSHU CHEMICAL INDUSTRY Co., Ltd.) and 37.62 g (0.14
mol) of 5-naphthoquinone diazide sulfonyl acid chloride were dissolved in 450 g of
1,4-dioxane, and the temperature was adjusted to room temperature. To this
solution, 15.58 g (0.154 mol) of triethylamine mixed with 50 g of 1,4-dioxane was
added dropwise such that the temperature in the system did not increase to 35°C or
10 higher. After completion of the dropwise addition, the resulting mixture was stirred
at 30°C for 2 hours. A triethylamine salt was filtered off, and the filtrate was
poured into water. Thereafter, the precipitates obtained were collected by filtration.
The precipitates were dried with a vacuum dryer to obtain a quinonediazide
compound (q-1).

15 [0083]

Evaluation methods in each Example/Comparative Example will be
described below.

(1) Measurement of Hardness

For a cured film with a film thickness of 1.5 μm prepared on a 5-cm square
20 glass substrate, the pencil hardness was measured in accordance with "JIS K5600-5-4
(1999)". The applied load was 500 g.

[0084]

(2) Evaluation of Adhesion to ITO

A substrate was formed such that ITO had a film thickness of 200 Angstrom
25 and a resistance value of 100 $\Omega/\square$ on an alkali-free glass substrate (glass thickness:
0.7 mm). For a cured film with a film thickness of 1.5 μm formed on this substrate
(hereinafter referred to as an ITO substrate), adhesion between ITO and the cured

film was evaluated in accordance with JIS "K5400" 8.5.2 (1990) Cross-cut tape method. On the cured film surface on the glass substrate, vertical and horizontal 11 parallel straight lines perpendicular to each other were drawn with a cutter knife at 1-mm intervals in such a manner that the cutter knife reached the base of the glass plate to form 100 squares of 1 mm × 1 mm. A cellophane adhesive tape (width = 5 18 mm, adhesive strength = 3.7 N/10 mm) was applied to the cured film surface with cuts and rubbed with an eraser (meeting JIS S6050) to cause a close adhesion. Then, the tape was picked up at one end and held perpendicular to the plate, and the number of the squares survived after instantaneous peeling was visually evaluated.

10 The assessment was made from the peeled area of the squares as follows:

5: Peeled area, 0%

4: Peeled area, 0 to less than 5%

3: Peeled area, 5 to 15%

2: Peeled area, 15 to 35%

15 1: Peeled area, 35 to 65%

0: Peeled area, 65 to 100%

[0085]

(3) Resolution

A line-and-space pattern mask at a width ratio of 1:1 was used to measure 20 the width of a mask pattern that is able to form a minimum pattern.

[0086]

(4) Evaluation of Planarization Performance

For a cured film formed on a silicon wafer by the method described in (1) above, cure shrinkage from before to after the curing was calculated. When the 25 value is 0 to 15%, the planarization performance can be said to be good. The cure shrinkage was calculated according to the equation below.

Cure shrinkage (%) = (1 - Film thickness of cured film obtained by curing /

Film thickness after development) $\times 100$

When calculating cure shrinkage of a non-photosensitive resin composition, the calculation was performed by substituting "Film thickness after pre-baking" for "Film thickness after development" because a developing process is not performed.

5 For the film thickness measurement, Lambda Ace STM-602 (trade name, manufactured by Dainippon Screen Mfg. Co., Ltd.) was used. The refractive index was set at 1.52 for every measured object, and film thickness after pre-baking, film thickness after development, and film thickness of a cured film obtained by curing were measured.

10 [0087]

Example 1

Under yellow light, 1.557 g of 2-methyl-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (trade name "Irgacure 907" available from Ciba Specialty Chemicals K. K., (hereinafter referred to as IC907)) and 0.173 g of 4,4-bis(diethylamino)benzophenone (hereinafter referred to as EK) were dissolved in 21.618 g of DAA and 34.489 g of PGMEA. To this solution, 10.382 g of dipentaerythritol hexaacrylate (trade name "KAYARAD DPHA" available from Nippon Kayaku Co., Ltd. (hereinafter referred to as DPHA), 4.326 g of the mixed silane coupling agent solution (a-1), 8.652 g of a 1% by mass solution of 4-t-butylcatechol in PGMEA, 17.303 g of the siloxane resin solution (b-1), and 1.500 g of a 1% by mass solution of silicone-based surfactant BYK-333 (available from BYK-Chemie Japan) in PGMEA were added, and the resulting mixture was stirred. Then, the resultant was filtered through a 0.45- μ m filter to obtain a negative-tone photosensitive resin composition (N-1).

25 [0088]

The negative-tone photosensitive resin composition (N-1) obtained was spin-coated on a glass substrate and on an ITO substrate each using a spin coater

(1H-360S manufactured by MIKASA CO., LTD.) at any rotation speed. Thereafter, these substrates were pre-baked at 110°C for 2 minutes using a hot plate (SCW-636 manufactured by Dainippon Screen Mfg. Co., Ltd.) to produce a film with a film thickness of 1.5 μm .

5 [0089]

Using a parallel light mask aligner (PLA-501F manufactured by Canon Inc.) and an ultra-high pressure mercury lamp as a light source, the film produced was exposed to light at an exposure amount of 200 mJ (i-ray) using 5-, 10-, 20-, 30-, 40-, and 50- μm wide masks at a width ratio of 1:1 with a mask gap of 100 μm .

10 Thereafter, using an automatic developing apparatus (AD-2000, manufactured by Takizawa Sangyo Co., Ltd.), the film was developed by showering of an aqueous solution of 0.4% by mass tetramethylammonium hydroxide, ELM-D (available from MITSUBISHI GAS CHEMICAL COMPANY, INC.), for 90 seconds and then rinsed with water for 30 seconds. Finally, the film was cured in air at 220°C for 1 hour
15 using an oven (IHPS-222 manufactured by ESPEC CORP.) to produce a cured film. The cured film obtained was evaluated for hardness, adhesion, and resolution by the method described above.

[0090]

Example 2

20 A negative-tone photosensitive resin composition (N-2) was obtained in the same manner as in Example 1 except using the mixed silane coupling agent solution (a-2) in place of the mixed silane coupling agent solution (a-1). Using the negative-tone photosensitive resin composition (N-2) obtained, evaluations were performed in the same manner as in Example 1.

25 [0091]

Example 3

A negative-tone photosensitive resin composition (N-3) was obtained in the

same manner as in Example 1 except using the mixed silane coupling agent solution (a-3) in place of the mixed silane coupling agent solution (a-1). Using the negative-tone photosensitive resin composition (N-3) obtained, evaluations were performed in the same manner as in Example 1.

5 [0092]

Example 4

A negative-tone photosensitive resin composition (N-4) was obtained in the same manner as in Example 1 except that the amount of the mixed silane coupling agent solution (a-1) was changed to 0.433 g and the amount of PGMEA to 38.382 g.

10 Using the negative-tone photosensitive resin composition (N-4) obtained, evaluations were performed in the same manner as in Example 1.

[0093]

Example 5

A negative-tone photosensitive resin composition (N-5) was obtained in the same manner as in Example 1 except that the amount of the mixed silane coupling agent solution (a-1) was 1.730 g and the amount of PGMEA was 37.085 g. Using the negative-tone photosensitive resin composition (N-5) obtained, evaluations were performed in the same manner as in Example 1.

[0094]

20 Example 6

A negative-tone photosensitive resin composition (N-6) was obtained in the same manner as in Example 1 except that the amount of the mixed silane coupling agent solution (a-1) was 10.382 g and the amount of PGMEA was 28.433 g. Using the negative-tone photosensitive resin composition (N-6) obtained, evaluations were performed in the same manner as in Example 1.

[0095]

Example 7

A negative-tone photosensitive resin composition (N-7) was obtained in the same manner as in Example 1 except that the amount of the mixed silane coupling agent solution (a-1) was 14.708 g and the amount of PGMEA was 24.107 g. Using the negative-tone photosensitive resin composition (N-7) obtained, evaluations were performed in the same manner as in Example 1.

[0096]

Example 8

To 30.000 g of the negative-tone photosensitive resin composition (N-1), 0.052 g of triphenylsulfonium trifluoromethanesulfonate (trade name "WPAG-281" available from BYK-Chemie Japan (hereinafter referred to as WPAG-281) was added, and the resulting mixture was stirred to obtain a negative-tone photosensitive resin composition (N-8). Using the negative-tone photosensitive resin composition (N-8) obtained, evaluations were performed in the same manner as in Example 1.

[0097]

Example 9

To 30.000 g of the negative-tone photosensitive resin composition (N-1), 0.208 g of WPAG-281 was added, and the resulting mixture was stirred to obtain a negative-tone photosensitive resin composition (N-9). Using the negative-tone photosensitive resin composition (N-9) obtained, evaluations were performed in the same manner as in Example 1.

[0098]

Example 10

Under yellow light, 1.557 g of IC907 and 0.173 g of EK were dissolved in 32.000 g of DAA and 21.629 g of PGMEA. To this solution, 8.652 g of DPHA, 4.326 g of the mixed silane coupling agent solution (a-1), 8.652 g of a 1% by mass solution of 4-t-butylcatechol in PGMEA, 21.629 g of the acrylic resin solution (b-2), and 1.500 g of a 1% by mass solution of BYK-333 in PGMEA were added, and the

resulting mixture was stirred. Then, the resultant was filtered through a 0.45- μ m filter to obtain a negative-tone photosensitive resin composition (N-10). Using the negative-tone photosensitive resin composition (N-10) obtained, evaluations were performed in the same manner as in Example 1.

5 [0099]

Example 11

A negative-tone photosensitive resin composition (N-11) was obtained in the same manner as in Example 10 except using the mixed silane coupling agent solution (a-2) in place of the mixed silane coupling agent solution (a-1). Using the
10 negative-tone photosensitive resin composition (N-11) obtained, evaluations were performed in the same manner as in Example 1.

[0100]

Example 12

A negative-tone photosensitive resin composition (N-12) was obtained in the
15 same manner as in Example 10 except using the mixed silane coupling agent solution (a-3) in place of the mixed silane coupling agent solution (a-1). Using the negative-tone photosensitive resin composition (N-12) obtained, evaluations were performed in the same manner as in Example 1.

[0101]

20 Example 13

Under yellow light, 1.557 g of IC907 and 0.173 g of EK were dissolved in 32.000 g of DAA and 24.108 g of PGMEA. To this solution, 10.382 g of DPHA, 4.326 g of the mixed silane coupling agent solution (a-1), 8.652 g of a 1% by mass solution of 4-t-butylcatechol in PGMEA, 17.303 g of the acrylic resin solution (b-2),
25 and 1.500 g of a 1% by mass solution of BYK-333 in PGMEA were added, and the resulting mixture was stirred. Then, the resultant was filtered through a 0.45- μ m filter to obtain a negative-tone photosensitive resin composition (N-13). Using the

negative-tone photosensitive resin composition (N-13) obtained, evaluations were performed in the same manner as in Example 1.

[0102]

Example 14

5 A negative-tone photosensitive resin composition (N-14) was obtained in the same manner as in Example 13 except that 0.052 g of WPAG-281 was added to 30.000 g of the negative-tone photosensitive resin composition (N-13). Using the negative-tone photosensitive resin composition (N-14) obtained, evaluations were performed in the same manner as in Example 1.

10 [0103]

Example 15

 Under yellow light, 1.557 g of IC907 and 0.173 g of EK were dissolved in 32.000 g of DAA and 18.917 g of PGMEA. To this solution, 6.921 g of DPHA, 4.326 g of the mixed silane coupling agent solution (a-1), 8.652 g of a 1% by mass
15 solution of 4-t-butylcatechol in PGMEA, 25.955 g of the acrylic resin solution (b-2), and 1.500 g of a 1% by mass solution of BYK-333 in PGMEA were added, and the resulting mixture was stirred. Then, the resultant was filtered through a 0.45- μ m filter to obtain a negative-tone photosensitive resin composition (N-15). Using the negative-tone photosensitive resin composition (N-15) obtained, evaluations were
20 performed in the same manner as in Example 1.

[0104]

Example 16

 Under yellow light, 1.730 g of the quinonediazide compound (q-1) was dissolved in 6.045 g of DAA and 43.141 g of PGMEA. To this solution, 4.326 g of
25 the mixed silane coupling agent solution (a-1), 43.258 g of the siloxane resin solution (b-1), and 1.500 g of a 1% by mass solution of silicone-based surfactant BYK-333 (available from BYK-Chemie Japan) in PGMEA were added, and the resulting

mixture was stirred. Then, the resultant was filtered through a 0.45- μm filter to obtain a positive-tone photosensitive resin composition (P-1).

The positive-tone photosensitive resin composition (P-1) obtained was spin-coated on a glass substrate and on an ITO substrate each using a spin coater (1H-360S manufactured by MIKASA CO., LTD.) at any rotation speed. Thereafter, these substrates were pre-baked at 110°C for 2 minutes using a hot plate (SCW-636 manufactured by Dainippon Screen Mfg. Co., Ltd.) to produce a film with a film thickness of 1.5 μm .

[0105]

Using a parallel light mask aligner (PLA-501F manufactured by Canon Inc.) and an ultra-high pressure mercury lamp as a light source, the film produced was exposed to light at an exposure amount of 200 mJ (i-ray) using 5-, 10-, 20-, 30-, 40-, and 50- μm wide masks at a width ratio of 1:1 with a mask gap of 100 μm . During the exposure, an unexposed portion large enough to measure hardness and adhesion was ensured. Thereafter, using an automatic developing apparatus (AD-2000, manufactured by Takizawa Sangyo Co., Ltd.), the film was developed by showering of an aqueous solution of 0.4% by mass tetramethylammonium hydroxide, ELM-D (available from MITSUBISHI GAS CHEMICAL COMPANY, INC.), for 90 seconds and then rinsed with water for 30 seconds. Next, using a parallel light mask aligner (PLA-501F manufactured by Canon Inc.) and an ultra-high pressure mercury lamp as a light source, the film was exposed to light at an exposure amount of 6000 mJ (i-ray). Finally, the film was cured in air at 220°C for 1 hour using an oven (IHPS-222 manufactured by ESPEC CORP.) to produce a cured film. The cured film obtained was evaluated for hardness, adhesion, and resolution by the method described above.

[0106]

Example 17

To 44.871 g of PGMEA, 6.045 g of DAA was added. To this solution, 4.326 g of the mixed silane coupling agent solution (a-1), 43.258 g of the siloxane resin solution (b-1), and 1.500 g of a 1% by mass solution of silicone-based surfactant BYK-333 (available from BYK-Chemie Japan) in PGMEA were added, and the resulting mixture was stirred. Then, the resultant was filtered through a 0.45- μ m filter to obtain a thermosetting resin composition (U-1).

The thermosetting resin composition (U-1) obtained was spin-coated on a glass substrate and on an ITO substrate each using a spin coater (1H-360S manufactured by MIKASA CO., LTD.) at any rotation speed to produce a film with a film thickness of 1.5 μ m. Thereafter, the film was pre-baked at 110°C for 2 minutes using a hot plate (SCW-636 manufactured by Dainippon Screen Mfg. Co., Ltd.). Finally, the film was cured in air at 260°C for 1 hour using an oven (IHPS-222 manufactured by ESPEC CORP.) to produce a cured film. Cure shrinkage was calculated by the method described above to evaluate hardness and adhesion.

[0107]

Comparative Example 1

Under yellow light, 1.557 g of IC907 and 0.173 g of EK were dissolved in 21.618 g of DAA and 38.815 g of PGMEA. To this solution, 10.382 g of DPHA, 8.652 g of a 1% by mass solution of 4-t-butylcatechol in PGMEA, 17.303 g of the siloxane resin solution (b-1), and 1.500 g of a 1% by mass solution of silicone-based surfactant BYK-333 (available from BYK-Chemie Japan) in PGMEA were added, and the resulting mixture was stirred. Then, the resultant was filtered through a 0.45- μ m filter to obtain a negative-tone photosensitive resin composition (N-16). Using the negative-tone photosensitive resin composition (N-16) obtained, evaluations were performed in the same manner as in Example 1.

[0108]

Comparative Example 2

A negative-tone photosensitive resin composition (N-17) was obtained in the same manner as in Example 1 except using the mixed silane coupling agent solution (a-4) in place of the mixed silane coupling agent solution (a-1). Using the negative-tone photosensitive resin composition (N-17) obtained, evaluations were performed in the same manner as in Example 1.

[0109]

Comparative Example 3

A negative-tone photosensitive resin composition (N-18) was obtained in the same manner as in Example 1 except using the mixed silane coupling agent solution (a-5) in place of the mixed silane coupling agent solution (a-1). Using the negative-tone photosensitive resin composition (N-18) obtained, evaluations were performed in the same manner as in Example 1.

[0110]

Comparative Example 4

To 30.000 g of the negative-tone photosensitive resin composition (N-17), 0.208 g of WPAG-281 was added, and the resulting mixture was stirred to obtain a negative-tone photosensitive resin composition (N-19). Using the negative-tone photosensitive resin composition (N-19) obtained, evaluations were performed in the same manner as in Example 1.

[0111]

Comparative Example 5

To 30.000 g of the negative-tone photosensitive resin composition (N-16), 0.208 g of WPAG-281 was added, and the resulting mixture was stirred to obtain a negative-tone photosensitive resin composition (N-20). Using the negative-tone photosensitive resin composition (N-20) obtained, evaluations were performed in the same manner as in Example 1.

[0112]

Comparative Example 6

Under yellow light, 1.557 g of IC907 and 0.173 g of EK were dissolved in 32.000 g of DAA and 25.955 g of PGMEA. To this solution, 8.652 g of DPHA, 8.652 g of a 1% by mass solution of 4-t-butylcatechol in PGMEA, 21.629 g of the acrylic resin solution (b-2), and 1.500 g of a 1% by mass solution of BYK-333 in PGMEA were added, and the resulting mixture was stirred. Then, the resultant was filtered through a 0.45- μ m filter to obtain a negative-tone photosensitive resin composition (N-21). Using the negative-tone photosensitive resin composition (N-21) obtained, evaluations were performed in the same manner as in Example 1.

[0113]

Comparative Example 7

Under yellow light, 1.557 g of IC907 and 0.173 g of EK were dissolved in 32.000 g of DAA and 28.434 g of PGMEA. To this solution, 10.382 g of DPHA, 8.652 g of a 1% by mass solution of 4-t-butylcatechol in PGMEA, 17.303 g of the acrylic resin solution (b-2), and 1.500 g of a 1% by mass solution of BYK-333 in PGMEA were added, and the resulting mixture was stirred. Then, the resultant was filtered through a 0.45- μ m filter to obtain a negative-tone photosensitive resin composition (N-22). Using the negative-tone photosensitive resin composition (N-22) obtained, evaluations were performed in the same manner as in Example 1.

[0114]

Comparative Example 8

Under yellow light, 1.557 g of IC907 and 0.173 g of EK were dissolved in 32.000 g of DAA and 23.243 g of PGMEA. To this solution, 6.921 g of DPHA, 8.652 g of a 1% by mass solution of 4-t-butylcatechol in PGMEA, 25.955 g of the acrylic resin solution (b-2), and 1.500 g of a 1% by mass solution of BYK-333 in PGMEA were added, and the resulting mixture was stirred. Then, the resultant was filtered through a 0.45- μ m filter to obtain a negative-tone photosensitive resin

composition (N-23). Using the negative-tone photosensitive resin composition (N-23) obtained, evaluations were performed in the same manner as in Example 1.

[0115]

Comparative Example 9

5 A negative-tone photosensitive resin composition (N-24) was obtained in the same manner as in Example 10 except using the mixed silane coupling agent solution (a-4) in place of the mixed silane coupling agent solution (a-1). Using the negative-tone photosensitive resin composition (N-24) obtained, evaluations were performed in the same manner as in Example 1.

10 [0116]

Comparative Example 10

 A negative-tone photosensitive resin composition (N-25) was obtained in the same manner as in Example 10 except using the mixed silane coupling agent solution (a-5) in place of the mixed silane coupling agent solution (a-1). Using the
15 negative-tone photosensitive resin composition (N-25) obtained, evaluations were performed in the same manner as in Example 1.

[0117]

Comparative Example 11

 A negative-tone photosensitive resin composition (N-26) was obtained in the
20 same manner as in Example 1 except using the mixed silane coupling agent solution (a-6) in place of the mixed silane coupling agent solution (a-1). Using the negative-tone photosensitive resin composition (N-26) obtained, evaluations were performed in the same manner as in Example 1.

[0118]

25 Comparative Example 12

 A negative-tone photosensitive resin composition (N-27) was obtained in the same manner as in Example 1 except using the mixed silane coupling agent solution

(a-7) in place of the mixed silane coupling agent solution (a-1). Using the negative-tone photosensitive resin composition (N-27) obtained, evaluations were performed in the same manner as in Example 1.

[0119]

5 Comparative Example 13

A positive-tone photosensitive resin composition (P-2) was obtained in the same manner as in Example 16 except using the mixed silane coupling agent solution (a-7) in place of the mixed silane coupling agent solution (a-1). Using the positive-tone photosensitive resin composition (P-2) obtained, evaluations were

10 performed in the same manner as in Example 16.

[0120]

Comparative Example 14

A thermosetting resin composition (U-2) was obtained in the same manner as in Example 17 except using the mixed silane coupling agent solution (a-7) in place

15 of the mixed silane coupling agent solution (a-1). Using the thermosetting resin composition (U-2) obtained, evaluations were performed in the same manner as in Example 17.

Table 1

	Resin Composition	Composition							Results		
		(A) Silane Coupling Agent			(B) Alkali-Soluble Resin		(E) Thermal Acid Generator		Hardness	Adhesion	Resolution (μm)
		Name	n [Formula (1)]	Weight Ratio (A)/{(B) + (C)}	Name	Weight Ratio (B)/(C)	Name	Weight Ratio (E)/{(B) + (C)}			
Example 1	N-1	a-1	0	5/100	b-1	40/60	-	-	6H	4	5
Example 2	N-2	a-2	0	5/100	b-1	40/60	-	-	6H	4	5
Example 3	N-3	a-3	1	5/100	b-1	40/60	-	-	6H	3	5
Example 4	N-4	a-1	0	0.5/100	b-1	40/60	-	-	6H	2	5
Example 5	N-5	a-1	0	2/100	b-1	40/60	-	-	6H	3	5
Example 6	N-6	a-1	0	12/100	b-1	40/60	-	-	6H	4	10
Example 7	N-7	a-1	0	17/100	b-1	40/60	-	-	6H	4	30
Example 8	N-8	a-1	0	5/100	b-1	40/60	WPAG-281	1/100	6H	5	10
Example 9	N-9	a-1	0	5/100	b-1	40/60	WPAG-281	4/100	6H	5	30
Example 10	N-10	a-1	0	5/100	b-2	50/50	-	-	6H	5	5
Example 11	N-11	a-2	0	5/100	b-2	50/50	-	-	6H	5	5
Example 12	N-12	a-3	1	5/100	b-2	50/50	-	-	6H	4	5
Example 13	N-13	a-1	0	5/100	b-2	40/60	-	-	7H	4	5
Example 14	N-14	a-1	0	5/100	b-2	40/60	WPAG-281	1/100	7H	5	10
Example 15	N-15	a-1	0	5/100	b-2	60/40	-	-	4H	5	10
Example 16	P-1	a-1	0	5/100	b-1	40/60	-	-	2H	5	5
Example 17	U-1	a-1	0	5/100	b-1	40/60	-	-	2H	5	-

[0121]

Table 1 (continued)

	Resin Composition	Composition							Results		
		(A) Silane Coupling Agent			(B) Alkali-Soluble Resin		(E) Thermal Acid Generator		Hardness	Adhesion	Resolution (μm)
		Name	n [Formula (1)]	Weight Ratio (A)/{(B) + (C)}	Name	Weight Ratio (B)/(C)	Name	Weight Ratio (E)/(B) + (C)}			
Comparative Example 1	N-16	-	-	-	b-1	40/60	-	-	6H	0	5
Comparative Example 2	N-17	a-4	2	5/100	b-1	40/60	-	-	6H	1	5
Comparative Example 3	N-18	a-5	2	5/100	b-1	40/60	-	-	6H	1	5
Comparative Example 4	N-19	a-4	2	5/100	b-1	40/60	WPAG-281	1/100	6H	1	10
Comparative Example 5	N-20	-	-	-	b-1	40/60	WPAG-281	1/100	6H	0	10
Comparative Example 6	N-21	-	-	-	b-2	50/50	-	-	6H	1	5
Comparative Example 7	N-22	-	-	-	b-2	40/60	-	-	7H	0	5
Comparative Example 8	N-23	-	-	-	b-2	60/40	-	-	4H	2	5
Comparative Example 9	N-24	a-4	2	5/100	b-2	50/50	-	-	6H	2	5
Comparative Example 10	N-25	a-5	2	5/100	b-2	50/50	-	-	6H	2	5
Comparative Example 11	N-26	a-6		5/100	b-1	40/60	-	-	6H	0	5
Comparative Example 12	N-27	a-7		5/100	b-1	40/60	-	-	6H	1	5
Comparative Example 13	P-2	a-7		5/100	b-1	40/60	-	-	2H	5	-
Comparative Example 14	U-2	a-7		5/100	b-1	40/60	-	-	2H	3	-

[0122]

To compare the difference in cure shrinkage and in planarization capability depending on the type of resin compositions to which the silane coupling agent of the present invention is added, the following reference experiments were performed.

5 [0123]

Reference Example 1

The negative-tone photosensitive resin composition (N-1 (using the silane coupling agent (a-1))) was spin-coated on a silicon wafer substrate using a spin coater (1H-360S manufactured by MIKASA CO., LTD.) at any rotation speed.

10 Thereafter, the resultant was pre-baked at 110°C for 2 minutes using a hot plate (SCW-636 manufactured by Dainippon Screen Mfg. Co., Ltd.) to produce a film with a film thickness of 1.5 μm . Using a parallel light mask aligner (PLA-501F manufactured by Canon Inc.) and an ultra-high pressure mercury lamp as a light source, the film produced was exposed to light at an exposure amount of 200 mJ

15 (i-ray). Thereafter, using an automatic developing apparatus (AD-2000, manufactured by Takizawa Sangyo Co., Ltd.), the film was developed by showering of an aqueous solution of 0.4% by mass tetramethylammonium hydroxide, ELM-D (available from MITSUBISHI GAS CHEMICAL COMPANY, INC.), for 90 seconds and then rinsed with water for 30 seconds. Finally, the film was cured in air at

20 220°C for 1 hour using an oven (IHPS-222 manufactured by ESPEC CORP.) to produce a cured film. Cure shrinkage was calculated by the method described above to evaluate planarization capability. The results were that the cure shrinkage was 11% and the planarization capability was good.

[0124]

25 Evaluations were performed in the same manner as described above except using (N-27) in place of the negative-tone photosensitive resin composition (N-1). The results were that the cure shrinkage was 9% and the planarization capability was

good.

[0125]

In other words, with respect to negative-tone photosensitive resin compositions, the addition of the silane coupling agent of the present invention (a-1) in place of a conventional silane coupling agent caused almost no reduction in cure shrinkage or planarization capability.

[0126]

Reference Example 2

The positive-tone photosensitive resin composition (P-1 (using the silane coupling agent (a-1))) was spin-coated on a silicon wafer substrate using a spin coater (1H-360S manufactured by MIKASA CO., LTD.) at any rotation speed to produce a film with a film thickness of 1.5 μm . Thereafter, the film was pre-baked at 110°C for 2 minutes using a hot plate (SCW-636 manufactured by Dainippon Screen Mfg. Co., Ltd.). Using an automatic developing apparatus (AD-2000, manufactured by Takizawa Sangyo Co., Ltd.), the film was developed by showering of an aqueous solution of 0.4% by mass tetramethylammonium hydroxide, ELM-D (available from MITSUBISHI GAS CHEMICAL COMPANY, INC.), for 90 seconds and then rinsed with water for 30 seconds. Next, using a parallel light mask aligner (PLA-501F manufactured by Canon Inc.) and an ultra-high pressure mercury lamp as a light source, the film was exposed to light at an exposure amount of 6000 mJ (i-ray). Finally, the film was cured in air at 220°C for 1 hour using an oven (IHPS-222 manufactured by ESPEC CORP.) to produce a cured film. Cure shrinkage was calculated by the method described above to evaluate planarization capability. The results were that the cure shrinkage was 16% and the planarization capability was poor.

Evaluations were performed in the same manner as described above except using (P-2) in place of the positive-tone photosensitive resin composition (P-1).

The results were that the cure shrinkage was 13% and the planarization capability was good.

[0127]

In other words, with respect to positive-tone photosensitive resin compositions, the addition of the silane coupling agent of the present invention (a-1) in place of a conventional silane coupling agent tended to reduce particularly planarization performance.

[0128]

Reference Example 3

The thermosetting resin composition (U-1 (using the silane coupling agent (a-1))) was spin-coated on a silicon wafer substrate using a spin coater (1H-360S manufactured by MIKASA CO., LTD.) at any rotation speed to produce a film with a film thickness of 1.5 μm . Thereafter, the film was pre-baked at 110°C for 2 minutes using a hot plate (SCW-636 manufactured by Dainippon Screen Mfg. Co., Ltd.).

Finally, the film was cured in air at 260°C for 1 hour using an oven (IHPS-222 manufactured by ESPEC CORP.) to produce a cured film. Cure shrinkage was calculated by the method described above to evaluate planarization capability. The results were that the cure shrinkage was 18% and the planarization capability was poor.

[0129]

Evaluations were performed in the same manner as described above except using (U-2) in place of the thermosetting resin composition (U-1). The results were that the cure shrinkage was 14% and the planarization capability was good.

[0130]

In other words, with respect to thermosetting resin compositions, the addition of the silane coupling agent of the present invention (a-1) in place of a conventional silane coupling agent tended to reduce cure shrinkage and planarization

performance.

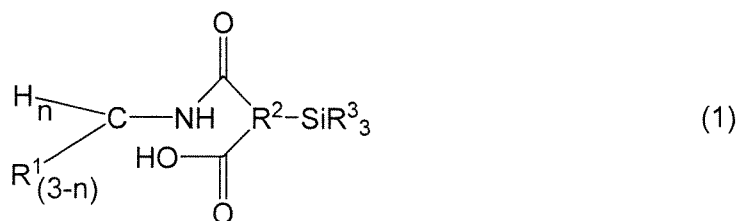
INDUSTRIAL APPLICABILITY

[0131]

5 The present invention is suitably used in a silane coupling agent, a
negative-tone photosensitive resin composition containing the same, a cured film
using the same, and a touch panel device having the same.

CLAIMS

1. A silane coupling agent represented by Formula (1),



wherein each R¹ may be the same or different from each other and

- 5 represents C₁-C₆ alkyl; the alkyl may further have a substituent(s); n represents 0 or 1; R² represents a C₃-C₃₀ trivalent organic group; and R³ may be the same or different from each other and represents C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, hydroxyl, and phenoxy, among which groups for R³ groups other than hydroxyl may further have a substituent(s).
- 10 2. The silane coupling agent according to claim 1, wherein n = 0 in Formula (1).
3. A negative-tone photosensitive resin composition, comprising at least (A) the silane coupling agent according to claim 1 or 2, (B) an alkali-soluble resin, (C) a polyfunctional acryl monomer, and (D) a photo-radical polymerization initiator.
- 15 4. The negative-tone photosensitive resin composition according to claim 3, wherein (B) the alkali-soluble resin is a siloxane resin having an ethylenically unsaturated group.
5. The negative-tone photosensitive resin composition according to claim 3, wherein (B) the alkali-soluble resin is an acrylic resin having an ethylenically unsaturated group.
- 20 6. A cured film obtained by curing the negative-tone photosensitive resin composition according to any one of claims 3 to 5.
7. A component for a touch panel having the cured film according to claim 6.