

METHOD FOR FORMING PROTECTIVE COATING

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a method for forming a protective coating for optical devices. More particularly, the present invention relates to a method for forming a highly transparent protective coating on a display part of optical devices, particularly liquid crystal display devices and the like.

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BACKGROUND ART

In preparing optical devices, particularly liquid crystal display devices and the like, it has become popular to use a method which comprises providing a color filter on a transparent substrate such as glass, vapor depositing an inorganic thin layer of indium tin oxide (hereinafter referred to as "ITO") on the color filter, patterning the thin layer by photolithography to form a transparent electrode, and then placing thereon a liquid crystal. In this method, however, since the color filter per se does not have heat resistance and chemical resistance high enough to withstand the process wherein ITO is vapor deposited followed by photolithography to form a transparent electrode, a protective coating should be previously formed on the color filter before the vapor deposition of ITO.

Properties required of the protective coating include heat resistance, chemical resistance, adhesion, and transparency. In particular, transparency, preferably a transparency of not less than 95% in terms of transmittance, is required of protective coatings for optical devices. Accordingly, to provide better transparency, studies have been made on various compositions for forming a protective coating. When a protective coating is formed by a conventional method for forming a protective coating, however, all the compositions for forming a protective coating have

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disadvantageously posed a problem that the transparency of the protective coating, specifically transmittance, is deteriorated upon heat curing in the production process.

5 Further, for photosensitive compositions for forming a protective coating, in many cases, a protective coating having satisfactory transparency cannot be provided after exposure and development. In this case, in order to further improve the transparency,
10 a process called "bleaching" is necessary wherein exposure is carried out again after the exposure process. The re-exposure is disadvantageous from the viewpoint of production efficiency.

To overcome the above problems, a method for
15 forming a protective coating, which can efficiently produce a highly transparent protective coating, has been desired in the art.

SUMMARY OF THE INVENTION

20 The present inventors have found that carrying out the heat curing process under an inert gas atmosphere with the use of the conventional composition for forming a protective coating can overcome the above problems of the prior art and can produce a protective coating
25 having excellent transparency without sacrificing any of the required properties.

Thus, according to the present invention, there is provided a method for forming a protective coating, comprising coating a composition for forming a
30 protective coating which comprises a polymer and a solvent onto a substrate to form a coating, and heating the coating on the substrate to cure the same thereby forming a protective coating on the substrate, wherein the heating process is carried out under an inert gas
35 atmosphere.

According to the method of the present invention, a highly transparent protective coating can be efficiently

produced with the use of conventional composition for forming a protective coating. In particular, in photosensitive compositions for forming a protective coating, in the method of the present invention, there
5 is no need to provide the re-exposure process which has hitherto been necessary in most cases.

DETAILED DESCRIPTION OF THE INVENTION

<Composition for forming protective coating>

10 The composition for forming a protective coating used in the method for forming a protective coating according to the present invention may be any conventional composition used for forming a protective coating. This composition for forming a protective
15 coating comprises a polymer, a solvent, and optional other component(s).

 The composition for forming a protective coating may be either a heat-curable composition or a photosensitive composition. The photosensitive
20 composition may be either a negative-working photosensitive composition or a positive-working photosensitive composition. The components of the composition for forming a protective coating may be properly selected according to the type of the
25 composition, and are not particularly limited so far as the effect of the present invention is not sacrificed. Ordinary components of the composition for forming a protective coating will be described according to the type of the composition.

30 1. Heat-curable composition

 When the composition for forming a protective coating used in the method of the present invention is a heat-curable composition, the composition comprises a polymer, a solvent, and, in addition, generally a
35 crosslinking agent.

(A) Polymer

 In the present invention, when the composition for

forming a protective coating is a heat-curable composition, upon heating, a crosslinking reaction takes place between polymers or between the polymer and the crosslinking agent to cure the polymer, thereby forming
5 a cured coating. The polymer may be properly selected according to purposes. A polymer containing carboxyl groups (hereinafter referred to as "carboxyl-containing polymer") may be mentioned as one of preferred polymers.

Specific examples of preferred polymers of this
10 type include copolymers of acrylic acid, methacrylic acid, or esters of acrylic acid or methacrylic acid with vinyl aromatic compounds. Regarding acrylic acid, methacrylic acid, or esters thereof, examples of esters of acrylic acid and methacrylic acid include methyl
15 acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, ethylhexyl methacrylate, and phenyl acrylate. Vinyl aromatic compounds include styrene, α -methylstyrene, and p-methylstyrene.

20 The form of copolymer is not particularly limited, and any of random copolymer, block copolymer and the like produced by addition polymerization may be used. The copolymerization method is also not particularly limited, and examples of copolymerization methods usable
25 herein include solution polymerization and emulsion polymerization.

The molecular weight of the carboxyl-containing polymer is not particularly limited. Preferably, however, the carboxyl-containing polymer has a weight average
30 molecular weight of 2,000 to 200,000 as determined using styrene as a standard. The weight average molecular weight of this polymer is more preferably about 7,000 to 100,000.

Other preferred polymers include hydroxyl-
35 containing polymers. Various hydroxyl-containing polymers are known, and any of these polymers may be used. More preferred are phenol novolak resins which are

produced by reacting phenols, for example, phenol, m-cresol, 3,5-xyleneol, p-alkylphenol, or resorcin, with aldehydes, for example, formaldehyde or acetaldehyde. For the production of phenol novolak resins, a proper method may be selected from conventional methods used in the production of phenol novolak resins. From the viewpoint of reaction rate, however, it is common practice to use an acid or an alkali as a catalyst.

(B) Solvent

10 In the present invention, an organic solvent is used as a solvent for dissolving a solid component such as the above-described polymer. According to a preferred embodiment of the present invention, the organic solvent is selected from the group consisting of propylene glycol, ethylene glycol, lactic acid, butyric acid, 15 acetic acid, formic acid, and γ -butyrolactone solvents and mixtures of these solvents. The utilization of these organic solvents can provide coating compositions, which are stable for about 6 months after the preparation thereof, and can realize the formation of an even coating free from unevenness. Consequently, a protective coating can be provided which has excellent adhesion, evenness, and transparency and, at the same time, possesses excellent durability, abrasion resistance, 20 contamination resistance, and chemical resistance.

Specific examples of organic solvents include: glycol ether and acetate solvents, such as propylene glycol methyl ether, propylene glycol ethyl ether, propylene glycol propyl ether, propylene glycol t-butyl ether, dipropylene glycol methyl ether, dipropylene glycol propyl ether, tripropylene glycol methyl ether, propylene glycol methyl ether acetate, dipropylene glycol methyl ether acetate, ethylene glycol ethyl ether, ethylene glycol methyl ether, ethylene glycol butyl ether, ethylene glycol isopropyl ether, ethylene glycol n-butyl ether, cellosolve acetate, methyl cellosolve acetate, ethyl cellosolve acetate, diethylene glycol 35

methyl ether, diethylene glycol ethyl ether, diethylene glycol butyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol monoacetate, diethylene glycol monoethyl ether acetate, 5 propylene glycol phenyl ether, propylene glycol ethyl ether acetate, triethylene glycol butyl ether, 3-methyl-3-methoxybutyl acetate, and 3-methyl-3-methoxybutanol; lactic acid solvents, such as ethyl lactate, methyl lactate, butyl lactate, and pentyl lactate; acetic acid 10 solvents, such as butyl acetate, amyl formate, isoamyl acetate, isobutyl acetate, methoxybutyl acetate, and butyl propionate; and butyric acid solvents include isobutyl butyrate, butyl butyrate, and ethyl pyruvate.

Further, according to a preferred embodiment of the 15 present invention, the organic solvent is propylene glycol methyl ether acetate or a mixed organic solvent containing at least propylene glycol methyl ether acetate. In the case of the mixed organic solvent containing propylene glycol methyl ether acetate, a 20 preferred organic solvent used in combination with propylene glycol methyl ether acetate is selected from the group consisting of propylene glycol, ethylene glycol, lactic acid, butyric acid, acetic acid, formic acid, and γ -butyrolactone solvents and mixtures of these 25 solvents.

(C) Crosslinking agent

In the present invention, when the composition for forming a protective coating is a heat-curable composition, this composition generally contains a 30 crosslinking agent component. Although the crosslinking agent component is not particularly limited, epoxy compounds are preferred. Epoxy compounds include novolak epoxy resins, bisphenol A epoxy resins, halogenated bisphenol A epoxy resins, and alicyclic epoxy resins.

35 Specific examples of preferred crosslinking agents include bisphenol acetone diglycidyl ether, phenol novolak epoxy resins, cresol novolak epoxy resins,

triglycidyl isocyanurate,
 tetraglycidyl diaminodiphenylene, tetraglycidyl-m-
 xylenediamine, tetraglycidyl-1,3-
 bis(aminoethyl)cyclohexane, tetraphenylglycidyl ether
 5 ethane, triphenylglycidyl ether ethane,
 bisphenolhexafluoroacetodiglycidyl ether, 1,3-bis(1-
 (2,3-epoxypropoxy)-1-trifluoromethyl-2,2,2-
 trifluoromethyl)benzene, 4,4-bis(2,3-
 epoxypropoxy)octafluorobiphenyl, triglycidyl-p-
 10 aminophenol, tetraglycidylmetaxylenediamine, 2-(4-(2,3-
 epoxypropoxy)phenyl)-2-(4-(1,1-bis(4-(2,3-
 epoxypropoxy)phenyl)ethyl)phenyl)propane, and 1,3-bis(4-
 (1-(4-(2,3-epoxypropoxy)phenyl)-1-(4-(1-(4-(2,3-
 epoxypropoxy)phenyl)-1-methylethyl)phenyl)ethoxy)-
 15 2-propanol.

The crosslinking agent component may be in the form
 of a substituent, which has been introduced into the
 carboxyl-containing polymer, rather than the form of a
 compound. In this case, the crosslinking agent component
 20 is preferably introduced either as an epoxy group or a
 residue of the crosslinking agent.

(D) Other components

In the present invention, the composition for
 forming a protective coating may comprise, in addition
 25 to the above components, optional various additives.

Here other additives include the above crosslinking
 agents and, in addition, sensitizers, leveling agents,
 adhesion promoters, surfactants, antioxidants,
 thickeners, ultraviolet absorbers, and reaction
 30 promoters.

The composition for forming a protective coating
 used in the method for forming a protective coating
 according to the present invention may contain a
 leveling agent from the viewpoint of forming a coating
 35 having an even surface upon coating of the composition
 for forming a protective coating onto a substrate.
 Leveling agents usable herein include silane leveling

agents and fluoro leveling agents.

The composition for forming a protective coating used in the method for forming a protective coating according to the present invention may contain an
5 adhesion promoter so that the composition for forming a protective coating, when coated onto a substrate, adheres to the substrate with satisfactory adhesion strength.

Any adhesion promoter may be used. Examples of
10 adhesion promoters include alkoxysilane compounds, alkoxytitanium compounds, alkoxyzirconium compounds, and alkoxyaluminum compounds. Amino-containing silane compounds represented by formula (I) are particularly preferred.

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$$\text{H}_2\text{N}-\text{R}^{11}-\text{Si}-(\text{OR}^{12})_3 \quad (\text{I})$$
 wherein R^{11} represents an unsubstituted alkylene group; and R^{12} s each independently represent an unsubstituted alkyl group.

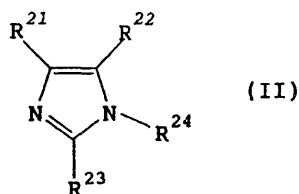
Among such amino-containing silane compounds,
20 particularly 3-aminopropyltriethoxysilane and 3-aminopropyltrimethoxysilane can realize the formation of a good protective coating.

The composition for forming a protective coating used in the method for forming a protective coating
25 according to the present invention may contain a surfactant or a thickener to improve coatability onto the substrate. Any of conventional surfactants and thickeners may be used.

Further, in the method according to the present
30 invention, when the composition is a heat-curable composition, the composition may comprise a reaction promoter for accelerating a polymerization reaction which takes place upon heating or light irradiation. Examples of reaction promoters usable herein include
35 imidazole compounds.

The use of the imidazole compound in the composition for forming a protective coating can realize

a protective coating having improved sputtering resistance. Preferred imidazole compounds are represented by formula (II):



5 wherein

R^{21} and R^{22} each independently represent a hydrogen atom or a substituted or unsubstituted alkyl group;

R^{23} represents a hydrogen atom, a substituted or unsubstituted alkyl group, or an aryl group; and

10 R^{24} represents a hydrogen atom or a substituted or unsubstituted alkyl group.

Among them, particularly preferred imidazole compounds are 2-methylimidazole, 2-ethyl-4-methylimidazole, 1-benzyl-2-methylimidazole, 2-phenyl-4-methylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 1,2-dimethylimidazole, 2-phenylimidazole, 1-benzyl-2-phenylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 2,4-diamino-6-(2'-methylimidazolyl-(1'))ethyl-s-triazine, 2,4-diamino-6-(2'-undecylimidazolyl)ethyl-s-triazine, 2,4-diamino-6-(2'-ethyl-4-methylimidazolyl-(1'))ethyl-s-triazine, 2-phenyl-4,5-dihydroxymethylimidazole, 2-phenyl-4-methyl-5-hydroxymethylimidazole, 1-cyanoethyl-2-phenyl-4,5-di(2-cyanoethoxy)methylimidazole.

2. Negative-working photosensitive composition

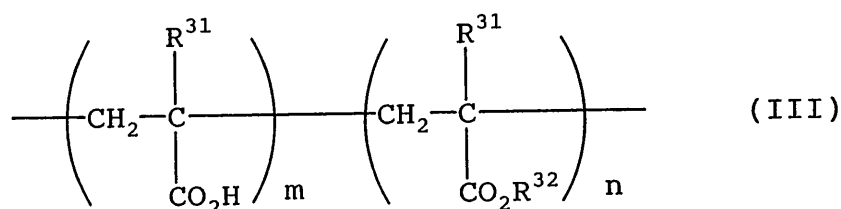
When the composition for forming a protective coating used in the method according to the present invention is a negative-working photosensitive composition, the composition comprises a polymer and a solvent and, in addition, generally a photopolymerization initiator and optionally a

crosslinking agent.

(A) Polymer

In the present invention, when the composition for forming a protective coating is a negative-working photosensitive composition, by virtue of the contribution of a photopolymerization initiator which will be described later, a crosslinking reaction takes place between polymers or between the polymer and the photopolymerization initiator to cure the polymer, thereby forming a cured coating. This type of polymer generally has a chain portion and a reaction site which can be bonded to a photopolymerization initiator or a reaction site in other polymer.

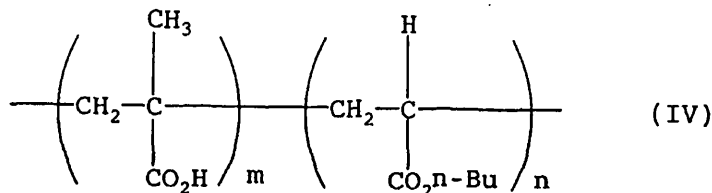
Such polymers are well known in the art, and may be properly selected according to purposes. Among these polymers, one polymer preferable in the method according to the present invention is a reaction product of a polymer comprising a segment represented by formula (III) with a compound selected from the group consisting of (3,4-epoxycyclohexyl) methacrylate and derivatives thereof.



wherein R^{31} s, which may be the same or different, represent a substituent selected from the group consisting of a hydrogen atom and a methyl group; R^{32} represents an alkyl group having a linear or branched structure containing 1 to 5 carbon atoms; and m and n represent a degree of polymerization, respectively, where the molar ratio m/n is 0.5 to 2.4.

In particular, in formula (III), R^{31} in at least one of the monomer units preferably represents a methyl group. R^{32} preferably represents an alkyl group having 1 to 4 carbon atoms, particularly preferably an *n*-butyl

group. Further, the polymer represented by formula (III) is more preferably a polymer comprising a segment represented by formula (IV):



5 wherein m and n are as defined above.

The molar ratio m/n is in the range of 0.5 to 2.4, preferably in the range of 0.6 to 1.7.

A phenol novolak resin may be used instead of the polymer represented by formula (III). Phenol novolak
10 resins usable herein are the same as those described above in connection with the heat-curable composition.

(3,4-Epoxy cyclohexyl) methacrylate and derivatives thereof include those having various substituents. Among them, (3,4-epoxycyclohexyl)methyl methacrylate is
15 preferred.

The molecular weight (M_w) of the reaction product of the polymer with (3,4-epoxycyclohexyl) methacrylate is preferably in the range of 10,000 to 80,000, more preferably in the range of 15,000 to 40,000. The acid
20 value of the reaction product is preferably 20 to 100 mg KOH/g, more preferably 45 to 70 mg KOH/g.

(B) Solvent

Also in the case where the composition for forming a protective coating is a negative-working
25 photosensitive composition, an organic solvent is used as a solvent for dissolving solid matter such as the polymer. Solvents usable herein may be the same as those described above in connection with the heat-curable composition.

(C) Photopolymerization initiator

30 The photopolymerization initiator may be any conventional photopolymerization initiator, and examples thereof include azide compounds, halomethyloxazole

compounds, halomethyl-s-triazine compounds, onium salts, benzoin ethers, xanthenes, and acetophenone derivatives.

Azide compounds include: (i) azidostilbenes and derivatives thereof, for example, 4,4'-diazidostilbene, 4,4'-diazidostilbene-2,2'-disulfonic acid N,N-diethyleneoxyethylamide, 4,4'-diazidostilbene-2,2'-disulfonic acid N-propylhydroxyamide, 4,4'-diazidostilbene-2,2'-disulfonic acid, 4,4'-diazidostilbene-2,2'-disulfonic acid N,N-diethylamide, and sodium 4,4'-diazidostilbene-2,2'-disulfonate; (ii) azido benzalcylohexanone and derivatives thereof, for example, 2,6-di-(p-azidobenzal)cylohexanone, 2,6-di-(p-azidobenzal)-4-methylcylohexanone, 2,6-di-(p-azidobenzal)-4-tert-amylcylohexanone, and 2,6-di-(p-azido cinnamylidene)-4-tert-aminocyclohexanone; (iii) azidocinnamylidenecyclohexanones and derivatives thereof; (iv) azidobenzalketones, p-azidobenzalacetophenone, p-azidobenzalacetone, 4,4'-diazidochalcone, 2,6-bis(4'-azidobenzal)acetone, 2,6-bis(4'-azidobenzal)acetone-2'-sulfonic acid N,N-diethyleneoxyethylamide, and 2,6-bis(4'-azidobenzal)acetone-2,2'-disulfonic acid N,N-diethyleneoxyethylamide. An azide group, which has been introduced into the polymer chain, may also be used.

Halomethyloxazole compounds include, for example, 2-trichloromethyl-5-styryl-1,3,4-oxadiazole, 2-trichloromethyl-5-(p-cyanostyryl)-1,3,4-oxadiazole, and 2-trichloromethyl-5-(p-methoxystyryl)-1,3,4-oxadiazole.

Halomethyl-s-triazine compounds include particularly trihalomethyl-s-triazine compounds, for example, 2,4-bis(trichloromethyl)-6-p-methoxystyryl-s-triazine, 2,4-bis(trichloromethyl)-6-(1-p-diethylaminophenyl-1,3-butadienyl)-s-triazine, 2,4-bis(trichloromethyl)-6-(p-phenylstyryl)-s-triazine, 2,4-bis(trichloromethyl)-6-styryl-s-triazine, 2,4-bis(trichloromethyl)-6-phenyl-s-triazine, 2[2'(5"-methylfuryl)ethylidene]-4,6-bis(trichloromethyl)-s-

triazine, 2(2'-furylethylidene)-4,6-(trichloromethyl)-s-triazine, and 5,7-bis(tribromomethyl)-s-triazolo[1,5-a]pyrimidine.

Benzoin ethers include, for example, benzoin methyl ether and benzoin isobutyl ether. Benzophenones include, for example, acetophenone, 2,2-dimethoxy-2-phenylacetophenone, 1,1-dichloroacetophenone, Michler's ketone, and o-benzoylmethyl benzoate. Xanthenes include, for example, xanthone, thioxanthone, 2-chlorothioxanthone, 2-alkylthioxanthone, and 2,4-dialkylthioxanthone.

Acetophenone derivatives include, for example, acetophenone, trichloroacetophenone, 2,2-diethoxyacetophenone, and 2,2-dimethoxy-2-phenylacetophenone.

Onium salts include various sulfonium salts, iodonium salts, and diazonium salts. Specific examples thereof include triphenylsulfonium trifluoromethanesulfonate, benzyl-4-hydroxyphenylmethylsulfonium hexafluorophosphate, α -naphthylmethyl-4-hydroxyphenylmethylsulfonium hexafluorophosphate (or hexafluoroantimonate), diphenyl-t-butylphenylsulfonium trifluoromethanesulfonate, diphenylmethoxyphenylsulfonium hexafluoroantimonate, triphenylsulfonium hexafluoroantimonate, di-t-butylphenyliodonium trifluoromethanesulfonate (or hexafluoroantimonate or tetrafluoroborate), methoxyphenyliodonium trifluoromethanesulfonate, diphenyliodonium trifluoromethanesulfonate, aminophenylbenzenediazonium tetrafluoroborate, and pyrenediazonium tetrafluoroborate.

In the method according to the present invention, the photopolymerization initiator may be properly selected from these compounds. They may be used solely or, if necessary, in a combination of two or more. These photopolymerization initiators may be added, to the composition for forming a protective coating, either as

a compound or as a substituent introduced into the above polymer. Among the above photopolymerization initiators, halomethyl-s-triazine compounds, particularly trihalomethyl-s-triazine compounds, are preferred.

5 (D) Crosslinking agent

In the method according to the present invention, when the composition for forming a protective coating is a negative-working photosensitive composition, if necessary, the composition may further comprise a
10 crosslinking agent.

Crosslinking agents usable herein are the same as those described above in connection with the heat-curable composition. Examples of additional crosslinking agents usable herein include: compounds containing at
15 least two residues, which may be the same or different and are reacted with the polymer to form a crosslinked matrix, such as alkoxy or acyloxy (for example, bis-, tris-, or tetra-(hydroxymethyl)-substituted aromatic compounds or heterocyclic aromatic compounds and bis-,
20 tris-, or tetra-(acetoxymethyl)-substituted aromatic compounds or heterocyclic aromatic compounds); melamine compounds (for example, N-hydroxymethyl-containing melamine, N-alkoxymethyl-containing melamine, or N-acyloxymethyl-containing melamine); acetal resins (for
25 example, polyvinyl butyral); peroxide compounds (for example, benzoyl peroxide, p-chlorobenzoyl peroxide, acetyl peroxide, and lauroyl peroxide); and blocked isocyanates (for example, isophorone diisocyanate, hexamethylene diisocyanate, cyclohexylene diisocyanate,
30 and the like that have been blocked by various blocking agents, for example, ethanol, butanol, dimethyl malonate, imidazole, ε-caprolactam, methyl cellosolve, ethylene glycol or the like). They may be used solely or in a combination of two or more.

35 (E) Other components

In the method according to the present invention, when the composition is a negative-working

photosensitive composition, the composition may comprise, in addition to the above components, other components. Other components usable herein may be the same as those described above in connection with other components used
5 in the heat-curable composition.

3. Positive-working photosensitive composition

When the composition for forming a protective coating used in the method according to the present invention is a positive-working photosensitive
10 composition, the composition comprises a polymer and a solvent and, in addition, generally a photosensitive component and a crosslinking agent.

(A) Polymer

In the present invention, when the composition for
15 forming a protective coating is a positive-working photosensitive composition, the polymer may be selected from polymers described above in connection with the heat-curable composition.

(B) Solvent

20 In the present invention, when the composition for forming a protective coating is a positive-working photosensitive composition, the solvent may be selected from solvents described above in connection with the heat-curable composition.

(C) Photosensitive component

25 When the composition for forming a protective coating used in the method according to the present invention is a positive-working photosensitive composition, the composition comprises a photosensitive
30 component. Here the photosensitive component refers to a component which absorbs light to induce a polymerization reaction of the components in the composition. The composition containing the photosensitive component for forming a protective coating acts as a photosensitive
35 composition.

The photosensitive component may be properly selected from photosensitive components commonly used in

positive-working photosensitive compositions. Preferably, however, a photosensitive component containing a quinonediazide group is used.

Any conventional photosensitive component may be used as the photosensitive component, and preferred examples thereof include those produced by reacting naphthoquinonediazidosulfonic acid chloride or benzoquinonediazidosulfonic acid chloride with a low-molecular or polymeric compound containing a functional group condensable with the acid chloride.

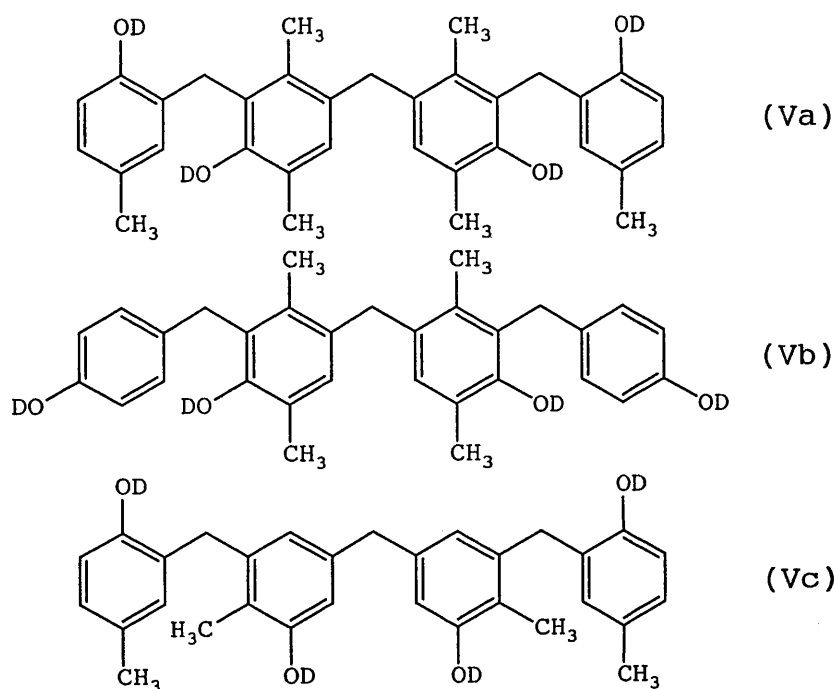
Here functional groups condensable with the acid chloride include hydroxyl and amino groups, and the hydroxyl group is preferred. Examples of hydroxyl-containing low-molecular compounds include: hydroquinone, resorcin, 2,4-dihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 2,4,6-trihydroxybenzophenone, 2,4,4'-trihydroxybenzophenone, 2,3,4,4'-tetrahydroxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2,2',3,4,6'-pentahydroxybenzophenone, and other polyhydroxybenzophenones; bis(2,4-dihydroxyphenyl)methane, bis(2,3,4-trihydroxyphenyl)methane, bis(2,4-dihydroxyphenyl)propane-1 and other bis((poly)hydroxyphenyl)alkanes; and 4,4',3'',4''-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane, 4,4',2'',3'',4''-pentahydroxy-3,5,3',5'-tetramethyltriphenylmethane, 2,3,4,2',3',4',3'',4''-octahydroxy-5,5'-diacetyltriphenylmethane and other polyhydroxytriphenylmethanes. Examples of hydroxyl-containing polymeric compounds include novolak resins and polyhydroxystyrene.

In particular, a compound having, in its structure, a methylene bridged product comprising a 1,2-naphthoquinonediazide skeleton and two or more methyl-substituted phenol derivatives is preferred as the photosensitive component. The use of this photosensitive

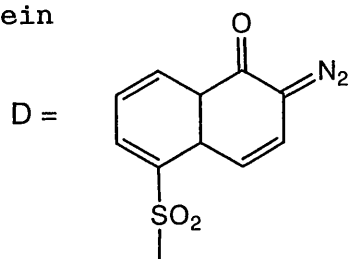
component can provide a protective coating having higher transparency. Here the methyl-substituted phenol derivative is a compound wherein any hydrogen atom attached to carbon in a phenol skeleton is substituted
5 by a methyl group. The present invention, however, embraces phenol not substituted by the methyl group (that is, phenol per se). Therefore, a methylene bridged product comprising two or more methyl-substituted phenol derivatives may refer to a compound wherein two or more
10 phenol skeletons are linked to each other or one another through a methylene group and any hydrogen atom on the phenol skeleton is substituted by a methyl group.

In the present invention, the photosensitive component may have a plurality of 1,2-
15 naphthoquinonediazide skeletons. The presence of at least one 1,2-naphthoquinonediazide skeleton in the structure of the photosensitive component suffices for contemplated effect. The number of 1,2-naphthoquinonediazide skeletons is not particularly
20 limited, and the maximum number of the 1,2-naphthoquinonediazide skeletons is equal to the number of hydroxyl groups present in the methylene bridged product comprising methyl-substituted phenol derivatives. The number of 1,2-naphthoquinonediazide skeletons,
25 however, is preferably 1 to 5, particularly preferably 2 to 4.

Among these photosensitive components, at least one compound selected from the group consisting of compounds represented by formulae (Va) to (Vc) is particularly
30 preferred as the photosensitive component used in the positive-working photosensitive composition utilized in the method according to the present invention:



wherein



or H, provided that at least one

of D is not H.

Among the photosensitive components represented by these formulae, photosensitive components, wherein three out of four D have been esterified with 1,2-naphthoquinonediazidosulfonic acid, are most preferred.

In the present invention, the photosensitive component has, in its structure, two or more methyl-substituted phenol derivatives. The number of methyl-substituted phenol derivatives in the structure is preferably 2 to 5, particularly preferably 4.

In the method according to the present invention, the photosensitive component may be properly selected from among the photosensitive components. They may be used either solely or, if necessary, in a combination of two or more. These photosensitive components may be added, to the composition for forming a protective coating, either as a compound or as a substituent

introduced into the above polymer.

(D) Crosslinking agent

In the method according to the present invention, when the composition for forming a protective coating is a positive-working photosensitive composition, if necessary, the composition may contain a crosslinking agent. The crosslinking agent may be selected from crosslinking agents described above in connection with the negative-working photosensitive composition. Among others, melamine compounds are preferred.

(E) Other components

In the method according to the present invention, when the composition for forming a protective coating is a positive-working photosensitive composition, the composition may comprise, in addition to the above components, optional various additives. Such additives include those described above in connection with other components of the heat-curable composition.

Further, when the composition for forming a protective coating is a positive-working photosensitive composition, a sensitizer may be added to improve sensitivity to light irradiation. Sensitizers include, for example, 2-nitrofluorene, 2,4,7-trinitrofluorene, benzanthrone, picramide, 1,2-benzanthraquinone, 11-chloro-6-hydroxybenzanthrone, phenanthraquinone, and 4-(4-butoxyphenyl)-2,6-diphenylthiopyrilium perchlorate.

4. Preparation of composition

In the method according to the present invention, the amount of the polymer added to the composition for forming a protective coating may be properly determined so that a good protective coating can be realized. The amount of the polymer added, however, is preferably 5 to 40% by weight, more preferably 10 to 30% by weight, based on the total weight of the composition for forming a protective coating.

The content of the organic solvent in the coating composition may be properly regulated according to the

concentration of the polymer and other additives. For example, the content of the organic solvent in the coating composition may be in the range of 45 to 95% by weight.

5 When the composition for forming a protective coating contains a crosslinking agent, the amount of the crosslinking agent added is not particularly limited. The amount of the crosslinking agent added, however, is preferably in the range of 1 to 50 parts by weight, more
10 preferably in the range of 5 to 40 parts by weight, based on 100 parts by weight of the polymer.

 When the composition for forming a protective coating contains a photopolymerization initiator, the amount of the crosslinking agent added is not
15 particularly limited. The amount of the crosslinking agent added, however, is preferably in the range of 1 to 50 parts by weight, more preferably in the range of 5 to 40 parts by weight, based on 100 parts by weight of the polymer.

20 When the composition for forming a protective coating contains a photosensitive component, the amount of the crosslinking agent added is not particularly limited. The amount of the crosslinking agent added, however, is preferably in the range of 1 to 50 parts by
25 weight, more preferably in the range of 5 to 40 parts by weight, based on 100 parts by weight of the polymer.

 The composition for forming a protective coating used in the method for forming a protective coating according to the present invention may be prepared by
30 dissolving or dispersing the above solid components in a solvent component. The sequence of mixing and the like in the preparation of the composition is not particularly limited. For example, from the viewpoint of stability of the composition, however, the composition
35 may be stored as a plurality of solutions, dispersions, or powders, and they may be properly mixed together immediately before use. Alternatively, the composition

may be prepared as a concentrated solution, and, immediately before use, the concentrated solution may be diluted with a solvent.

<Method for forming protective coating>

5 The method for forming a protective coating according to the present invention comprises coating the composition for forming a protective coating onto a substrate to form a coating and heating the coating under an inert gas atmosphere to cure the coating.

10 Where heat-curable composition is used

 In the present invention, when the heat-curable composition is used as the composition for forming a protective coating, a protective coating is generally formed by the following processes:

15 (a1) a process wherein the composition for forming a protective coating is coated onto a substrate; and

 (a2) a process wherein the coating of the composition for forming a protective coating applied onto the substrate is heated under an inert gas
20 atmosphere to cure the coating.

 Substrates, to which the method for forming a protective coating according to the present invention can be applied, include, but are not limited to, color filters, glasses, glass filters, black matrixes, various
25 polymers (for example, polyimides, polyamides, polyethylene, and acrylic resins), indium titanium oxide, silicon nitride, metal oxides (for example, titanium oxide, silicon oxide, and chromium oxide), and metals (for example, aluminum and copper).

30 The method for forming a protective coating according to the present invention comprises a process wherein the composition for forming a protective coating is coated onto the above substrate. Any method may be used for coating the composition for forming a
35 protective coating without particular limitation, and examples thereof include spin coating, roll coating, and spray coating. Among them, spin coating is useful from

the viewpoint of forming an even coating.

The method for forming a protective coating according to the present invention comprises a process wherein the coating of the composition for forming a protective coating applied onto the substrate is heated under an inert gas atmosphere. The coating may be heated by any proper method. Specific examples of heating means include hot plates, heating ovens, convection ovens, and infrared irradiation.

In the method for forming a protective coating according to the present invention, conditions for heating the composition for forming a protective coating may be properly determined by taking into consideration, for example, the type of polymer and the formulation of the composition for forming a protective coating. In general, however, heating may be carried out at 150 to 270°C, preferably 170 to 250°C, for about 10 min to 10 hr, preferably 20 to 120 min.

In the method for forming a protective coating according to the present invention, the heating is carried out under an inert gas atmosphere. In the present invention, the inert gas refers to gas which is not substantially chemically reactive with the composition for forming a protective coating, and specific examples thereof include nitrogen, argon, helium, neon, xenon and the like and mixed gases composed of these gases. Among them, nitrogen, argon, and a mixed gas composed of nitrogen and argon are preferred from the viewpoints of handleability, cost and the like.

Where photosensitive composition is used

When the composition for forming a protective coating is photosensitive, a protective coating may be generally formed by the following processes:

(b1) a process wherein the composition for forming a protective coating is coated onto a substrate;

(b2) a process wherein the coating of the

composition for forming a protective coating applied onto the substrate is exposed to light;

(b3) a process wherein the exposed coating is developed; and

5 (b4) a process wherein the developed coating is heat cured under an inert gas atmosphere.

Also in the case where the composition for forming a protective coating is a photosensitive composition, the substrate may be selected from substrates described
10 above in connection with the use of the heat-curable composition. The process (b1) and the process (b4) may be carried out in the same manner as described above in connection with the use of the heat-curable composition.

When the composition for forming a protective
15 coating is a photosensitive composition, the exposure process (b2) can induce a polymerization reaction of the components of the composition for forming a protective coating. For the light irradiation, it is common practice to adopt imagewise exposure in such a manner
20 that only desired sites of the coating of the composition for forming a protective coating applied to the substrate are exposed to light. Alternatively, the whole area of the coating of the composition for forming a protective coating may be evenly exposed.

25 The exposure may be carried out by any conventional method without particular limitation. Examples of exposure methods usable herein include exposure through a photomask and scanning exposure using a stepper or the like.

30 Light used in the exposure may be any radiation with a wavelength to which the photosensitive component is sensitive. In general, however, ultraviolet light with wavelengths of 250 to 500 nm is used. The exposure dose is regulated so that a satisfactory crosslinking
35 reaction takes place in the exposed portion. In general, however, the exposure dose is in the range of 10 to 500 mJ/cm².

In the development process (b3), the exposed photosensitive resin composition layer is generally developed with an alkaline solution. When the photosensitive composition is a positive-working composition, upon the development, the photosensitive resin composition layer in its portion exposed to the actinic radiation may be removed to form a positive image. On the other hand, when the photosensitive composition is a negative-working composition, upon the development, the photosensitive resin composition layer in its portion exposed to the actinic radiation remains unremoved while the portion not exposed to the actinic radiation is removed, whereby a negative image is formed. The development solution may be any one commonly used in the development of photoresists. In general, an aqueous solution of an inorganic alkali compound, a primary amine, a secondary amine, a tertiary amine, an alcoholamine, or a quaternary ammonium salt is used. More specifically, an aqueous solution of tetramethylammonium hydride (hereinafter referred to as "TMAH"), potassium hydroxide, sodium hydroxide, sodium carbonate, sodium silicate, ammonia, ethylamine, n-propylamine, diethylamine, di-n-propylamine, triethanolamine, dimethylethanolamine, tetramethylammonium, tetraethylammonium, or choline may be used. If necessary, these development solutions may contain optional additives, for example, water-soluble organic solvents (specifically methanol, ethanol and the like) and surfactants.

When the composition for forming a protective coating is a photosensitive composition, if necessary, the coating of the composition applied to the substrate may be preheated (prebaked) before the exposure process (b2). The purpose of the preheating is to remove the whole or a part of the solvent from the coating of the composition for forming a protective coating applied to the substrate. Upon the preheating, the photosensitive

resin composition layer is fixed onto the substrate, and, also in the subsequent exposure or development processing, the coating is not separated from the substrate. The prebaking may be carried out under any
5 conditions so far as the above purpose can be attained. In general, however, the prebaking is carried out by heating the photosensitive resin composition layer at 50 to 120°C for 30 sec to 2 min.

When the composition for forming a protective
10 coating is a photosensitive composition, the protective coating, which has been heat cured in the process (b4), may be exposed again, that is, re-exposed. In the method for forming a protective coating according to the present invention, satisfactory transparency can be
15 realized without the provision of the re-exposure process. However, the transparency can be further improved by the re-exposure.

Substrates, on which a protective coating has been formed by the method for forming a protective coating
20 according to the present invention, may be used, for example, in semiconductors, flat panel displays, and electronic equipment. The applications thereof, however, are not limited to these only.

The following examples further illustrate the
25 present invention, but are not intended to limit it.

EXAMPLES

Examples 1 to 3 and Comparative Examples 1a to 3b

A photosensitive composition for forming a
30 protective coating was prepared according to the following formulation.

(Sample A)

Polymer: SU 007*	18.0 wt%
Photoactive compound: Bis[4-hydroxy-3-(2-hydroxy-5-methylbenzyl)-5-methylphenyl]-methane 6-diazo-5,6-dihydro-5-oxonaphthalene-1-sulfonate	3.6 wt%

35

Solvent: Propylene glycol methyl ether 78.4 wt%
 (Sample B)
 Polymer: SU 007 18.0 wt%
 Photoactive compound: 4,4'-[1-[4-[1-(4-
 5 Hydroxyphenyl)-1-methylethyl]phenyl]-
 ethylidene]bisphenol 6-diazo-5,6-dihydro-
 5-oxonaphthalene-1-sulfonate 3.6 wt%
 Solvent: Propylene glycol methyl ether 78.4 wt%
 (Sample C)
 10 Polymer: SU 007 18.0 wt%
 Photoactive compound: Bis[4-hydroxy-3-
 (2-hydroxy-5-methylbenzyl)-5-methylphenyl]-
 methane 6-diazo-5,6-dihydro-5-
 oxonaphthalene-1-sulfonate 3.6 wt%
 15 Dissolution aid:
 4,4-(2-Hydroxyphenyl)methylenebis-
 (2,6-xyleneol) 3.0 wt%
 Solvent: Propylene glycol methyl ether 78.4 wt%
 * Polymer, manufactured by Clariant Japan: monomer
 20 composition = methyl methacrylate 13%, hydroxypropyl
 methacrylate 20%, methacrylic acid 61%, and n-butyl
 acrylate 6% (molar ratio); acid value = 85 mg KOH/g; OH
 value = 78 mg KOH/g; and molecular weight = 40,000.

Each of the samples was coated on a glass substrate
 25 by means of a spin coater (1H-DX2, manufactured by
 Mikasa Corp.) at 700 r.p.m. for 30 sec. The coated
 substrates were heat dried on a hot plate at 90°C for one
 min.

Subsequently, the heat dried, coated substrates
 30 were dip developed with a 0.4% aqueous TMAH solution as
 a developing solution for one min.

Thereafter, the glass substrates having thereon a
 developed protective coating were heated at 250°C for 30
 min in a heating oven set under an air atmosphere or
 35 under a nitrogen atmosphere to cure the coating.

The glass substrates having thereon a protective
 coating thus obtained were measured for transmittance at

400 nm and transmittance at 500 nm. The results were as follows.

	Sample	Atmosphere in heating oven	Transmittance at 400 nm, %	Transmittance at 500 nm, %
Ex. 1	A	Nitrogen	78.6	95.6
Comp. Ex. 1a	A	Air	63.8	90.0
Ex. 2	B	Nitrogen	87.4	97.1
Comp. Ex. 2a	B	Air	58.2	83.6
Ex. 3	C	Nitrogen	82.4	97.2
Comp. Ex. 3a	C	Air	60.4	88.6

5 As is apparent from the results, according to the method of the present invention, when an identical photosensitive composition for a protective coating is used, a protective coating having higher transparency can be formed as compared with that of the comparative
10 examples.

Separately, the procedure of Comparative Examples 1a to 3a, was repeated, except that, at a stage between after the development and before the heat curing, the coatings were exposed to i-line at 200 mJ/cm², that is,
15 were bleached. The glass substrates having thereon a protective coating thus obtained were measured for transmittance. The results were as follows.

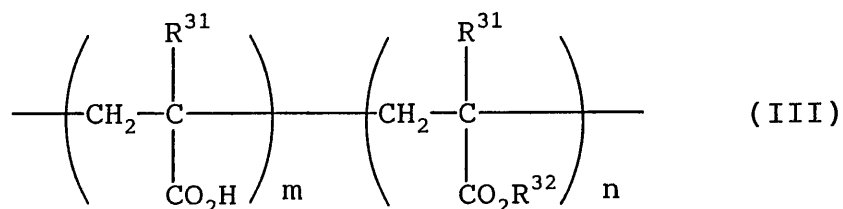
	Sample	Transmittance at 400 nm, %	Transmittance at 500 nm, %
Ex. 1	Not re-exposed	78.6	95.6
Comp. Ex. 1b	Re-exposed	73.2	94.2
Ex. 2	Not re-exposed	87.4	97.1
Comp. Ex. 2b	Re-exposed	74.1	93.8
Ex. 3	Not re-exposed	82.4	97.2
Comp. Ex. 3b	Re-exposed	71.5	93.7

20 As is apparent from the results, the method of the

present invention can produce protective coatings having a higher transparency than bleached coatings and thus can eliminate the need to provide a bleaching process.

Claims

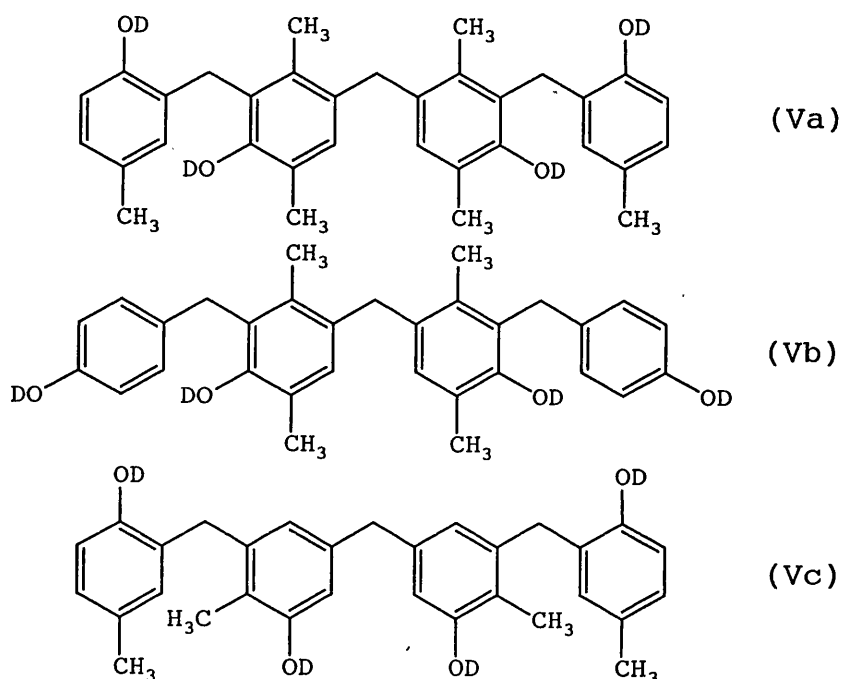
1. A method for forming a protective coating, comprising coating a composition for forming a protective coating which comprises a polymer and a solvent onto a substrate to form a coating, and heating the coating on the substrate to cure the same thereby forming a protective coating on the substrate, wherein the heating process is carried out under an inert gas atmosphere.
2. A method for producing a protective coating according to claim 1, wherein the composition is a heat-curable composition.
3. A method for producing a protective coating according to claim 1, wherein the polymer is a carboxyl-containing polymer.
4. A method for producing a protective coating according to claim 1, wherein the composition is a photosensitive composition and the coating formed is exposed to light prior to the heating process.
5. A method for producing a protective coating according to claim 4, wherein the photosensitive composition is a negative-working photosensitive composition.
6. A method for producing a protective coating according to claim 5, wherein the polymer is represented by the following formula (III):



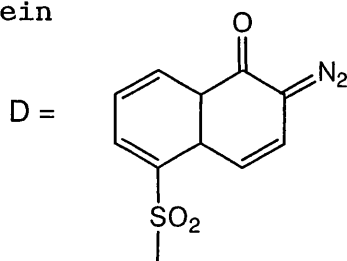
wherein R^{31} , which may be the same or different, represents a substituent selected from the group consisting of a hydrogen atom or a methyl group; R^{32} is an alkyl group having a linear or branched structure containing 1 to 5 carbon atoms; and m and n represent a degree of polymerization, respectively, where the molar ratio m/n is 0.5 to 2.4.

7. A method for producing a protective coating according to claim 4, wherein the photosensitive composition is a positive-working photosensitive composition.

8. A method for producing a protective coating according to claim 7, wherein a photosensitive component is at least one member selected from the group consisting of the following formulas (Va) - (Vc):



wherein



or H, provided that at least one

of D is not H.

9. A method for producing a protective coating according to claim 4, wherein the coating is exposed again after the heating process.

10. A method for producing a protective coating according to claim 1, wherein the substrate is a display part of an optical device.

11. A method for producing a protective coating according to claim 1, wherein the inert gas is selected from the group consisting of nitrogen, argon, and a mixture of nitrogen with argon.

12. An article comprising a protective coating produced by a method according to claim 1.