

DESCRIPTION

PHOTOSENSITIVE RESIN COMPOSITIONS, CURED ARTICLES OF THE COMPOSITIONS, AND FILMS CONTAINING THE COMPOSITIONS

Technical Field

The present invention relates to a photosensitive resin composition for forming a cured coating (a cured material) with high stress at break point and excellent in abrasion-resistance, and a cured coating (a cured material) thereof. The present invention further relates to a film having the cured coating that improves surface hardness of plastics such as polyester, acryl, polycarbonate, polyether sulfone, etc. and that is less susceptible to curling caused by curing shrinkage. Further the present invention relates to a next-generation high density optical disc using the resin composition and the cured material especially with low water absorbability and low shrinkage on curing, as well as excellent in transparency and durability.

Background Art

At present, plastics are used in great quantities in the industrial field including the automobile industry, the consumer-electronics industry and the electric and electronics industries. Reasons for massive use of plastics are, in addition to easiness in processing, transparency and etc., their properties of reduced weight, low price, excellent optical characteristics, and the like. However, plastics have disadvantages such that they are softer than glass and the like, and their surfaces are easy to be scratched.

In order to improve the plastics having such disadvantages, coating with a hard-coating agent on the surface thereof is generally performed as conventional means. Examples of such hard-coating agent which can be used are thermosetting

hard-coating agents of silicones, acrylics or melamines. Among them, silicone hard-coating agents have been widely used due to their superior quality of high hardness. The silicone hard-coating agents are used for most of high value-added products such as spectacles and lenses. However, silicone hard-coating agents require a long curing time and are expensive, and consequently they are not preferable as hard-coating agents for continuous processing film. Although attempts have been made to add an antireflective filler to the silicone hard-coating agents, coagulation of the filler may occur upon heating, since the hard-coating agents are thermosetting resins. Consequently, there are no low-reflective silicone hard-coating agents that do not impair transparency at present.

Recently, a radiation-curing acryl hard-coating agent was developed. Since the radiation-curing hard-coating agent is immediately cured to form a hard film by exposure to radiation (activation energy ray) such as ultraviolet light, processing speed is high. In addition, the product has excellent properties such as hardness and abrasion resistance, thereby bringing the total cost low, and as a result, it predominates in the field of hard-coating. The radiation-curing hard-coating agent is especially preferable for continuous processing of polyester films, polyacrylate films, acryl films, polycarbonate films, vinyl chloride films, triacetyl cellulose films, polyether sulfone films, and the like. Polyester films are widely used for antiscattering films for glass or lightproof film for automobile, films for electronic materials such as for touch-sensitive panels, liquid crystal displays, CRT flat TVs (CRT display) or laminated films for a steel sheet of a housing of home electric appliances such as refrigerator to improve decoration properties, or films for whiteboard surface. In all such applications, hard-coating is required so as to the surface thereof not to be scratched.

Further, recently, displays such as a CRT display and a liquid crystal display having a film coated with a hard-coating agent on the surface thereof, have problems

that it is difficult to see the display screen due to reflection and causing eyestrain, since the surface of the film is smooth and flat. Consequently, hard-coating treatment capable of preventing the surface reflection is required in some cases depending on the usage thereof. In order to prevent surface reflection, there can be mentioned a method for preventing surface reflection comprising coating, on a film, a radiation-curing resin into which an inorganic filler or organic microparticle filler is dispersed thereby forming unevenness on the surface (AG treatment), a method comprising providing a multi-layer structure on the film in the order of a high refractive layer and a low refractive layer thereby preventing shadowing and reflection by difference in refractive index (AR treatment), a method combining the above two methods (AG/AR treatment) and the like.

While, the hard-coating provided with functionality is desired, a large number of studies are on going at present for further improvement on the hardness of the hard-coat itself. For example, it is described in JP2001-113648A that the hardness is enhanced by adding polyfunctional urethane acrylate in the resin composition. However, since generation of cracks and film curling tend to be caused by large shrinkage on curing of the used polyfunctional urethane acrylate, the amount of addition or the composition thereof has to be limited.

General examples of an optical recording medium used in practice include CD (compact disc), MO (magneto optic disc), CD-R (CD recordable), CD-RW (CD rewritable), etc. These are constructed by forming recording layer film and reflection coating on the polycarbonate substrate of 1.2 mm in thickness, as well as forming the protective layer of an ultraviolet-curing coating agent for protecting them from external factors. In addition, recently, DVD-R, DVD-RW, DVD-RAM, DVD+R, DVD+RW, and the like can be used in practice as a result of solving problems on birefringence of the polycarbonate substrate and making a diameter of laser spots smaller by preparing the polycarbonate substrate of 0.6 mm in thickness,

i.e., a half of the conventional substrate thickness, and bonding the two substrates for further improvement of recording capacity. All of these discs are constructed by forming the recording layer film and the reflection coating on the polycarbonate substrate of 0.6 mm in thickness, as well as constructing a protective layer or an adhesive layer of ultraviolet-curing type for the purpose of protection and adhesion by the same manner as above.

However, DVD recording medium is still in the state of recording capacity shortage for use as the recording medium addressing massive storage capacity in the age of digital broadcasting. Consequently, an optical disc of a type such that a recording layer and a transparent layer of 100 μm in thickness are laminated on a substrate, and writing and reading data by blue laser light not from the polycarbonate substrate but from the transparent cover layer, is proposed (JP11-273147A) and used in practice as the next-generation high density optical disc.

With regard to a method for forming the cover layer, there are a method for bonding a transparent film of 100 μm in thickness and a method for forming a layer of 100 μm in thickness on a recording layer by using the ultraviolet-curing resin. For forming an ultraviolet-curing resin layer a 2P method and spin coater method have been proposed. Examples of the ultraviolet-curing resin for forming on a recording film are 2P agents such as compositions described in JP5-059139A and JP5-132534A. In addition, protective coating agents such as compositions described in JP3-131605A, JP3-172358A and JP2003-268263A are proposed.

Disclosure of Invention

Problems to be solved by the invention

In order to develop a stronger hard-coat under a condition where a thickness of a base film is limited, although various measures including use of a material which itself is hard, increase in degree of crosslinkage, and setting film thickness relatively

high are performed, there is such a problem as generation of cracks and curling as a result of increased crosslinkage and thickness of the film.

An object of the present invention is to provide an activated energy ray-curing resin composition which enables thick film coating with low curling and which is suitable for preparing a hard coat without generation of cracks, a cured coating thereof and a film with the cured coating. A further object of the present invention is to provide a resin composition which has a low cure shrinkage rate and is suitable for use in a transparent cover layer of a high density optical disc with little warping and excellent in endurance.

Means to solve the problems

The present inventors have studied extensively a way to achieve the above objects and found a photosensitive resin composition having a specific composition, thereby completed the present invention.

Specifically, the present invention relates to:

(1) a photosensitive resin obtained by reacting:

an isocyanate compound (A) that is a reaction product of a diisocyanate compound (a) and an alcohol compound (b) having at least two hydroxyl groups in its molecule, or an isocyanate compound (A') derived from the diisocyanate compound (a), in which either of the isocyanate groups forms an isocyanurate ring structure, with

a mixture (B) of polyfunctional (meth)acrylate compounds, as (meth)acrylate compounds of polyhydric alcohol, comprising a polyfunctional (meth)acrylate compound having one or more hydroxyl groups and a polyfunctional (meth)acrylate compound having all hydroxyl groups thereof esterified;

- (2) the photosensitive resin according to the above (1) wherein a weight-average molecular weight of the alcohol compound (b) having at least two hydroxyl groups in its molecule is 100 - 1500;
- (3) the photosensitive resin according to the above (1) or (2) wherein the polyfunctional (meth)acrylate compound having one or more hydroxyl group is pentaerythritol tri(meth)acrylate and/or dipentaerythritol penta(meth)acrylate;
- (4) the photosensitive resin according to any one of the above (1) to (3) wherein the mixture (B) is a mixture of pentaerythritol triacrylate and pentaerythritol tetraacrylate;
- (5) a photosensitive resin composition comprising the photosensitive resin as described in any one of the above (1) to (4) and a photopolymerization initiator (C);
- (6) the photosensitive resin composition according to the above (5) comprising a polymerizable compound (D);
- (7) the photosensitive resin composition according to the above (6) wherein the polymerizable compound (D) is one or plural compounds selected from the group consisting of (poly)ester (meth)acrylates (D-1), urethane (meth)acrylates (D-2), epoxy (meth)acrylates (D-3), (poly)ether (meth)acrylates (D-4), alkyl (meth)acrylates or alkylene (meth)acrylates (D-5), (meth)acrylates having an aromatic ring (D-6), (meth)acrylates having an alicyclic structure (D-7), compounds having a maleimide group, (meth)acrylamide compounds and unsaturated polyesters;
- (8) a cured material of the photosensitive resin composition as described in any one of the above (5) to (7);
- (9) a film comprising the cured material as described in the above (8);
- (10) the photosensitive resin composition according to any one of the above (5) to (7) which is a protective coating agent for an optical disc;

- (11) the cured material of the photosensitive resin composition according to the above (8) wherein a water absorption rate of the cured material measured at 25°C is 2.0% or less and a shrinkage rate on curing is 6% or less;
- (12) the cured material according to the above (8) or (11) wherein a blue laser transmission rate at a film thickness of 50 - 150 μm of the cured material is 70% or more;
- (13) an optical disc having a layer of the cured material according to the above (8), (11) or (12); and
- (14) the optical disc according to the above (13) wherein the layer of the cured material is constructed on the incident side of recording light and/or reproducing light.

Advantages of the Invention

The cured coating (cured material) of the photosensitive resin composition of the present invention has low curling and little generation of cracks, and is able to improve hardness of the cured coating. The coating can be applied to various fields requiring high hardness other than the hard coat film, i.e. ink, plastic coating, paper printing, metal coating, various fields of coating such as furniture coating, lining, adhesives, as well as electronics fields such as insulating varnish, insulating sheet, laminated plate, printed-circuit board, resist ink, semiconductor sealant, and the like.

Further, the resin composition and cured material thereof of the present invention make possible to provide a protective coating agent and cured material thereof for high-density optical discs having excellent transparency and low water absorbability, as well as exhibiting high endurance with little warping, and hence they are extremely useful in optical discs for reading and/or writing by using blue laser.

Best Mode for Carrying Out the Invention

The photosensitive resin of the present invention can be obtained by reacting an isocyanate compound (A) that is a reaction product of a diisocyanate compound (a) and an alcohol compound (b) having at least two hydroxyl groups in its molecule, or an isocyanate compound (A') derived from the diisocyanate compound (a), in which either of the isocyanate groups forms an isocyanurate ring structure, with a mixture (B) of polyfunctional (meth)acrylate compounds, as (meth)acrylate compounds of polyhydric alcohol, comprising a polyfunctional (meth)acrylate compound having one or more hydroxyl groups and a polyfunctional (meth)acrylate compound having all hydroxyl groups thereof esterified.

Examples of the diisocyanate compound (a) according to the present invention are the compounds in which two isocyanate groups are substituted in a linear saturated hydrocarbon, a cyclic saturated hydrocarbon or an aromatic hydrocarbon. Specific examples thereof include but are not limited to linear saturated hydrocarbon diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate, 2,2,4- or 2,4,4-trimethylhexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, lysine diisocyanate, and the like; cyclic saturated hydrocarbon diisocyanates such as isophorone diisocyanate, dicyclohexylmethane diisocyanate, methylene bis(4-cyclohexylisocyanate), hydrogenated diphenylmethane diisocyanate, hydrogenated xylene diisocyanate, hydrogenated toluene diisocyanate, norbornene diisocyanate and the like; and aromatic diisocyanates such as 2,4-tolylene diisocyanate, 1,3-xylene diisocyanate, p-phenylene diisocyanate, 6-isopropyl-1,3-phenyl diisocyanate, 1,5-naphthalene diisocyanate and the like. These may be used alone or as a mixture of two or more compounds.

The alcohol compound (b) having at least two hydroxyl groups in its molecule is not specifically limited, but is preferably compounds with weight-average

molecular weight of 100 - 1500. Specific examples include polyether polyols such as polybutylene glycol, polytetramethylene glycol, polypropylene glycol, polyethylene glycol and the like; polyester polyols such as polyethylene glycol adipate, poly-1,4-butanediol adipate, polycaprolactone and the like; glycols such as ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, neopentyl glycol and the like; alicyclic alcohols such as cyclohexane dimethylol, hydrogenated bisphenol A, hydrogenated bisphenol F, alcohols containing spiro skeleton, tricyclodecane dimethylol, pentacyclopentadecane dimethylol and the like or alkylene oxides thereof; branched or linear long chain alkyldiols such as hydrogenated polybutadiene and the like; bisphenols such as bisphenol A, bisphenol F and the like; alkylene oxide addition products of bisphenols; polyols such as trimethylolpropane, ditrimethylolpropane, pentaerythritol, dipentaerythritol and the like; and alkylene oxide addition products of these polyols; polyester polyols obtained by reaction of these polyols with polybasic acids such as adipic acid; and polycarbonate polyols.

The reaction of the diisocyanate compound (a) with the alcohol compound (b) having at least two hydroxyl groups in its molecule for obtaining the isocyanate compound (A) used for production of the photosensitive resin of the present invention is performed by feeding in such an equivalent relation that an isocyanate group remains after the reaction. When the amount of feeding of the alcohol compound (b) is reduced and the feeding ratio is increased, a substance derived from the alcohol compound hardly remains in the generated isocyanate compound (A), and as a result, generation of cracks of the photosensitive resin composition tends to increase. Further, when the ratio of feeding is reduced, a molecular weight increases, which tends to influence the curing property of the photosensitive resin composition.

Specifically, the OH group in the alcohol compound (b) may be set to 0.1 - 0.9 mol, preferably 0.20 - 0.85 mol to 1.0 mol of the NCO group in the diisocyanate compound (a).

Although the reaction can be performed without a solvent, the reaction may be performed in a solvent in order to improve workability when viscosity of the product is high. Specific examples of the solvent are ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone and the like; aromatic hydrocarbons such as benzene, toluene, xylene, tetramethylbenzene and the like; glycol diethers such as ethylene glycol dimethyl ether, ethylene glycol diethyl ether, dipropylene glycol dimethyl ether, dipropylene glycol diethyl ether, triethylene glycol dimethyl ether, triethylene glycol diethyl ether and the like; esters such as ethyl acetate, butyl acetate, methyl cellosolve acetate, ethyl cellosolve acetate, butyl cellosolve acetate, carbitol acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, dipropylene glycol monomethyl ether acetate, dialkyl glutarate (e.g. dimethyl glutarate, and the like), dialkyl succinate (e.g. dimethyl succinate) and the like; dialkyl adipate (e.g. dimethyl adipate); cyclic esters such as γ -butyl lactone; and petroleum solvents such as petroleum ether, petroleum naphtha, hydrogenated petroleum naphtha, solvent naphtha and the like. Further, a mixture of these solvents may be used.

The reaction temperature generally ranges from 30 to 150°C, and preferably ranges 50 to 100°C.

The end point of the reaction may be confirmed as a decrease in an amount of the isocyanate, for example, by IR (infrared absorption spectrum) or by back titration with an acid after a reaction of remaining isocyanate with an excess base.

Catalysts may be added for shortening the reaction time, and either of a basic catalyst or an acidic catalyst may be used.

Examples of the basic catalyst are amines such as pyridine, pyrrole, triethylamine, diethylamine, dibutylamine, ammonium and the like; and phosphines such as tributylphosphine, triphenylphosphine and the like.

Examples of the acidic catalyst are Lewis acid catalysts such as copper naphthenate, cobalt naphthenate, zinc naphthenate, tributoxyaluminum, titanium tetraisopropoxide, zirconium tetrabutoxide, aluminum chloride, tin 2-ethylhexanate, octyltin trilaurate, dibutyltin dilaurate, octyltin diacetate, and the like. When the catalyst is added, the amount of addition is generally 0.1 - 1 part by weight with respect to 100 parts by weight of the isocyanate compound (A) to be generated.

The isocyanate compound (A') used for production of the photosensitive resin of the present invention is a compound having an isocyanurate ring structure, which is a trimer formed by using one of the isocyanate groups in the above diisocyanate compound (a). Specifically, the trimer of tolylene diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate can be mentioned.

The mixture (B) of a polyfunctional (meth)acrylate compound having one or more hydroxyl groups and a polyfunctional (meth)acrylate compound having all hydroxyl groups thereof esterified, as (meth)acrylate compounds of polyhydric alcohol, used for production of the photosensitive resin of the present invention is not specifically limited. Specific examples thereof are a mixture of pentaerythritol (meth)acrylate with pentaerythritol tetra(meth)acrylate; a mixture of one or more polyfunctional (meth)acrylates selected from the group consisting of dipentaerythritol penta(meth)acrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritol tri(meth)acrylate and dipentaerythritol di(meth)acrylate, with dipentaerythritol hexa(meth)acrylate; and a mixture of trimethylol propane di(meth)acrylate with trimethylol propane tri(meth)acrylate. Further plurality of these mixtures may be used in combination.

Examples of the mixture (B) include preferably a mixture containing pentaerythritol tri(meth)acrylate and/or dipentaerythritol penta(meth)acrylate, and specifically a mixture of pentaerythritol triacrylate and pentaerythritol tetraacrylate is preferable. A ratio of the polyfunctional (meth)acrylate compound having one or more hydroxy groups in the mixture (B) accounts for about 20 - 95% by weight in total of the mixture (B) containing the polyfunctional (meth)acrylate compound having all hydroxyl groups thereof esterified.

With regard to the mixture (B), as (meth)acrylate compounds of polyhydric alcohol, comprising a polyfunctional (meth)acrylate compound having one or more hydroxyl groups and a polyfunctional (meth)acrylate compound having all hydroxyl groups thereof esterified, which is used for production of the photosensitive resin of the present invention, a reaction product obtained by (meth)acrylation of a polyhydric alcohol may be used.

Further, a polymerizable compound (D) hereinbelow may be added therein and used.

The photosensitive resin of the present invention can be obtained by a reaction of the above isocyanate compound (A) or isocyanate compound (A') with the mixture (B) of polyfunctional (meth)acrylate compounds, and the reaction is performed by feeding in such an equivalent relation that no isocyanate group remains after the reaction. Specifically, the mixture (B) of polyfunctional (meth)acrylate compounds is fed preferably so that the OH group thereof is 1.0 - 3.0 mol, more preferably 1.0 - 2.0 mol to 1.0 mol of the NCO group in the isocyanate compound.

Although the reaction can be performed without a solvent, it may be performed in a solvent similar to the solvent which may be used in the reaction with the above mentioned diisocyanate compound (a) and the alcohol compound (b) having at least two hydroxyl groups in its molecule, or may be performed by adding

the polymerizable compound (D) hereinbelow mentioned, or further may be performed in the polymerizable compound (D).

The reaction temperature generally ranges from 30 to 150°C, and preferably ranges 50 to 100°C.

The end point of the reaction may be confirmed as a decrease in the amount of isocyanate, for example, by IR or by back titration with an acid after a reaction of remaining isocyanate and an excess base.

For shortening the reaction time, a compound similar to the catalyst, which may be used in the reaction with the above-described diisocyanate compound (a) and the alcohol compound (b) having at least two hydroxyl groups in its molecule, may be added, and the amount thereof is the same as above.

To the above mixture (B) of polyfunctional (meth)acrylate compounds, it is conventional to previously add a polymerization-inhibitor such as p-methoxyphenol. However, the polymerization-inhibitor such as hydroquinone, p-methoxyphenol, 2,4-dimethyl-6-t-butylphenol, 3-hydroxythiophenol, p-benzoquinone, 2,5-dihydroxy-p-benzoquinone, phenothiazine and the like may be added during the reaction. When the polymerization-inhibitor is added, the amount thereof is 0.01 - 1% by weight with respect to the mixture (B) of polyfunctional (meth)acrylate compounds. Further, the amount of the photosensitive resin in the photosensitive resin composition of the present invention is generally about 5 - 90% by weight, preferably 10 - 86% by weight, when the solid content of the photosensitive resin composition is set as 100% by weight.

The photosensitive resin composition of the present invention may contain a photopolymerization initiator (C). Examples of the photopolymerization initiator (C) is not limited, and specifically, benzoin such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin propyl ether, benzoin isobutyl ether and the like; acetophenones such as acetophenone, 2,2-diethoxy-2-phenylacetophenone, 1,1-

dichloroacetophenone, 2-hydroxy-2-methyl-phenylpropane-1-one, diethoxyacetophenone, 1-hydroxy cyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one and the like; anthraquinones such as 2-ethylanthraquinone, 2-tert-butylanthraquinone, 2-chloroanthraquinone, 2-amylanthraquinone and the like; thioxanthenes such as 2,4-diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone and the like; ketals such as acetophenone dimethyl ketal, benzyl dimethyl ketal and the like; benzophenones such as benzophenone, 4-benzoyl-4'-methyldiphenyl sulfide, 4,4'-bismethylaminobenzophenone and the like; phosphine oxides such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide and the like can be mentioned. The addition ratio thereof is generally 0.01 - 30% by weight, preferably 0.1 - 25% by weight, when the solid content of the photosensitive resin composition is set as 100% by weight.

These may be used alone or as a mixture of two or more thereof, further these may be used in combination with a reaction promoter, for example, tertiary amines such as triethanolamine, methyldiethanolamine and the like; and benzoic acid derivatives such as ethyl N,N-dimethylamino benzoate, isoamyl N,N-dimethylamino benzoate and the like. When such reaction promoter is used, the addition amount thereof is 100% by weight or less to the photopolymerization initiator (C).

The photosensitive resin composition of the present invention may further contain the polymerizable compound (D). Examples of the polymerizable compound (D) are compounds having a (meth)acryloyloxy group, compounds having a maleimide group, (meth)acrylamide compounds, unsaturated polyesters, and the like.

Examples of the compound having a (meth)acryloyloxy group include (poly)ester (meth)acrylates (D-1), urethane (meth)acrylates (D-2), epoxy (meth)acrylates (D-3), (poly)ether (meth)acrylates (D-4), alkyl (meth)acrylates or

alkylene (meth)acrylates (D-5), (meth)acrylates having an aromatic ring (D-6), (meth)acrylates having an alicyclic structure (D-7), and the like.

Examples of the compound having a maleimide group include monofunctional aliphatic maleimides such as N-n-butylmaleimide, N-n-hexylmaleimide, 2-maleimidoethyl-ethylcarbonate, 2-maleimidoethyl-propylcarbonate, N-ethyl-(2-maleimidoethyl)carbamate and the like; alicyclic monofunctional maleimides such as N-cyclohexylmaleimide and the like; aliphatic bismaleimides such as N,N-hexamethylene bismaleimide, polypropylene glycol bis(3-maleimidopropyl) ether, bis(2-maleimidoethyl)carbonate and the like; alicyclic bismaleimides such as 1,4-dimaleimide cyclohexane, isophorone bisurethane bis(N-ethyl maleimide) and the like; (poly)ester (poly)maleimide compounds obtained by esterification of various (poly)ols with carboxymaleimide derivatives, such as a maleimide compound obtained by esterification of maleimideacetic acid and polytetramethylene glycol, a maleimide compound obtained by esterification of maleimidecaproic acid with tetraethylene oxide addition product of pentaerythritol, and the like.

Examples of the (meth)acrylamide compound include monofunctional (meth)acrylamides such as acryloylmorpholine, N-isopropyl (meth)acrylamide and the like; polyfunctional (meth)acrylamides such as methylene bis(meth)acrylamide and the like.

Examples of the unsaturated polyester are fumarate esters such as dimethyl fumarate, diethyl fumarate and the like; and esterification reaction products of a polyvalent unsaturated carboxylic acid such as maleic acid, fumaric acid, and the like, with a polyhydric alcohol.

The (poly)ester (meth)acrylate (D-1) as the compound having a (meth)acryloyloxy group is a generic designation of (meth)acrylate having one or more ester bonds in its main chain. Examples thereof include monofunctional

(poly)ester (meth)acrylates such as caprolactone modified 2-hydroxyethyl (meth)acrylate, (meth)acrylate of ethylene oxide and/or propylene oxide modified phthalic acid, (meth)acrylate of ethylene oxide modified succinic acid, caprolactone modified tetrahydrofurfuryl (meth)acrylate and the like; di(meth)acrylic acid ester of neopentylglycol-hydroxypivalate; caprolactone modified hydroxypivalate ester neopentylglycol di(meth)acrylate and the like; epichlorohydrin modified phthalate di(meth)acrylate; mono-, di- or tri(meth)acrylate of triol obtained by adding one or more moles of a cyclic lactone compound such as ϵ -caprolactone, γ -butyrolactone, δ -valerolactone and the like to one mole of trimethylol propane or glycerol; mono-, di-, tri- or tetra(meth)acrylate of tetraol obtained by adding one or more moles of a cyclic lactone compound such as ϵ -caprolactone, γ -butyrolactone, δ -valerolactone and the like to one mole of pentaerythritol or ditrimethylolpropane; mono(meth)acrylate or poly(meth)acrylate of polyhydric alcohol such as triol, tetraol, pentaol or hexaol obtained by adding one or more moles of a cyclic lactone compound such as ϵ -caprolactone, γ -butyrolactone, δ -valerolactone and the like to one mole of dipentaerythritol; (meth)acrylate of polyester polyol, which is a reaction product of diol component such as (poly)ethylene glycol, (poly)propylene glycol, (poly)tetramethylene glycol, (poly)butylene glycol, 3-methyl-1,5-pentanediol, hexanediol, and the like, with polybasic acid such as maleic acid, fumaric acid, succinic acid, adipic acid, phthalic acid, isophthalic acid, hexahydrophthalic acid, tetrahydrophthalic acid, dimer acid, sebacic acid, azelaic acid, 5-sodiumsulfoisophthalic acid, and the like, or anhydride thereof; and polyfunctional (poly)ester (meth)acrylate such as (meth)acrylate of cyclic lactone modified polyester diol formed with the diol hereinbefore, polybasic acid or anhydride thereof and ϵ -caprolactone, γ -butyrolactone or δ -valerolactone.

The urethane (meth)acrylate (D-2) as the compound having a (meth)acryloyloxy group is a generic designation of (meth)acrylate having one or

more urethane bond in its main chain, and is a (meth)acrylate compound obtained by reaction of a hydroxy compound (D-2-A) having at least one (meth)acryloyloxy group with an isocyanate compound (D-2-B).

Examples of the hydroxy compound (D-2-A) having at least one (meth)acryloyloxy group include 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 4-hydroxyethyl (meth)acrylate, cyclohexanedimethanol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, pentaerythritol tri(meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, and a ring-opening reaction products of such (meth)acrylate compounds having a hydroxyl group with ϵ -caprolactone.

Examples of the isocyanate compound (D-2-B) include aromatic diisocyanates such as p-phenylene diisocyanate, m-phenylene diisocyanate, p-xylene diisocyanate, m-xylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, naphthalene diisocyanate and the like; aliphatic or alicyclic structure diisocyanates such as isophorone diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, hydrogenated xylene diisocyanate, norbornene diisocyanate, lysine diisocyanate and the like; one or more burette-modified forms of isocyanate monomer; polyisocyanate such as trimerized isocyanurate of these diisocyanate compounds; polyisocyanate compounds obtained by urethanization reaction of diisocyanate compounds with the above polyol compounds.

A reaction of the hydroxy compound (D-2-A) having at least one (meth)acryloyloxy group with the isocyanate compound (D-2-B) may be performed in the same manner as in the reaction of the above isocyanate compound (A) or isocyanate compound (A') with the mixture (B) of polyfunctional (meth)acrylate compounds.

The epoxy(meth)acrylate (D-3) as the compound having a (meth)acryloyloxy group is a generic designation of a (meth)acrylate compound obtained by reacting a compound containing one or more epoxy group with (meth)acrylic acid.

Examples of the compound containing one or more epoxy group include phenyl diglycidyl ethers such as hydroquinone diglycidyl ether, catechol diglycidyl ether, resorcinol diglycidyl ether and the like; bisphenol epoxy compounds such as bisphenol A epoxy resin, bisphenol F epoxy resin, bisphenol S epoxy resin, epoxy compound of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane, and the like; hydrogenated bisphenol epoxy compounds such as hydrogenated bisphenol A epoxy resin, hydrogenated bisphenol F epoxy resin, hydrogenated bisphenol S epoxy resin, epoxy compounds of hydrogenated 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane and the like; halogenated bisphenol epoxy compounds such as brominated bisphenol A epoxy resin, brominated bisphenol F epoxy resin; alicyclic diglycidyl ether compounds such as cyclohexane dimethanol diglycidyl ether compound and the like; aliphatic diglycidyl ether compounds such as 1,6-hexanediol diglycidyl ether, 1,4-butanediol diglycidyl ether, diethylene glycol diglycidyl ether and the like; polysulfide diglycidyl ether compounds such as polysulfide diglycidyl ether and the like; phenol novolac epoxy resin, cresol novolac epoxy resin, tris(hydroxyphenyl) methane epoxy resin, dicyclopentadiene phenol epoxy resin, biphenol epoxy resin, bisphenol A novolac epoxy resin, naphthalene skeleton containing epoxy resin, heterocyclic epoxy resin and the like.

The epoxy (meth)acrylate (D-3) can be obtained by subjecting the compound containing one or more epoxy group and (meth)acrylic acid to conventional reaction condition.

The (poly)ether (meth)acrylate (D-4) as the compound having a (meth)acryloyloxy group is a generic designation of (meth)acrylate having one or more ether bond in its main chain. Examples thereof include: monofunctional

(poly)ether (meth)acrylates such as butoxyethyl (meth)acrylate, butoxytriethylene glycol (meth)acrylate, epichlorohydrin modified butyl (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, ethyl carbitol (meth)acrylate, phenoxyethyl (meth)acrylate, nonylphenoxy polyethylene glycol (meth)acrylate and the like; alkylene glycol di(meth)acrylates such as polyethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, polybutylene glycol di(meth)acrylate, polytetramethylene glycol di(meth)acrylate and the like; polyfunctional (meth)acrylates derived from (meth)acrylic acid and polyvalent hydroxy compounds such as a copolymer of ethylene oxide and propylene oxide, a copolymer of propylene glycol and tetrahydrofuran, hydrocarbon polyols, for example, polyisoprene glycol, hydrogenated polyisoprene glycol, polybutadiene glycol and hydrogenated polybutadiene glycol, and the like; di(meth)acrylate of diol in which one or more mole of cyclic ether such as ethylene oxide, propylene oxide, and butylene oxide is added to one mole of neopentyl glycol; alkylene oxide modified di(meth)acrylate of bisphenols such as bisphenol A, bisphenol F, bisphenol S; alkylene oxide modified di(meth)acrylate of hydrogenated bisphenols such as hydrogenated bisphenol A, hydrogenated bisphenol F, hydrogenated bisphenol S; mono-, di- or tri(meth)acrylate of triol obtained by adding one or more mole of cyclic ether compound such as ethylene oxide, propylene oxide and butylene oxide to one mole of trimethylol propane or glycerol; mono-, di- or tri(meth)acrylate of triol in which one or more mole of cyclic ether compound such as ethylene oxide, propylene oxide and butylene oxide is added to one mole of pentaerythritol or ditrimethylolpropane; polyfunctional (poly)ether (meth)acrylates such as tri- to hexafunctional (meth)acrylate of hexaol in which one or more mole of cyclic ether compound such as ethylene oxide, propylene oxide and butylene oxide is added to one mole of dipentaerythritol.

The alkyl (meth)acrylate or alkylene (meth)acrylate (D-5) as a compound having a (meth)acryloyloxy group is a generic designation of a straight chain alkyl (meth)acrylate which may be substituted with a halogen atom and/or hydroxyl group, or a branched chain alkyl (meth)acrylate which may be substituted with a halogen atom and/or hydroxyl group. Examples thereof include monofunctional (meth)acrylates such as octyl (meth)acrylate, isooctyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, and the like; di(meth)acrylates of hydrocarbon diol such as ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentylglycol di(meth)acrylate, 2-methyl-1,8-octanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate and the like; mono- or poly(meth)acrylates of polyhydric alcohol such as triol, tetraol and hexaol, such as mono(meth)acrylate, di(meth)acrylate, or tri(meth)acrylate of trimethylolpropane (hereinafter "poly" is used as a total designation for polyfunctional group such as di-, tri-, tetra-, etc.), mono(meth)acrylate or poly(meth)acrylate of glycerol, mono- or poly(meth)acrylate of pentaerythritol, mono- or poly(meth)acrylate of ditrimethylolpropane, and mono- or poly(meth)acrylate of dipentaerythritol; and (meth)acrylates containing a hydroxyl group, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate and the like.

The (meth)acrylate having an aromatic ring (D-6) as a compound having a (meth)acryloyloxy group is a generic designation of (meth)acrylate having an aromatic ring in its main chain or side chain. Examples thereof include monofunctional (meth)acrylates such as phenyl (meth)acrylate, benzyl (meth)acrylate and the like; and di(meth)acrylates such as bisphenol A di(meth)acrylate, bisphenol F di(meth)acrylate and the like.

The (meth)acrylate having alicyclic structure (D-7) as a compound having a (meth)acryloyloxy group is a generic designation of (meth)acrylate having an

alicyclic structure which may contain an oxygen atom or a nitrogen atom, as a constituent unit, in its main chain or side chain. Examples thereof include monofunctional (meth)acrylate having an alicyclic structure such as cyclohexyl (meth)acrylate, cyclopentyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentenyl (meth)acrylate and the like; di(meth)acrylate of hydrogenated bisphenols such as hydrogenated bisphenol A, hydrogenated bisphenol F and the like; polyfunctional (meth)acrylates having an alicyclic structure such as tricyclodecane dimethylol di(meth)acrylate and the like; alicyclic (meth)acrylate having an oxygen atom, etc. in the structure such as tetrafurfuryl (meth)acrylate and the like.

Examples of the polymerizable compound (D) which may be contained in the photosensitive resin composition of the present invention are, in addition to the above described compounds, poly(meth)acryl polymer (meth)acrylate such as reaction products of (meth)acrylate polymer and glycidyl (meth)acrylate, or reaction products of glycidyl (meth)acrylate polymer and (meth)acrylic acid; (meth)acrylate having an amino group such as dimethylaminoethyl (meth)acrylate and the like; isocyanurate (meth)acrylate such as tris(meth)acryloxyethyl isocyanurate and the like; (meth)acrylate having polysiloxane skeleton; polybutadiene (meth)acrylate; melamine (meth)acrylate, and the like. Further, a compound having copolymerizable property with the photosensitive resin composition obtained by reacting the isocyanate compound (A) or the isocyanate compound (A') with the mixture (B) of polyfunctional (meth)acrylate compounds, may be used without specific limitation.

Preferable polymerizable compounds (D) used in the photosensitive resin composition of the present invention for curing after spreading on the film include: a mixture of pentaerythritol tri(meth)acrylate with pentaerythritol tetraacrylate; a mixture of dipentaerythritol penta(meth)acrylate, dipentaerythritol

tetra(meth)acrylate, dipentaerythritol tri(meth)acrylate or dipentaerythritol di(meth)acrylate with dipentaerythritol hexa(meth)acrylate, a mixture of trimethylolpropane di(meth)acrylate with trimethylolpropane tri(meth)acrylate, and the like.

In the photosensitive resin composition of the present invention, when the photosensitive resin composition of the present invention is used as a protective coat agent for optical discs, preferable compounds for the polymerizable compound (D) are neopentyl glycol di(meth)acrylate, tricyclodecane dimethylol di(meth)acrylate, hydroxypivalaldehyde modified trimethylol propane di(meth)acrylate, di(meth)acrylate of neopentylglycol-hydroxypivalate, polyethylene glycol di(meth)acrylate, dicyclopentanyl di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, polypropylene glycol di(meth)acrylate, ethylene oxide modified bisphenol A di(meth)acrylate, ethylene oxide modified trimethylolpropane tri(meth)acrylate, ethylene oxide modified pentaerythritol tetra(meth)acrylate, tris[(meth)acryloxyethyl] isocyanurate, and the like.

When the photosensitive resin composition of the present invention contains the polymerizable compound (D), the content thereof is preferably about 10 - 2000% by weight, specifically preferably about 50 - 1000% by weight to 100% by weight of the resin composition obtained by reacting the isocyanate compound (A) or the isocyanate compound (A') with the mixture (B) of polyfunctional (meth)acrylate compounds.

The photosensitive resin composition of the present invention can contain appropriately, depending on use, unreactive compounds, inorganic fillers, organic fillers, silane coupling agents, tackifiers, antifoaming agents, leveling agents, plasticizers, antioxidants, ultraviolet absorbers, fire retardants, pigments, dyes and the like.

The unreactive compound is a low reactive or non-reactive liquid or solid oligomer or resin, for example, (meth)acrylate alkyl copolymer, epoxy resin, liquid polybutadiene, dicyclopentane diene derivative, saturated polyester oligomer, xylene resin, polyurethane polymer, ketone resin, diallylphthalate polymer (DAP resin), petroleum resin, rosin resin, fluorine oligomer, silicone oligomer and the like.

Examples of the inorganic filler include silicon dioxide, silicon oxide, calcium carbonate, calcium silicate, magnesium carbonate, magnesium oxide, talc, kaolin clay, calcined clay, zinc oxide, zinc sulfate, aluminum hydroxide, aluminum oxide, glass, mica, barium sulfate, alumina white, zeolite, silica balloon, glass balloon, and the like. To these inorganic fillers, a functional group such as a halogen atom, epoxy group, hydroxyl group and thiol group can be imparted by a method of adding a silane coupling agent, titanate coupling agent, aluminum coupling agent, zirconate coupling agent and the like, and reacting with the inorganic fillers.

Examples of the organic fillers include benzoguanamine resin, silicone resin, low-density polyethylene, high-density polyethylene, polyolefin resin, ethylene/acrylic acid copolymer, polystyrene, acrylate copolymer, polymethyl methacrylate resin, fluorocarbon resin, nylon 12, nylon 6/66, phenol resin, epoxy resin, urethane resin, polyimide resin and the like.

The photosensitive resin composition of the present invention may contain any conventionally known and commonly used tackifiers, antifoaming agents, leveling agents, plasticizers, antioxidants, ultraviolet absorbers, fire retardants, pigments and dyes can be contained without limitation, if they do not deteriorate curability and characteristic properties of the photosensitive resin composition.

The photosensitive resin composition of the present invention can be obtained by mixing the respective components hereinabove described, and orders and methods of mixing are not specifically limited.

Although the photosensitive resin composition of the present invention is not specifically required to contain a solvent, it may be used after dilution in an organic solvent, for example, ketones such as methyl ethyl ketone and methyl isobutyl ketone, acetate esters such as ethyl acetate and butyl acetate, aromatic hydrocarbon such as benzene, toluene and xylene, and other solvents commonly used for dissolving the photosensitive resin composition.

The photosensitive resin composition of the present invention can be polymerized by irradiating ultraviolet light or visible light having wavelength of 180 - 500 nm, i.e. active energy ray, and the cured material thereof is encompassed by the present invention.

Examples of a source of release of the active energy ray are low-pressure mercury vapor lamp, high-pressure mercury vapor lamp, extra high pressure mercury lamp, metal halide lamp, chemical lamp, black light lamp, mercury xenon lamp, excimer lamp, short arc lamp, helium-cadmium laser, argon laser, excimer laser, solar light, and the like.

The photosensitive resin composition of the present invention can be used as a coating agent, a surface preparation agent, a binder, a plastic material, a molding material, a laminate, an adhesion bond, an adhesive for ink, metals such as aluminum, iron and copper; plastics such as vinyl chloride, acryl, polycarbonate, polyethylene terephthalate, polyethylene, polypropylene, and the like; ceramics such as glass; woods; printing paper; and fiber. The film containing the cured material of the photosensitive resin composition of the present invention is also encompassed by the present invention.

Specifically, it is used in the field of ink such as planographic and typographic ink, flexographic ink, gravure ink, screen ink and the like, a field of varnish, a field of paper coating agent, the field of coating material for woodcraft, coating material or printing ink for beverage can, coating agent for soft packaging film, printing ink

or adhesion bond, thermal paper, coating agent for thermal film, printing ink, adhesive, adhesion bond or optical fiber coating agent.

When the resin composition of the present invention is used as the resin composition for optical discs, viscosity of the resin composition is preferably 100 - 5000 mPa·S measured by B-type viscometer at 25°C. Further, a shrinkage rate on curing at the time of curing is preferably 6% or less, and a rate of water absorption (measured at 25°C) of the cured material is preferably 2.0% or less.

A coating method of the protective coating agent for optical discs using the resin composition of the present invention is not limited, if film thickness can be made to 50 - 100 μm . Practical coating methods are, for example, a spin coat method, a 2P method, a roll coat method, a screen printing method and the like.

Since blue laser of about 400 nm is used for reading and/or writing in the next generation high-density optical disc, a transmittance at about 400 - 500 nm in the cured material of film thickness 50 - 150 μm is preferably 70% or more.

Further, in the optical disc of the present invention, preferable construction of the disc is such that the cured material layer of the ultraviolet ray-curing type resin composition is constructed on the incident side of recording light and/or reproducing light.

EXAMPLES

The present invention will be explained more specifically by examples, however the present invention is not limited to the following examples. Molecular weight is weight-average molecular weight, and is measured by GPC (gel-permeation chromatography).

Example 1

In a reactor vessel equipped with a reflux condenser, a stirrer, a thermometer and a thermoregulator, Takelac U-24 10T (Mitsui Takeda Chemicals Inc., poly-1,4-

butanediol adipate, hydroxyl group value 114.8 mgKOH/g) (97.8 g) (OH: 0.2 mol equivalent) and isophorone diisocyanate (44.5 g) (NCO: 0.4 mol equivalent) were added, and reacted at 80°C, until the content of NCO reached to a theoretical value by reacting with the OH group. Subsequently, inner temperature was reduced to 50°C, then 4-methoxyphenol (0.122 g) as the polymerization inhibitor and dibutyltin dilaurate (0.122 g) as the urethanization reaction catalyst were added, and stirred to be uniformly combined. A mixture (101.0 g) (OH: 0.22 mol equivalent) of pentaerythritol triacrylate and pentaerythritol tetraacrylate (mixing ratio, parts by weight: 65/35, hydroxyl group equivalent: 458.9 Eq) was fed by dividing it into three parts in order for the inner temperature not to exceed 70°C. After finishing the addition, the reaction was continued at 70°C, and the end point of the reaction was set when the content of the above NCO reached to 0.1% or less. The thus obtained photosensitive resin (C-1) had viscosity 33.1 Pa·s (E type viscometer, 60°C) and $M_w = 7,400$ (measured by GPC, conversion to polystyrene).

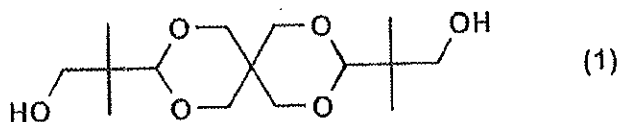
Example 2

In a reactor vessel equipped with a reflux condenser, a stirrer, a thermometer and a thermoregulator, PTG-850 (Hodogaya Chemical Co., Ltd., polytetramethylene glycol, hydroxyl group value 127.9 mgKOH/g) (87.7 g) (OH: 0.2 mol equivalent) and isophorone diisocyanate (44.5 g) (NCO: 0.4 mol equivalent) were added, and reacted at 80°C, until the content of NCO reached to a theoretical value by reacting with the OH group. Subsequently, inner temperature was reduced to 50°C, then 4-methoxyphenol (0.117 g) as the polymerization inhibitor and dibutyltin dilaurate (0.117 g) as the urethanization reaction catalyst were added, and stirred to be uniformly combined. A mixture (101.0 g) (OH: 0.22 mol equivalent) of pentaerythritol triacrylate and pentaerythritol tetraacrylate (mixing ratio, parts by weight: 65/35, hydroxyl group equivalent: 458.9 Eq) was fed by dividing it into three parts in order for the inner temperature not to exceed 70°C. After finishing the

addition, the reaction was continued at 70°C, and the end point of the reaction was set when the content of the above NCO reached to 0.1% or less. The thus obtained photosensitive resin (C-2) had viscosity 23.9 Pa·s (E type viscometer, 60°C) and Mw = 7,800 (measured by GPC, conversion to polystyrene).

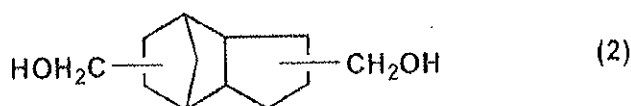
Example 3

In a reactor vessel equipped with a reflux condenser, a stirrer, a thermometer and a thermoregulator, a diol compound represented by the formula (1) hereinbelow (30.4 g) (OH: 0.2 mol equivalent) and isophorone diisocyanate (44.5 g) (NCO: 0.4 mol equivalent) were added, and reacted at 90°C, until the content of NCO reached to a theoretical value by reacting with the OH group. Subsequently, inner temperature was reduced to 50°C, then 4-methoxyphenol (0.088 g) as the polymerization inhibitor, dibutyltin dilaurate (0.088 g) as the urethanization reaction catalyst and MEK (2-butanone) (44.0 g) as the reaction solvent were added, and stirred to be uniformly combined. A mixture (101.0 g) (OH: 0.22 mol equivalent) of pentaerythritol triacrylate and pentaerythritol tetraacrylate (mixing ratio, parts by weight: 65/35, hydroxyl group equivalent: 458.9 Eq) was fed by dividing it into three parts in order for the inner temperature not to exceed 70°C. After finishing the addition, the reaction was continued at 70°C, and the end point of the reaction was set when the content of the above NCO reached to 0.1% or less. The thus obtained photosensitive resin (C-3) had viscosity 14.0 Pa·s (E type viscometer, 25°C) and Mw = 3,500 (measured by GPC, conversion to polystyrene).



Example 4

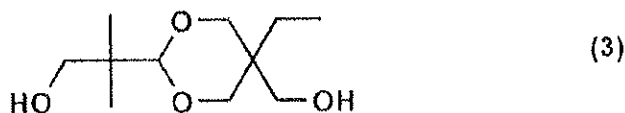
In a reactor vessel equipped with a reflux condenser, a stirrer, a thermometer and a thermoregulator, a diol compound represented by the formula (2) hereinbelow (39.3 g) (OH: 0.4 mol equivalent) and isophorone diisocyanate (88.9 g) (NCO: 0.8 mol equivalent) were added, and reacted at 90°C, until the content of NCO reached to a theoretical value by reacting with the OH group. Subsequently, inner temperature was reduced to 50°C, then 4-methoxyphenol (0.165 g) as the polymerization inhibitor, dibutyltin dilaurate (0.165 g) as the urethanization reaction catalyst and MEK (2-butanone) (82.5 g) as the reaction solvent were added, and stirred to be uniformly combined. A mixture (201.9 g) (OH: 0.44 mol equivalent) of pentaerythritol triacrylate and pentaerythritol tetraacrylate (mixing ratio, parts by weight: 65/35, hydroxyl group equivalent: 458.9 Eq) was fed by dividing it into three parts in order for the inner temperature not to exceed 70°C. After finishing the addition, the reaction was continued at 70°C, and the end point of the reaction was set when the content of the above NCO reached to 0.1% or less. The thus obtained photosensitive resin (C-4) had viscosity 5.8 Pa·s (E type viscometer, 25°C) and Mw = 2,900 (measured by GPC, conversion to polystyrene).



Example 5

In a reactor vessel equipped with a reflux condenser, a stirrer, a thermometer and a thermoregulator, a diol compound represented by the formula (3) hereinbelow (43.7 g) (OH: 0.4 mol equivalent) and isophorone diisocyanate (88.9 g) (NCO: 0.8 mol equivalent) were added, and reacted at 90°C, until the content of NCO reached to a theoretical value by reacting with the OH group. Subsequently, inner temperature was reduced to 50°C, then 4-methoxyphenol (0.167 g) as the polymerization inhibitor, dibutyltin dilaurate (0.167 g) as the urethanization reaction

catalyst and MEK (2-butanone) (83.6 g) as the reaction solvent were added, and stirred to be uniformly combined. A mixture (201.9 g) (OH: 0.44 mol equivalent) of pentaerythritol triacrylate and pentaerythritol tetraacrylate (mixing ratio, parts by weight: 65/35, hydroxyl group equivalent: 458.9 Eq) was fed by dividing it into three parts in order for the inner temperature not to exceed 70°C. After finishing the addition, the reaction was continued at 70°C, and the end point of the reaction was set when the content of the above NCO reached to 0.1% or less. The thus obtained photosensitive resin (C-5) had viscosity 15.2 Pa·s (E type viscometer, 25°C) and $M_w = 3,000$ (measured by GPC, conversion to polystyrene).



Example 6

In a reactor vessel equipped with a reflux condenser, a stirrer, a thermometer and a thermoregulator, 4-methoxyphenol (0.067 g) as the polymerization inhibitor and dibutyltin dilaurate (0.067 g) as the urethanization reaction catalyst were added, and stirred to be uniformly combined. A mixture (101.0 g) (OH: 0.22 mol equivalent) of pentaerythritol triacrylate and pentaerythritol tetraacrylate (mixing ratio, parts by weight: 65/35, hydroxyl group equivalent: 458.9 Eq) was added, and the inner temperature was set at 50°C. Subsequently, TPA-100 (hexamethylene diisocyanate trimer: a compound containing an isocyanurate ring) (33.6 g) (NCO: 0.2 mol equivalent) was fed by dividing it into three parts in order for the inner temperature not to exceed 70°C. After finishing the addition, the reaction was continued at 70°C, and the end point of the reaction was set when the content of the above NCO reached to 0.1% or less. The thus obtained photosensitive resin (C-6) had viscosity 12.6 Pa·s (E type viscometer, 60°C) and $M_w = 6,200$ (measured by GPC, conversion to polystyrene).

Example 7

In a reactor vessel equipped with a reflux condenser, a stirrer, a thermometer and a thermoregulator, 4-methoxyphenol (0.161 g) as the polymerization inhibitor and dibutyltin dilaurate (0.161 g) as the urethanization reaction catalyst were added, and stirred to be uniformly combined. A mixture (288.5 g) (OH: 0.22 mol equivalent) of dipentaerythritol pentaacrylate and dipentaerythritol hexaacrylate (mixing ratio, parts by weight: 40/60, hydroxyl group equivalent: 1311.3 g/Eq) was added and the inner temperature was set at 50°C. Subsequently, TPA-100 (hexamethylene diisocyanate trimer: a compound containing an isocyanurate ring) (33.6 g) (NCO: 0.2 mol equivalent) was fed by dividing it into three parts in order for the inner temperature not to exceed 70°C. After finishing the addition, the reaction was continued at 70°C, and the end point of the reaction was set when the content of above NCO reached to 0.1% or less. The thus obtained photosensitive resin (C-7) had viscosity 36.0 Pa·s (E type viscometer, 60°C) and $M_w = 11,200$ (measured by GPC, conversion to polystyrene).

Comparative Synthesis Example

In a reactor vessel equipped with a reflux condenser, a stirrer, a thermometer and a thermoregulator, a mixture (101.0 g) (OH: 0.22 mol equivalent) of pentaerythritol triacrylate and pentaerythritol tetraacrylate (mixing ratio, parts by weight: 65/35, hydroxyl group equivalent: 458.9 Eq), 4-methoxyphenol (0.067 g) as the polymerization inhibitor and dibutyltin dilaurate (0.067 g) as the urethanization reaction catalyst were added, and stirred at 70°C to be uniformly combined, then isophorone diisocyanate (17.8 g) (NCO: 0.16 mole equivalent) was added dropwise over a period of 3 hours. After finishing the addition, the reaction was continued at 70°C, and the end point of the reaction was set when the content of the above NCO reached to 0.1% or less to obtain the photosensitive resin (H-1).

Examples 8 - 13 and Comparative Example 1

From the photosensitive resins (C-3) and (C-4) obtained in Examples 3 and 4, respectively, the solvent MEK had previously been distilled off to obtain the resin components alone. Other resins were not treated to remain as it is. The resin compositions as shown in Table 1 below were prepared. These resin compositions were smeared by using a bar-coater on a stainless steel plate, on which a wall was constructed using sealing tape (thickness: 200 μm). The resin compositions on the plate were exposed to ultraviolet irradiation from the distance of the UV lamp height at 10 cm under nitrogen atmosphere with a carrying speed at 5 m/minute to obtain the cured coatings having about 200 μm in thickness.

Table 1

Content (g)		Example						Comparative Example
		8	9	10	11	12	13	1
(C-1)		80						
(C-2)			80					
(C-3)				80				
(C-4)					80			
(C-5)						80		
(C-6)							80	
(H-1)								80
HDDA	*1	20	20	20	20	20	20	20
Irg. 184	*2	5	5	5	5	5	5	5

*1: HDDA; a product of Nippon Kayaku Co., Ltd., 1,6-hexanediol diacrylate
 *2: Irg. 184 (Irgacure 184); a product of Ciba Specialty Chemicals, 1-hydroxy-cyclohexyl-phenyl-ketone

Test Example 1

Films obtained in Examples 8 - 13 or Comparative Example 1 were evaluated on the following items. Results are shown in Table 2.

(Pencil hardness)

Pencil hardness of the coated films was measured by using a pencil scratcher according to JIS K 5400. Specifically, the pencil was set at the angle 45° on the

film to be tested, and the film was scratched for about 5 mm with applying load 1 kg on the top to confirm the scratching.

(Tensile test)

The film was cut at 1.0 cm × 4.0 cm, and the following data was measured by using Tensilon (tensile tester).

1. Young's modulus
2. Stress at break point
3. Elongation at break point

Table 2: Result of Evaluation

	Pencil hardness	Young's modulus (MPa)	Stress at break point (MPa)	Elongation at break point (%)
Example 8	HB	715	33.7	8.1
Example 9	HB	631	27.8	6.9
Example 10	4H	1260	23.3	2.8
Example 11	5H	1346	28.8	3.5
Example 12	4H	1246	22.7	3.4
Example 13	6H	1340	34.4	4.1
Comparative Example 1	6H	1070	17.8	2.0

The results in Table 2 indicate that films capable of elongating while maintaining relatively high Young's modulus and high stress at break point can be obtained by using the photosensitive resin compositions of the present invention.

Examples 14 - 19, and Comparative Example 2

From the photosensitive resins (C-3) and (C-4) obtained in Examples 3 and 4, respectively, the solvent MEK had previously been distilled off to obtain the resin components alone. Other resins were not treated to remain as it is. The resin compositions as shown in Table 3 below were prepared. The thus obtained resin compositions were smeared by using a bar-coater (No. 20) on the easily adhesive treated polyester film (Toyobo K. K., A-4300, film thickness: 188 μ m), and allowed to leave for one minute in the dry oven at 80°C. The resin compositions on the film

were exposed to ultraviolet irradiation from the distance of a UV lamp height at 10 cm under air atmosphere using a high-pressure mercury lamp, 120 W/cm, with a carrying speed at 5 m/minute to obtain the films having cured coatings (10 - 15 μ m).

Table 3

Content (g)		Example						Comparative Example 2
		14	15	16	17	18	19	
(C-1)		30						
(C-2)			30					
(C-3)				30				
(C-4)					30			
(C-5)						30		
(C-6)							30	
(H-1)								30
R-551	*3	10	10	10	10	10	10	10
PRT-30	*4	10	10	10	10	10	10	10
Irg. 184		3	3	3	3	3	3	3
MEK	*5	50	50	50	50	50	50	50

*3: R-551; a product of Nippon Kayaku Co., Ltd., KAYARAD R-551; bisphenol A poly (n $\approx$ 4) ethoxy diacrylate
 *4: PET-30; a product of Nippon Kayaku Co., Ltd., KAYARAD PET-30; pentaerythritol triacrylate
 *5: MEK; 2-butanone

Test Example 2

Films obtained in Examples 14 - 19 or Comparative Example 2 were evaluated on the following items. Results are shown in Table 4.

(Pencil hardness)

Pencil hardness of the coated film was measured by using a pencil scratcher according to JIS K 5400. Specifically, the pencil was set at the angle 45° on the polyester film having the cured coating to be tested, and the film was scratched for about 5 mm with applying a load 1 kg on the top to confirm the scratching. Measurements were performed for five times, and the number of non-scratching films was counted.

Evaluation 5/5: no scratching for 5 times out of 5 times

0/5: generation of scratching for all cases out of 5 times

(Abrasion-resistant test)

Film loaded at 200 g/cm^2 was subjected to 10 reciprocations on steel wool #0000, and generation of scratching was observed macroscopically.

Evaluation ○: no scratching

× : generation of scratching

(Adhesiveness)

Eleven horizontal and vertical cut lines with 1 mm distance were nicked on the surface of the film to prepare 100 meshes according to JIS K 5400. When the film was swiftly detached after adhered with Cellophane tape (Registered Trademark) on the surface, numbers of remained meshes without detached were indicated.

(Curl)

Polyester film having cured membrane to be measured was cut at $5 \text{ cm} \times 5 \text{ cm}$, and allowed to leave in the drying oven at 80°C for 1 hour, and then reduce to room temperature. Each height of the four edges of the quadrate uplifted was measured on the horizontal board and mean height (unit: mm) was set as a measured value. Curling of the substrate was observed to be 0 mm in that time.

(Appearance)

Conditions such as surface cracks, stress whitening and haze were checked with eyes.

Evaluation ○: Good

△: slight crack generation

×: significant crack generation

Table 4: Result of Evaluation

	Pencil hardness 3H	Abrasion	Adhesiveness	Curl	Appearance
Example 14	5/5	○	80	5	○
Example 15	5/5	○	80	7	○
Example 16	5/5	○	100	17	○
Example 17	5/5	○	100	15	○
Example 18	5/5	○	100	18	○
Example 19	5/5	○	100	25	○
Comparative Example 2	5/5	○	100	26	△

The results in Table 4 indicate that the films coated with the photosensitive resin compositions of the present invention exhibit excellent properties including high pencil hardness and abrasion resistance as well as little generation of curl with almost no generation of cracks.

Test Example 3

(Examples 20 - 25 and Comparative Example 3)

The compound (C-1) obtained in Example 1 and the compound (C-6) obtained in Example 6 were used to prepare the resin compositions having the blending ratios as shown in Table 5 below, and evaluation as the protective coating agent for an optical disc was performed. In Table 5, parts indicate parts by weight.

Table 5

	Example						Comparative example 3
	20	21	22	23	24	25	
C-1	50	50	60				
C-6				50	50	65	
UX-6101							20
R-684	30			40			
R-604		25			40		70
PHE	20			10			10
LA		25	40		10	35	
Irg. 184	5	5	5	5	5	5	5
Viscosity (mPa·S/25°C)	3700	2200	2100	2900	3600	3100	2100
Shrinkage rate on curing (%)	5.3	5.2	4.5	4.9	4.8	4.2	7.2
Water absorption rate (%)	1.1	0.9	0.8	1.1	1.0	0.8	1.6
Transmission rate (%)	80	80	80	80	80	80	80
Warping	○	○	○	○	○	○	×
Endurance	○	○	○	○	○	○	○

Abbreviations for each composition shown in the table are as follows.

UX-6101: polyester urethane acrylate (molecular weight; 2700 ± 500), a product of Nippon Kayaku Co., Ltd.

R-684: dicyclopentanyl di(meth)acrylate, a product of Nippon Kayaku Co., Ltd.

R-604: hydroxypivalaldehyde modified trimethylolpropane di(meth)acrylate, a product of Nippon Kayaku Co., Ltd.

PHE: phenoxyethyl (meth)acrylate, a product of Dai-ichi Kogyo Seiyaku Co., Ltd.

LA: lauryl acrylate, a product of NOF Corporation

Irg. 184: 1-hydroxycyclohexyl phenyl ketone, a product of Ciba Specialty Chemicals, photopolymerization initiator
(Viscosity)

Data measured by B type viscometer was used as standard.

(Shrinkage rate on curing)

A value was determined by calculating from specific gravity (SG) of liquid before curing at 25°C and specific gravity (SG) of film obtained after curing at 25°C by the following equation (1).

$$\text{Shrinkage rate on curing} = (\text{film SG} - \text{liquid SG}) / \text{film SG} \times 100 \quad (1)$$

(Water absorption rate)

A value obtained by a method according to JIS K-7209 7.2.1 was defined as a water absorption rate.

(Transmission rate)

Transmission rate was measured by such that the resin was smeared with thickness $100 \pm 10 \mu\text{m}$ by using spin coat on the polycarbonate substrate, cured by irradiation of UV, and measured for transmission rate at 405 nm with the reference of polycarbonate substrate.

(Warping)

DVD substrate sputtered with aluminum was used. Each composition described in Table 5 was smeared on DVD substrate sputtered with aluminum by using spin coater to prepare coated film having mean film thickness $100 \mu\text{m}$. The coated film was cured by irradiating with the amount of energy of integral light intensity $1000 \text{ mJ}/\text{cm}^2$ after having set the height of lamp of UV irradiator (Japan Storage Battery Co., Ltd., CS-30L, 80 w/cm, high-pressure mercury lamp) to 10 cm. The obtained test pieces were allowed to leave for 24 hours, put on a glass plate, and evaluated the warping.

○: Almost no warping was recognizable

△: When one side of the test piece was held with a finger, the other side is pushed up to 2 mm or less.

×: When one side of the test piece was held with a finger, the other side is pushed up to 5 mm or more.

(Endurance)

Test pieces used in the evaluation of warping hereinabove were used, and allowed to leave at 80°C for 500 hours under 85% RH atmosphere. Condition of the reflection coating was observed with eyes.

○: No changes was observed on the reflection coating immediately after adhesion.

△: Slight change in color or pinhole was observed on the reflection coating.

×: Large change in color or pinhole was observed on the reflection coating.

The resin composition and the cured material thereof of the present invention can provide a protective coating agent and cured material thereof for a high-density optical disc having excellent transparency and low water absorbability, as well as exhibiting high endurance with little warping, and are extremely useful as a optical disc for reading and/or writing by using blue laser.

CLAIMS

1. A protective coating agent for an optical disc comprising:
a photosensitive resin obtained by reacting
an isocyanate compound (A) that is a reaction product of a diisocyanate compound (a) and an alcohol compound (b) having at least two hydroxyl groups in its molecule, or an isocyanate compound (A') derived from the diisocyanate compound (a), in which either of the isocyanate groups forms an isocyanurate ring structure, with
a mixture (B) of polyfunctional (meth)acrylate compounds, as
(meth)acrylate compounds of polyhydric alcohol, comprising a polyfunctional (meth)acrylate compound having one or more hydroxyl groups and a polyfunctional (meth)acrylate compound having all hydroxyl groups thereof esterified;
a photopolymerization initiator (C); and
a polymerizable compound (D).
2. The protective coating agent for an optical disc according to claim 1 wherein a weight-average molecular weight of the alcohol compound (b) having at least two hydroxyl groups in its molecule is 100 - 1500.
3. The protective coating agent for an optical disc according to claim 1 or 2 wherein the polyfunctional (meth)acrylate compound having one or more hydroxyl group is pentaerythritol tri(meth)acrylate and/or dipentaerythritol penta(meth)acrylate.

4. The protective coating agent for an optical disc according to any one of claim 1 to 3 wherein the mixture (B) is a mixture of pentaerythritol triacrylate and pentaerythritol tetraacrylate.
5. The protective coating agent for an optical disc according to any one of claims 1 to 4 wherein the polymerizable compound (D) is one or plural compounds selected from the group consisting of (poly)ester (meth)acrylates (D-1), urethane (meth)acrylates (D-2), epoxy (meth)acrylates (D-3), (poly)ether (meth)acrylates (D-4), alkyl (meth)acrylates or alkylene (meth)acrylates (D-5), (meth)acrylates having an aromatic ring (D-6), (meth)acrylates having an alicyclic structure (D-7), compounds having a maleimide group, (meth)acrylamide compounds and unsaturated polyesters.
6. A cured material of the protective coating agent for an optical disc according to any one of claim 1 to 5.
7. A film comprising the cured material according to claim 6.
8. The cured material of protective coating agent for an optical disc according to claim 6 wherein a water absorption rate of the cured material measured at 25°C is 2.0% or less and a shrinkage rate on curing is 6% or less.
9. The cured material according to claim 6 or 8 wherein a blue laser transmission rate at a film thickness of 50 - 150 μm of the cured material is 70% or more.
10. An optical disc having a layer of the cured material according to claim 6, 8 or 9.

11. The optical disc according to claim 10 wherein the layer of the cured material is constructed on the incident side of recording light and/or reproducing light.