

Description

Title of the Invention: ULTRAVIOLET-CURABLE RESIN COMPOSITION FOR
MULTILAYER OPTICAL DISK

5

Technical Field

[0001]

The present invention relates to an ultraviolet-curable resin composition for an optical disk and a cured material thereof, and relates to a resin composition for efficiently
10 producing a next-generation high-density optical disk, which has a high close adhesive force to a reflective film layer or a dielectric layer and is excellent in releasability from a stamper.

Background Art

15 [0002]

In recent years, there is a remarkable demand for a large capacity optical disk. Technologies for increasing recording capacity of an optical disk include shortening of wavelengths of recording/reproducing beams, increase of NA (numerical aperture) of an objective lens in an irradiation optical system for recording/reproducing beams, use of a
20 multilayered recording layer, and the like. Of these, the capacity increase by the use of multilayered recording layer enables capacity increase at low costs as compared with the shortening of wavelengths and the increase of NA.

For example, a DVD disk having two recording layers has a structure that the two recording layers are laminated via a transparent resin intermediate layer. Specifically, it is
25 a structure that a first transparent resin substrate of 0.6 mm, a first recording layer, a first semi-transparent reflective film layer, a transparent resin intermediate layer, a second recording layer, a second reflective film layer, an adhesive layer, and a second transparent resin substrate of 0.6 mm are laminated in this order. In this case, the transparent resin intermediate layer is formed by applying an ultraviolet-curable resin composition for
30 forming the transparent resin intermediate layer on the first semi-transparent reflective film layer, pressing the composition to a transparent resin stamper having a concavoconvex pattern such as a guiding groove for recording/reproducing beams, curing the ultraviolet-curable resin composition, and then peeling off the stamper to transfer the concavity and convexity to the surface of the ultraviolet-curable resin composition.

[0003]

With regard to the blu-ray disk, in the case of a read-only disk, for example, a pit-like recorded pattern is transferred to one surface of a polycarbonate substrate having a diameter of 120 mm and a thickness of 1.1 mm as a substrate, and a first reflective layer to be a first recording layer, for example, a silver alloy reflective film layer is formed on the surface of the substrate. Furthermore, a transparent resin intermediate layer to which a pit-like recorded pattern has been transferred is formed on the first reflective layer, and a second reflective layer to be a second recording layer, for example, a silver alloy reflective film layer is formed on the intermediate film. Then, a transparent resin layer is laminated, thereby the disk being configured. In this regard, there is proposed a procedure that the silver alloy reflective film layer is formed under vacuum, for example, by a sputtering method.

A recording type disk has a structure that a pit-like recorded pattern is transferred to one surface of a polycarbonate substrate having a diameter of 120 mm and a thickness of 1.1 mm as a base, a first reflective layer, a first dielectric layer, a first recording layer, and a second dielectric layer are laminate on the surface of the base, and further a transparent resin intermediate layer, a second reflective layer, a third dielectric layer, a second recording layer, a fourth dielectric layer, and a transparent resin layer are laminated in this order.

In these cases, the transparent resin intermediate layer is formed by applying an ultraviolet-curable resin composition for forming the transparent resin intermediate layer on the reflective film layer or the dielectric layer, pressing the composition to a transparent resin stamper having a concavoconvex pattern such as a guiding groove for recording/reproducing beams, curing the ultraviolet-curable resin composition, and then peeling off the stamper to transfer the concavity and convexity to the surface of the ultraviolet-curable resin composition. Usually, the transparent resin intermediate layer is composed of a release layer adhered to the second reflective layer and an adhesive layer adhered to the first reflective layer in the read-only disk, or is composed of a release layer adhered to the second reflective layer and an adhesive layer adhered to the second dielectric layer in the recoding type disk.

[0004]

In general, the transferring method is called a 2P (Photo Polymerization) method and the ultraviolet-curable resin composition to be used is called a 2P resin.

Examples of the transparent resin stamper include an acrylic resin, a methacrylic resin, a polycarbonate resin, a polyolefin-based resin (particularly, an amorphous polyolefin), a polyester resin, a polystyrene resin, an epoxy resin, or the like. Of these, in view of releasability, low moisture absorption, shape stability, and the like after curing of the 2P resin, an amorphous polyolefin is preferred. In view of the costs of the materials, a polycarbonate resin is preferred.

In general, a polycarbonate resin is used for the resin substrate of 0.6 mm for DVD and the resin substrate of 1.1 mm for a blu-ray disk. In the case where a polycarbonate resin is used as the transparent resin stamper, the releasability of the polycarbonate-made resin stamper from the 2P resin layer after curing is enhanced by using an ultraviolet-curable resin different from the 2P resin at the resin substrate side. [0005]

When the releasability from the transparent resin stamper is poor, a part of the transparent resin intermediate layer is peeled off together with the transparent resin stamper and a defect is generated. When transferring ability is poor, an error occurs at recording/reproduction. When warp is large after ultraviolet curing, a recording layer or a reflective layer cannot be uniformly formed on the concavoconvex pattern formed and/or the second substrate cannot be attached thereto in the case of DVD or a light transmitting layer of 0.1 mm cannot be uniformly formed in the case of a blu-ray disk. Moreover, when the concavoconvex pattern is deformed under high temperature and high humidity, recording properties (for example, a jitter property) of the first and second recording layers do not become equal.

The 2P resin described in each of Patent Documents 1 to 4 forms a concavoconvex pattern on a glass substrate using a metal-made stamper and there is no description on the concavoconvex pattern formation by a transparent resin stamper. Moreover, although the 2P resins are described in Patent Documents 5 to 8, there is no description on the resin of the present invention.

Prior Art Documents

Patent Documents

[0006]

Patent Document 1: JP-A-5-59139

Patent Document 2: JP-A-5-132534

Patent Document 3: JP-A-5-140254

Patent Document 4: JP-A-5-132506

Patent Document 5: JP-A-2003-331463

Patent Document 6: JP-A-2004-288242

Patent Document 7: JP-A-2004-288264

5 Patent Document 8: JP-A-2005-332564

Summary of the Invention

Problems that the Invention is to Solve

[0007]

10 Usually, the ultraviolet-curable resin to be used as a 2P agent should be easily releasable from a stamper on which a concavoconvex pattern has been formed, with maintaining the pattern. At that time, when the resin is difficult to be released from the stamper, there arises a problem that the resin attaches to the stamper and does not adhere to the reflective layer or the dielectric layer, and thus causing a decrease in production
15 efficiency. Moreover, even if the resin is a resin highly releasable from the stamper, when it is released at the time when it is placed under high temperature and high humidity, there arise a problem that a read error occurs.

[0008]

Accordingly, in consideration of such circumstances, the present invention
20 provides a resin composition which exhibits a particularly excellent releasability from a stamper and closely adheres to a reflective film layer or a dielectric layer even under high temperature and high humidity using a polyfunctional acrylate-modified urethane acrylate and a (meth)acrylate monomer.

[0009]

25 Furthermore, since selective adhesion to the reflective film layer or dielectric layer can be achieved upon the release from the stamper, the present invention enables omission of the adhesive layer of the ultraviolet-curable resin as the 2P agent.

Means for Solving the Problems

30 [0010]

The present inventors have found a resin composition which enhances releasability from a stamper and tightly adheres to a reflective film layer or a dielectric layer even when placed under high temperature and high humidity by using a urethane (meth)acrylate ultraviolet-curable resin composition obtained by reacting an organic

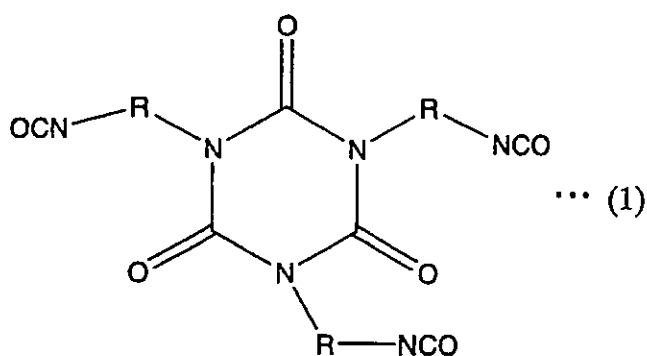
isocyanate with a polyfunctional acrylate having a hydroxyl group. Thereby, they have developed an ultraviolet-curable resin composition which exhibits a high releasability from a stamper and excellent in close adhesiveness to a reflective film layer or a recording film. [0011]

5 The present invention relates to the following (1) to (7).

(1) An ultraviolet-curable resin composition for a multilayer optical disk, comprising (A) a hexa- or higher-functional urethane (meth)acrylate obtained by reacting an organic isocyanate having two or more isocyanate groups in one molecule thereof with a tri- or higher-functional (meth)acrylate having a hydroxyl group, (B) a tri- or lower-
10 functional (meth)acrylate monomer, and (C) a photopolymerization initiator.

(2) The ultraviolet-curable resin composition for a multilayer optical disk according to the item (1) above, wherein in the hexa- or higher-functional urethane (meth)acrylate (A) obtained by reacting an organic isocyanate having two or more isocyanate groups in one molecule thereof with a tri- or higher-functional (meth)acrylate having a hydroxyl group, the organic isocyanate is one or two or more compounds selected from the group consisting of isophorone diisocyanate, hexamethylene diisocyanate, tolylene diisocyanate, xylene diisocyanate, diphenylmethane-4,4'-diisocyanate, dicyclopentanyl diisocyanate, and a trifunctional isocyanate represented by the formula
15 (1):

20 [0012]
[Chem. 1]

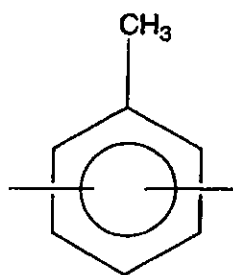


[0013]

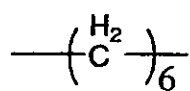
[0014]

25 where R represents:

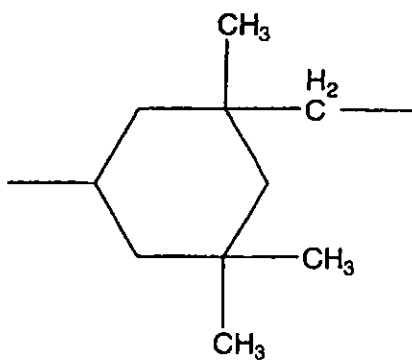
[Chem. 2]



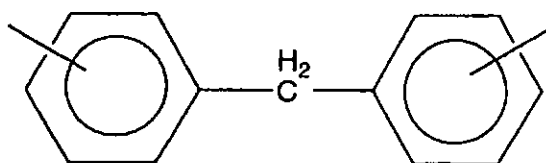
[Chem. 3]



5 [Chem. 4]

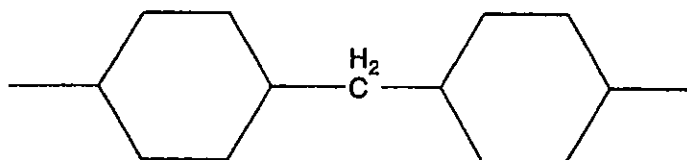


[Chem. 5]



or

[Chem. 6]



(3) The ultraviolet-curable resin composition for a multilayer optical disk according to the item (1) or (2) above, wherein in the hexa- or higher-functional urethane (meth)acrylate (A) obtained by reacting an organic isocyanate having two or more isocyanate groups in one molecule thereof with a tri- or higher-functional (meth)acrylate having a hydroxyl group, the tri- or higher-functional (meth)acrylate having a hydroxyl group is one or two or more compounds selected from the group consisting of pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, tri(meth)acrylate of ϵ -caprolactone adduct of pentaerythritol, and tri-, tetra- or penta-(meth)acrylate of ϵ -caprolactone adduct of dipentaerythritol.

(4) The ultraviolet-curable resin composition for a multilayer optical disk according to any one of the items (1) to (3) above, wherein the tri- or lower-functional (meth)acrylate monomer (B) is one or two or more compounds selected from the group consisting of isobornyl acrylate, neopentyl glycol diacrylate, propylene oxide-modified neopentyl glycol diacrylate, tricyclodecanedimethanol diacrylate, and hydropivalaldehyde-modified trimethylolpropane diacrylate.

(5) The ultraviolet-curable resin composition for a multilayer optical disk according to any one of the items (1) to (4) above, which contains 5 to 80% by weight of the (A) component, 10 to 80% by weight of the (B) component, and 1 to 15% by weight of the (C) component based on the whole resin composition.

(6) A cured material obtainable by irradiating the ultraviolet-curable resin composition for a multilayer optical disk according to any one of items (1) to (5) above with an active energy ray.

(7) A multilayer optical disk comprising the cured material according to the item (6) above.

Effect of the Invention

[0015]

The ultraviolet-curable resin composition of the present invention and a cured material thereof are excellent in releasability from a stamper and are useful as a 2P agent which closely adheres to a reflective film layer or a dielectric layer under high temperature and high humidity. Moreover, it is possible to provide an ultraviolet-curable resin composition which enables formation of an intermediate layer by one liquid with omitting an adhesive layer.

10 Best Mode for Carrying Out the Invention

[0016]

The present invention provides an ultraviolet-curable resin composition for an optical disk, comprising (A) a hexa- or higher-functional urethane (meth)acrylate obtained by reacting an organic isocyanate having two or more isocyanate groups in one molecule thereof with a tri- or higher-functional (meth)acrylate having a hydroxyl group, (B) a tri- or lower-functional (meth)acrylate monomer, and (C) a photopolymerization initiator.

[0017]

In the ultraviolet-curable resin composition of the present invention, (A) a hexa- or higher-functional urethane (meth)acrylate obtained by reacting an organic isocyanate having two or more isocyanate groups in one molecule thereof with a tri- or higher-functional (meth)acrylate having a hydroxyl group is used.

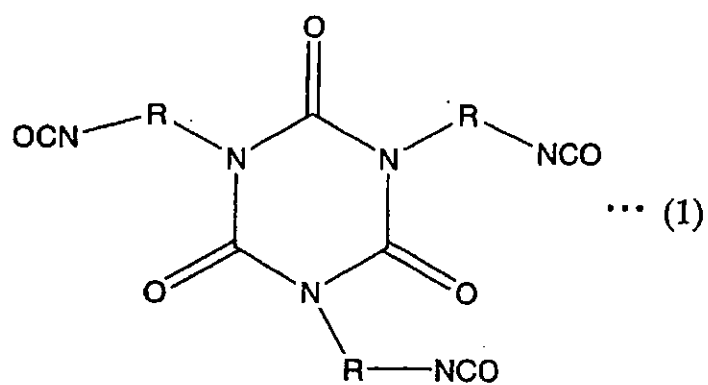
The organic isocyanate to be used in the present invention is a compound having two or more isocyanate groups in one molecule thereof and any known ones may be used without particular limitation. Examples thereof include diisocyanates such as isophorone diisocyanate, hexamethylene diisocyanate, tolylene diisocyanate, xylene diisocyanate, diphenylmethane-4,4'-diisocyanate, and dicyclopentanyl diisocyanate.

[0018]

Furthermore, in the present invention, as a modified isocyanate, use is made of a trifunctional isocyanate represented by the following formula (1):

[0019]

[Chem. 7]

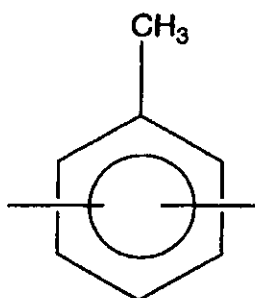


[0020]

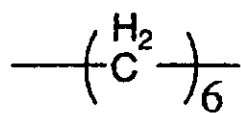
5 where R represents:

[0021]

[Chem. 8]

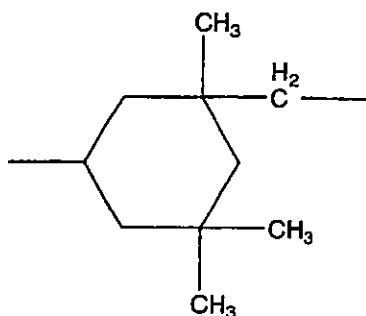


[Chem. 9]

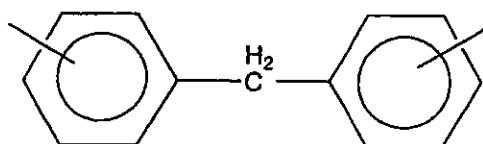


10

[Chem. 10]

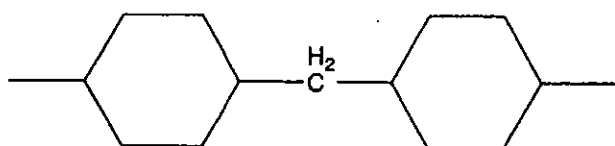


[Chem. 11]



5 or

[Chem. 12]



in which a diisocyanate monomer is subjected to isocyanurate modification.

[0022]

10 These compounds are obtained through synthesis by any appropriate and known methods but examples of commercially available products thereof include Takenate D-170N manufactured by Takeda Chemical Industries, Ltd.; Sumidur N-3300, Desmodur L, Desmodur HL manufactured by Sumitomo Chemical Bayer Ltd.; T-1890 manufactured by Degussa.

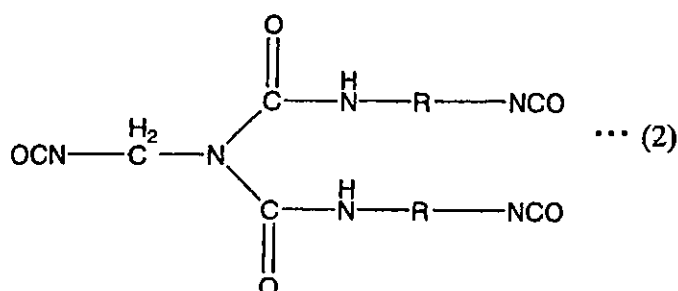
15 As the organic isocyanate, the trifunctional isocyanate represented by the formula (1) is preferred, and particularly, an isocyanurate trimer of hexamethylene diisocyanate (R = -(CH₂)₆-) is preferred.

[0023]

Furthermore, as a modified isocyanate, it is also possible to use an isocyanate represented by the following formula (2):

[0024]

5 [Chem. 13]



[0025]

wherein R is the same as R in the above formula (1),

as a modified isocyanate, in which a diisocyanate monomer is subjected to a biuret
10 reaction.

[0026]

The tri- or higher-functional (meth)acrylate having a hydroxyl group specifically
refers to a tri- to octa-functional (meth)acrylate having a hydroxyl group and any known
ones can be used without particular limitation. Examples thereof include pentaerythritol
15 tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, tri(meth)acrylate of ϵ -caprolactone
adduct of pentaerythritol, tri-, tetra- or penta-(meth)acrylate of ϵ -caprolactone adduct of
dipentaerythritol, and the like. In the present invention, particularly, pentaerythritol
tri(meth)acrylate and dipentaerythritol penta(meth)acrylate are preferred.

[0027]

20 The reaction was carried out as follows. Namely, an organic polyisocyanate is
mixed so that the isocyanate group thereof is 1.1 to 2.0 equivalents per equivalent of the
hydroxyl group of a tri- or higher-functional (meth)acrylate having a hydroxyl group, and
is reacted at a reaction temperature of preferably 70 to 90°C. Thereby, an objective
urethane (meth)acrylate (A) can be obtained.

25 One or two kinds of the above (A) urethane (meth)acrylate can be mixed and used
in an arbitrary ratio. The amount of the (A) urethane (meth)acrylate to be used in the
composition is 5 to 80% by weight, preferably 15 to 75% by weight, and particularly
preferably about 20 to 70% by weight as a ratio to the composition.

[0028]

As the (B) tri- or lower-functional (meth)acrylate monomer to be used in the present invention, any known one may be used without particular limitation. Examples thereof include tricyclodecane (meth)acrylate, benzyl acrylate, dicyclopentanyl (meth)acrylate, isobornyl (meth)acrylate, adamantyl (meth)acrylate, benzyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, morpholine (meth)acrylate, neopentyl glycol di(meth)acrylate, propylene oxide-modified neopentyl glycol di(meth)acrylate, tricyclodecanedimethanol di(meth)acrylate, hydropivalaldehyde-modified trimethylolpropane di(meth)acrylate, hydroxypivalic acid neopentyl glycol di(meth)acrylate, and the like.

In order to enhance the releasability, as the (meth)acrylate monomer, it is preferred to use isobornyl acrylate, neopentyl glycol diacrylate, propylene oxide-modified neopentyl glycol diacrylate, tricyclodecanedimethanol diacrylate, and hydropivalaldehyde-modified trimethylolpropane diacrylate. The amount thereof to be used in the composition is 10 to 80% by weight, preferably 15 to 75% by weight, and more preferably 20 to 70% by weight as a ratio to the composition.

[0029]

Examples of the (C) photopolymerization initiator to be contained in the ultraviolet-curable resin composition of the present invention include 1-hydroxycyclohexyl phenyl ketone (IRGACURE 184; manufactured by Ciba Specialty Chemicals), 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (IRGACURE 2959; manufactured by Ciba Specialty Chemicals), 2-hydroxy-1-{4-[4-(2-hydroxy-2-methylpropionyl)-benzyl]-phenyl}-2-methyl-propane-1-one (IRGACURE 127; manufactured by Ciba Specialty Chemicals), 2,2-dimethoxy-2-phenylacetophenone (IRGACURE 651; manufactured by Ciba Specialty Chemicals), oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl]propanone] (ESACURE ONE; manufactured by Fratelli Lamberti), 2-hydroxy-2-methyl-1-phenyl-propane-1-one (DAROCURE 1173; manufactured by Ciba Specialty Chemicals), 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one (IRGACURE 907; manufactured by Ciba Specialty Chemicals), 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butane-1-one, 2-chlorothioxanthone, 2,4-dimethylthioxanthone, 2,4-diisopropylthioxanthone, isopropylthioxanthone, 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Lucilin TPO; manufactured by BASF), bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (IRGACURE 819; manufactured by

Ciba Specialty Chemicals), bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, and the like.

[0030]

One kind or plural kinds of these photopolymerization initiators can be mixed and used in an arbitrary ratio and also it is possible to use it in combination with a photopolymerization initiator aid such as an amine.

The amount of the (C) photopolymerization initiator in the ultraviolet-curable resin composition of the present invention is 1 to 15% by weight, preferably about 1 to 10% by weight.

Examples of the photopolymerization initiator aid such as an amine include diethanolamine, 2-dimethylaminoethyl benzoate, dimethylaminoacetophenone, p-dimethylaminobenzoic acid ethyl ester, p-dimethylaminobenzoic acid isoamyl ester, and the like. In the case where the photopolymerization initiator aid is used in combination, the content thereof in the ultraviolet-curable resin composition of the present invention is preferably 0.05 to 5% by weight, particularly preferably about 0.1 to 3% by weight.

[0031]

In the ultraviolet-curable resin composition of the present invention, phosphoric acid (meth)acrylate can be added, if necessary. The phosphoric acid (meth)acrylate enhances adhesiveness of aluminum, silver, or a silver alloy to an adhesive cured material but there is a concern that a metal film is corroded, so that the amount is limited.

Furthermore, in the present invention, in addition to the above components, if necessary, additives such as a silane coupling agent, a leveling agent, an antifoaming agent, a polymerization inhibitor, a photostabilizer (hindered amine-based one or the like), an antioxidant, an antistatic agent, a surface lubricant, and a filler may be used in combination. Examples of the additives include KBM-502, KBM-503, KBM-5103, KBM-802, and KBM-803 manufactured by Shin-Etsu Chemical Co., Ltd.; BYK-333, BYK-307, BYK-3500, BYK-3530, and BYK-3570 manufactured by Big Chemie; Z-6062, SH-6062, and SH-29PA manufactured by Dow Corning Toray Co., Ltd.; LA-82 manufactured by Adeka Corporation; and the like.

[0032]

The ultraviolet-curable resin composition of the present invention can be obtained by mixing and dissolving the above components at room temperature to 80°C, followed by filtration, if necessary.

The viscosity of the ultraviolet-curable resin composition of the present invention is 10 to 800 mPa·s, preferably 40 to 500 mPa·s upon measurement at 25°C on a B type viscometer.

[0033]

5 In the case of DVD, the transparent resin intermediate layer is formed by (1) applying the resin composition of the present invention to at least one of the substrate having the first transparent resin substrate, the first recording layer and the first semi-transparent reflective film layer laminated thereon and the transparent resin stamper by a method such as a spin coating method, a screen printing method, or a roll coating method,
10 then attaching the substrate to the stamper, and irradiating the attached one with an ultraviolet ray from the transparent resin stamper side. Alternatively, the layer is also formed by (2) applying the resin composition of the present invention to the transparent resin stamper by the above method, then subjecting the resin composition to ultraviolet curing, and attaching it to the substrate having the first transparent resin substrate, the first
15 recording layer and the first semi-transparent reflective film layer laminated thereon with an arbitrary ultraviolet-curable resin. The forming method of (1) is preferred since reduction of production costs is expectable in view that production efficiency can be omitted. Moreover, in the case of a Blu-ray disk, the transparent resin intermediate layer is also formed in the same manner as in the case of DVD. In general, a polycarbonate
20 resin is used for the first transparent resin substrate of 0.6 mm for DVD or HD-DVD and for the resin substrate of 1.1 mm for a Blu-ray disk. In the case where a polycarbonate-made transparent resin stamper is used, the method of (1) is also preferred in view of the releasability.

[0034]

25 As the transparent resin stamper, there may be mentioned an acrylic resin, a methacrylic resin, a polycarbonate resin, a polyolefin-based resin (particularly, a non-crystalline polyolefin), a polyester-based resin, a polystyrene resin, an epoxy resin, or the like. Of these, in view of the releasability, low moisture absorption, shape stability, and the like after curing of the 2P resin, a non-crystalline polyolefin is preferred and, in view of
30 material costs, a polycarbonate resin is preferred. The 2P-curable resin composition of the present invention can use either transparent resin stamper.

The ultraviolet-curable resin composition of the present invention affords a cured material by irradiation with an active energy ray. Examples of the active energy ray include a low-pressure, high-pressure, or ultra high-pressure mercury lamp, a metal halide

lamp, a (pulse) xenon lamp, an electrodeless lamp, an ultraviolet light-emitting diode, and the like. The above cured material is also included in the present invention.

[0035]

In the recording layer formed on the transparent resin intermediate layer by the above cured material, both of an organic coloring matter and a phase change material can be used. Examples of the organic coloring matter include metal-containing azo, polymethine, phthalocyanine coloring matters, and examples of the phase change material include those obtained by adding any one or more of In, Ag, Au, Bi, Se, Al, P, Ge, H, Si, C, V, W, Ta, Zn, Ti, Ce, Tb, Sn, and Pb to Sb and Te.

Moreover, the resin composition of the present invention can be used for both of an optical disk or a blu-ray disk having a structure that a polycarbonate-made substrate is attached.

[0036]

Examples of the applying method include a spin coating method, a 2P method, a roll coating method, a screen printing method, and the like.

[0037]

Moreover, since a blue laser of about 400 nm is used for read and/or write in a next-generation high density optical disk, it is preferred that the transmittance at 405 nm in the cured material having a film thickness of 90 to 100 μm is 80% or more.

Examples

[0038]

The following will describe the present invention in detail with reference to Examples.

Synthetic Example 1: Synthesis of urethane acrylate (A-1)

Into a round-bottom flask fitted with a stirring apparatus, a cooling tube, and a thermometer were charged 0.63 part by weight of isophorone diisocyanate, 93.9 parts by weight of pentaerythritol triacrylate, 0.03 part by weight of methoquinone as a polymerization inhibitor, and 0.05 part by weight of dibutyltin dilaurate, and the whole was mixed at room temperature for 30 minutes and reacted at 80°C for 5 hours. When isocyanate concentration decreased to 0.1% or less, the reaction was finished and an objective urethane acrylate was obtained.

Synthetic Example 2: Synthesis of urethane acrylate (A-2)

Into a round-bottom flask fitted with a stirring apparatus, a cooling tube, and a thermometer were charged 11.6 parts by weight of isocyanurate modified type of hexamethylene diisocyanate (Takenate D-170N manufactured by Takeda Chemical Industries, Ltd.; formula (1) $R = -(CH_2)_6-$), 88.4 parts by weight of dipentaerythritol pentaacrylate, 0.05 part by weight of methoquinone as a polymerization inhibitor, and 0.05 part by weight of dibutyltin dilaurate, and the whole was mixed at room temperature for 30 minutes and reacted at 80°C for 5 hours. When isocyanate concentration decreased to 0.1% or less, the reaction was finished and an objective urethane acrylate was obtained.

Synthetic Example 3: Synthesis of urethane acrylate (A-3)

Into a round-bottom flask fitted with a stirring apparatus, a cooling tube, and a thermometer were charged 14.8 parts by weight of hexamethylene diisocyanate, 85.1 parts by weight of dipentaerythritol pentaacrylate, 0.03 part by weight of methoquinone as a polymerization inhibitor, and 0.05 part by weight of dibutyltin dilaurate, and the whole was mixed at room temperature for 30 minutes and reacted at 80°C for 5 hours. When isocyanate concentration decreased to 0.1% or less, the reaction was finished and an objective urethane acrylate was obtained.

Examples and Test Examples

For the resin compositions of Examples 1 to 3 and Comparative Examples 1 to 3, constituting materials and amounts thereof as well as results of evaluation of described items are shown in Table 1. In this regard, "part(s)" described in the table indicates part(s) by weight.

[0039]

[Table 1]

Table 1. Resin Composition and Evaluation Results

	Example 1	Example 2	Example 3	Compar- ative Example 1	Compar- ative Example 2	Compar- ative Example 3
Component (A) (parts)						
A-1	43					
A-2		43				
A-3			43			
Component (B) (parts)						
IBA	52	52	52	43	19	19
BP-1040					76	
THE-330						76
DPHA				52		
Component (C) (Parts)						
IRGACURE 184	5	5	5	5	5	5
Other component (parts)						
(Releasability test)						
Peel strength (Kgf)	0.9	0.7	0.8	0.9	2.4	2.6
Releasability judgment	Good	Good	Good	Good	Bad	Bad
(Durability test close adhesive force)						
Adhesiveness judgment	Good	Good	Good	Bad	Good	Good

5 [0040]

Incidentally, each component shown by an abbreviated name in Table 1 is as follows:

A-1: the urethane acrylate obtained in Synthetic Example 1

A-2: the urethane acrylate obtained in Synthetic Example 2

A-3: the urethane acrylate obtained in Synthetic Example 3

IBA: isobornyl acrylate manufactured by Dai-ichi Kogyo Kagaku

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RP-1040: pentaerythritol ethylene oxide-modified tetraacrylate manufactured by Nippon Kayaku Co., Ltd.

THE-330: ethylene oxide-modified trimethylolpropane triacrylate manufactured by Nippon Kayaku Co., Ltd.

5 DPHA: dipentaerythritol hexaacrylate manufactured by Nippon Kayaku Co., Ltd.

IRGACURE 184: 1-hydroxycyclohexyl phenyl ketone manufactured by Ciba Specialty Chemicals

[0041]

(Preparation of samples for evaluation)

10 Using each of the ultraviolet-curable resin compositions obtained, a sample disk for evaluation was prepared by the following methods 1 to 3.

1. A transparent resin prepared so that air bubbles were not included was placed on an inner periphery of a polycarbonate-made substrate (first substrate) having a diameter of 120 mm and a thickness of 0.6 mm on which an azo coloring matter layer as a recording
15 layer, a reflective film layer, and a ZnS·SiO₂ layer as a dielectric layer formed thereon. A stamper was placed on the resin and was attached thereto by spin coating at 2000 rpm for 4 seconds.

2. The second ultraviolet-curable resin composition was cured by irradiation with a high-pressure mercury lamp (80 W/cm) at 400 mJ/cm² from the transparent stamper side.

20 3. Using a disk peeling apparatus (manufactured by Origin Electric Co., Ltd.), the transparent resin stamper was peeled off to prepare a sample disk for evaluation.

[0042]

(a) Releasability test

25 Using a disk peeling apparatus (manufactured by Origin Electric Co., Ltd.), peel strength at an inner diameter of 60 mm at which releasability was poor was measured on a measuring instrument (FGC-5B manufactured by NIDEC-SHIMPO Corporation). The judgment of releasability was performed according to the following standards.

Good: a peel strength of 1.5 kgf or less

Bad: a peel strength of more than 1.5 kgf

30 [0043]

(b) Durability (moisture resistance) test

As the moisture resistance test, after the sample disk after peeling prepared in the above step was allowed to stand under high temperature and high humidity of 80°C and 85% for 96 hours, they were stored at room temperature for 24 hours. The moisture

resistance was judged whether exfoliation from the recording film was observed before placed under the high temperature and high humidity and after stored at room temperature.

Good: closely adhered

Bad: exfoliated

5 [0044]

As is apparent from Table 1, Examples 1 to 3 which are the ultraviolet-curable resin compositions of the present invention and cured materials thereof are excellent in close adhesive force even in the situation under high temperature and high humidity as compared with Comparative Example 1. Moreover, as compared with Comparative
10 Examples 2 and 3 where polyfunctional acrylate monomers were used, it was confirmed that Examples were resin compositions particularly excellent in releasability.

Industrial Applicability

[0045]

15 The ultraviolet-curable resin composition of the present invention and a cured material thereof are excellent in releasability and are useful as a 2P agent which closely adhere to a reflective film layer or a dielectric layer even when placed under high-temperature high-humidity conditions. Moreover, it is possible to provide an ultraviolet-curable resin which enables formation of an intermediate layer by one liquid with omitting
20 an adhesive layer.

[0046]

While the invention has been described in detail with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

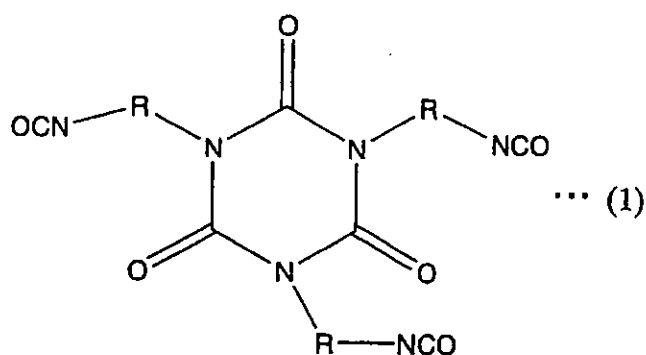
25 The present application is based on Japanese Patent Application No. 2009-084534 filed on March 31, 2009, and all the contents are incorporated herein by reference. Also, all the references cited herein are incorporated as a whole.

Claims

1. An ultraviolet-curable resin composition for a multilayer optical disk,
comprising (A) a hexa- or higher-functional urethane (meth)acrylate obtained by reacting
5 an organic isocyanate having two or more isocyanate groups in one molecule thereof with
a tri- or higher-functional (meth)acrylate having a hydroxyl group, (B) a tri- or lower-
functional (meth)acrylate monomer, and (C) a photopolymerization initiator.

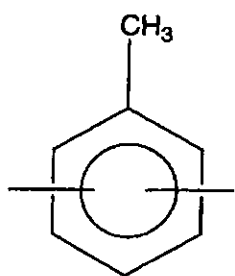
2. The ultraviolet-curable resin composition for a multilayer optical disk
10 according to claim 1, wherein in the hexa- or higher-functional urethane (meth)acrylate (A)
obtained by reacting an organic isocyanate having two or more isocyanate groups in one
molecule thereof with a tri- or higher-functional (meth)acrylate having a hydroxyl group,
the organic isocyanate is one or two or more compounds selected from the group
consisting of isophorone diisocyanate, hexamethylene diisocyanate, tolylene diisocyanate,
15 xylene diisocyanate, diphenylmethane-4,4'-diisocyanate, dicyclopentanyl diisocyanate, and
a trifunctional isocyanate represented by the formula (1):

[Chem. 1]

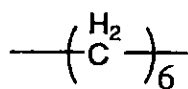


where R represents:

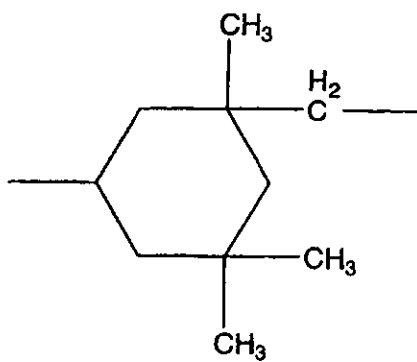
[Chem. 2]



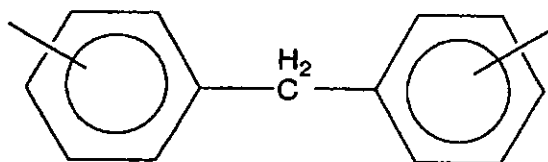
[Chem. 3]



5 [Chem. 4]

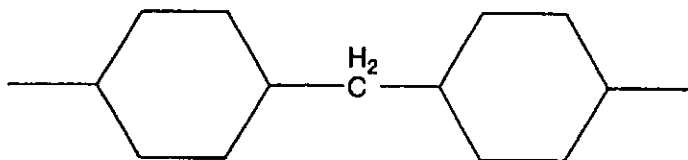


[Chem. 5]



or

[Chem. 6]



3. The ultraviolet-curable resin composition for a multilayer optical disk
5 according to claim 1 or 2, wherein in the hexa- or higher-functional urethane
(meth)acrylate (A) obtained by reacting an organic isocyanate having two or more
isocyanate groups in one molecule thereof with a tri- or higher-functional (meth)acrylate
having a hydroxyl group, the tri- or higher-functional (meth)acrylate having a hydroxyl
group is one or two or more compounds selected from the group consisting of
10 pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, tri(meth)acrylate of
 ϵ -caprolactone adduct of pentaerythritol, and tri-, tetra- or penta-(meth)acrylate of ϵ -
caprolactone adduct of dipentaerythritol.

4. The ultraviolet-curable resin composition for a multilayer optical disk
15 according to any one of claims 1 to 3, wherein the tri- or lower-functional (meth)acrylate
monomer (B) is one or two or more compounds selected from the group consisting of
isobornyl acrylate, neopentyl glycol diacrylate, propylene oxide-modified neopentyl glycol
diacrylate, tricyclodecanedimethanol diacrylate, and hydropivalaldehyde-modified
trimethylolpropane diacrylate.

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5. The ultraviolet-curable resin composition for a multilayer optical disk
according to any one of claims 1 to 4, which contains 5 to 80% by weight of the (A)
component, 10 to 80% by weight of the (B) component, and 1 to 15% by weight of the (C)
component based on the whole resin composition.

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6. A cured material obtainable by irradiating the ultraviolet-curable resin
composition for a multilayer optical disk according to any one of claims 1 to 5 with an
active energy ray.

7. A multilayer optical disk comprising the cured material according to claim 6.