DESCRIPTION

TITLE OF THE INVENTION

PROCESS FOR PRODUCTION OF REPLICA MOLD FOR IMPRINTING USE

Technical Field

[0001]

The present invention relates to a method for producing a replica of a mold for imprinting use. The present application claims the benefit of Japanese Patent Application No. 2010-143118 filed on June 23, 2010. ~~The entire disclosure of the application is hereby incorporated by reference herein in its entirety.~~

Background Art

[0002]

In recent years, a technique which is referred to as an imprinting method and can faithfully transfer a microscopic pattern is developed as a method for forming a fine raised and depressed pattern (see Non-patent Document 1). In many cases, an imprinting method of a nano meter order is referred to as a nano imprinting method, and an imprinting method of a micro meter order is referred to as an imprinting method. Herein, both the methods are referred to as the imprinting method.

[0003]

In the imprinting process, a mold is pressed against a resin to transfer a pattern formed on the mold onto the resin. It is difficult to use a mold material used herein for a long period of time because the mold material is

imprinting use, a fine raised and depressed pattern having excellent storage stability before use and providing a certain extent of flexibility can be formed, and the surface has a significantly high hardness as the surface is mineralized with the fine raised and depressed pattern maintained after curing, and thus having an excellent abrasion resistance. The present invention has been thus completed.

[0008]

That is, the present invention relates to the following items:

(1) a method for producing a replica mold comprising the steps of:

(A) coating a substrate with an organic-inorganic hybrid material;

(B) semi-curing a coated surface with heat and/or an electromagnetic ray to produce a substrate for fine raised and depressed pattern formation;

(C) pressing a master mold having a predetermined fine raised and depressed pattern formed thereon against the substrate for fine raised and depressed pattern formation by an imprinting method to transfer the fine raised and depressed pattern onto the substrate; and

(D) irradiating the substrate for fine raised and depressed pattern formation onto which the fine raised and depressed pattern is transferred with an electromagnetic ray to cure the substrate, wherein the organic-inorganic hybrid material comprises:

a) an organosilicon compound consisting of

a compound represented by the formula (I):

$R^1_nSiX_{4-n}$ ... (I)

(wherein n represents 1 or 2; when n is 2, each R^1 is optionally the same or different; R^1 represents an organic group; and one or more of R^1 represent a vinyl group-containing hydrocarbon group; X represents a hydroxyl group or a hydrolyzable group; and each X is optionally the same or different),

a compound represented by the formula (II):

$R^2_nSiX_{4-n}$ ... (II)

(wherein n represents 1 or 2; when n is 2, each R^2 is optionally the same or different; R^2 represents an organic group excluding a vinyl group-containing hydrocarbon group, which has a carbon atom bonded directly to Si in the formula; X represents a hydroxyl group or a hydrolyzable group; and each X is optionally the same or different), and

a hydrolysis condensate thereof if present,

wherein {[the compound of the formula (I)] + [a unit derived from the compound of the formula (I) in the hydrolysis condensate if present]} / {[the compound of the formula (I)] + [the compound of the formula (II)] + [a unit derived from the compound of the formula (I) in the hydrolysis condensate if present] + [a unit derived from the compound of the formula (II) in the hydrolysis condensate if present]} × 100 is 30 to 100 mol%; and

{[the compound of the formula (II)] + [a unit derived from the compound of the formula (II) in the hydrolysis condensate if present]} / {[the compound of the formula (I)] + [the compound of the formula (II)] + [a unit derived from the compound of the formula (I) in the

hydrolysis condensate if present] + [a unit derived from the compound of the formula (II) in the hydrolysis condensate if present]} × 100 is 0 to 70 mol%;

b) an electromagnetic ray-curable compound; and

c) a silanol condensation catalyst;

~~(2) the method for producing a replica mold according to the item (1), further comprising the step of (E) applying a mold releasing layer onto a surface of the~~

~~fine raised and depressed pattern obtained in the step (D);~~

~~(3) the method for producing a replica mold according to the item (1), wherein the organic inorganic hybrid material comprises a material for a mold releasing layer;~~

~~(4) the method for producing a replica mold according to any one of the items (1) to (3), wherein the organic inorganic hybrid material comprises:~~

~~a) an organosilicon compound comprising:~~

~~a compound represented by the formula (I):~~

~~$R^1_nSiX_{4-n}$ ... (I)~~

~~(wherein n represents 1 or 2; when n is 2, each R^1 may be the same or different; R^1 represents an organic group; and one or more of R^1 represent a vinyl group-containing hydrocarbon group; X represents a hydroxyl group or a hydrolyzable group; and each X may be the same or different,)~~

~~a compound represented by the formula (II):~~

~~$R^2_nSiX_{4-n}$ ... (II)~~

~~(wherein n represents 1 or 2; when n is 2, each R^2 may be the same or different; R^2 represents an organic group excluding a vinyl group containing hydrocarbon group, which has a carbon atom bonded directly to Si in the formula; X represents a hydroxyl group or a hydrolyzable group; and each X may be the same or different), and~~

~~a hydrolysis condensate thereof if present,~~

~~wherein {[the compound of the formula (I)] + [a unit derived from the compound of the formula (I) in the hydrolysis condensate if present]} / {[the compound of the~~

~~formula (I)] + [the compound of the formula (II)] + [a unit derived from the compound of the formula (I) in the hydrolysis condensate if present] + [a unit derived from the compound of the formula (II) in the hydrolysis condensate if present]} × 100 is 30 to 100 mol%; and~~

~~{[the compound of the formula (II)] + [a unit derived from the compound of the formula (II) in the hydrolysis condensate if present]} / {[the compound of the formula (I)] + [the compound of the formula (II)] + [a unit derived from the compound of the formula (I) in the hydrolysis condensate if present] + [a unit derived from the compound of the formula (II) in the hydrolysis condensate if present]} × 100 is 0 to 70 mol%;~~

~~b) an electromagnetic ray-curable compound; and~~

~~c) a silanol condensation catalyst;~~

(~~5~~2) the method for producing a replica mold according to the item (~~4~~1), wherein {[the compound of the formula (I)] + [a unit derived from the compound of the formula (I) in the hydrolysis condensate if present]} / {[the compound of the formula (I)] + [the compound of the formula (II)] + [a unit derived from the compound of the formula (I) in the hydrolysis condensate if present] + [a unit derived from the compound of the formula (II) in the hydrolysis condensate if present]} × 100 is 30 to 95 mol%; and

{[the compound of the formula (II)] + [a unit derived from the compound of the formula (II) in the hydrolysis condensate if present]} / {[the compound of the formula (I)] + [the compound of the formula (II)] + [a unit derived from the compound of the formula (I) in the

hydrolysis condensate if present] + [a unit derived from the compound of the formula (II) in the hydrolysis condensate if present]} × 100 is 5 to 70 mol%;

(3~~6~~) the method for producing a replica mold according to the item (1~~4~~) or (2~~5~~), wherein the electromagnetic ray-curable compound is 80 mass % or less based on the total mass of the solid content of the composition; ~~and~~

(4~~7~~) the method for producing a replica mold according to any one of the items (1~~4~~) to (3~~6~~), wherein the silanol condensation catalyst is a photosensitive compound;~~.~~

(5) the method for producing a replica mold according to any one of items (1) to (4), further comprising the step of (E) applying a mold releasing layer onto a surface of the fine raised and depressed pattern obtained in the step (D); and

(6) the method for producing a replica mold according to any one of items (1) to (5), wherein the organic-inorganic hybrid material comprises a material for a mold releasing layer.

[0009]

The present invention also relates to (7~~8~~) a replica mold obtained by a method according to any one of the items (1) to (6~~7~~).

Brief Description of Drawings

[0010]

[Figure 1] Figure 1 is a photograph obtained by photographing a surface of a slide glass with an organic-inorganic hybrid material according to the present invention after pressing and removing a master mold, by means of a digital microscope in Example 1.

[Figure 2] Figure 2 is a photograph obtained by photographing a polycarbonate surface with an organic-inorganic hybrid material according to the present invention after pressing and removing a master mold, by means of a digital microscope in Example 1.

[Figure 3] Figure 3 is a photograph obtained by photographing a surface of a substrate after pressing a

1. Organic-Inorganic Hybrid Material

An organic-inorganic hybrid material of the present invention is a composition for forming an organic-inorganic hybrid material layer to produce a fine raised and depressed pattern by laminating it on a substrate. The organic-inorganic hybrid material is an~~not particularly limited as long as the~~ organic-inorganic hybrid material that can be irradiated with an electromagnetic ray to cure the organic-inorganic hybrid material without removing a master mold from a substrate for fine raised and depressed pattern formation onto which the fine raised and depressed pattern is transferred, as usual, and the organic-inorganic hybrid material can be irradiated with the electromagnetic ray, with the master mold removed from the substrate for fine raised and depressed pattern formation onto which the fine raised and depressed pattern is transferred, to cure the organic-inorganic hybrid material. The organic-inorganic hybrid material particularly preferably contains the following components.

[0013]

a) Organosilicon Compound

An organosilicon compound in the organic-inorganic hybrid material of the present invention contains the following components:

a-1) a compound represented by the formula (I):

$R^1_nSiX_{4-n}$ ... (I)

(wherein n represents 1 or 2; when n is 2, R^1 may be the same or different; R^1 represents an organic group; and one or more of R^1 represent a vinyl group-containing

The electromagnetic ray-curable compound of the present invention is a compound polymerizing by irradiation with an active energy ray. Particularly, it is a compound or resin having a functional group which causes a polymerization reaction by irradiation with an ultraviolet ray in the presence of a photopolymerization initiator. Examples thereof include (meth)acrylate compounds, epoxy resin, and vinyl compounds excluding acrylate compounds. The number of functional group is ~~not particularly limited as long as it is~~ 1 or more.

Examples of the acrylate compounds include polyurethane(meth)acrylate, polyester(meth)acrylate, epoxy(meth)acrylate, polyamido(meth)acrylate, polybutadiene(meth)acrylate, polystyryl(meth)acrylate, polycarbonate diacrylate, tripropylene glycol di(meth)acrylate, hexane dioldi(meth)acrylate, trimethylol propane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, and siloxane polymers having a (meth)acryloyloxy group. Polyester(meth)acrylate, polyurethane(meth)acrylate, and epoxypoly(meth)acrylate are preferred, and polyurethane(meth)acrylate is more preferred.

The electromagnetic ray-curable compound ~~molecular weight is not limited as long as it~~ has compatibility with other hard coat layer compositions. Usually, a mass-average molecular weight is 500 to 50,000, and preferably 1,000 to 10,000.

[0029]

An epoxy(meth)acrylate can be obtained, for example, from an esterification reaction of an oxirane ring of a

In the present invention, a sensitizing agent may be added according to need. For example, trimethylamine, methyldimethanolamine, triethanolamine, p-dimethylaminoacetophenone, p-dimethylamino benzoic acid ethyl, p-dimethylamino benzoic acid isoamyl, N,N-dimethylbenzylamine, and 4,4'-bis(diethylamino)benzophenone can be used.

[0037]

It is preferred that the ultraviolet ray-curable compound is 80 mass % or less based on the total mass of the solid content of the organic-inorganic hybrid material.

[0038]

c) Silanol Condensation Catalyst

The silanol condensation catalyst ~~is not particularly limited as long as it~~ hydrolyses a hydrolyzable group in the compound represented by the formula (I), and condensates silanol to make a siloxane bond. Examples thereof include an organic metal, an organic acid metal salt, an acid, a base and a metal chelate compound. The silanol condensation catalysts can be used alone or two or more kinds of them can be used in combination.

Examples of the organic metal include alkyl metal compounds such as tetramethyl titanium and tetrapropyl zirconium, and metal alcoholates such as tetraisopropoxy titanium and tetrabutoxy zirconium.

Examples of the organic acid metal salt include carboxylic acid metal salts, sulfonic acid metal salts, and phenol metal salts.

2. Preparation of Organic-Inorganic Hybrid Material

A method for preparing the organic-inorganic hybrid material of the present invention comprises adding water and a solvent according to need, and mixing an organosilicon compound, an electromagnetic ray-curable compound, and a silanol condensation catalyst.

Specifically, known conditions and methods may be employed. It may be prepared according to the method described in, for example, WO2008/69217 pamphlet.

[0051]

~~The solvent to be used is not particularly limited.~~ The ~~E~~examples of the solvent to be used~~thereof~~ include: aromatic hydrocarbon atoms such as benzene, toluene, and xylene; aliphatic hydrocarbon atoms such as hexane and octane; alicyclic hydrocarbon atoms such as cyclohexane and cyclopentane; ketones such as acetone, methylethylketone, and cyclohexanone; ethers such as tetrahydrofuran and dioxane; esters such as ethyl acetate and butyl acetate; amides such as N,N-dimethylformamide and N,N-dimethylacetoamide; sulfoxides such as dimethylsulfoxide; alcohols such as methanol, ethanol, propanol, and butanol; polyalcohol derivatives such as ethylene glycol monomethyl ether and ethylene glycol monomethyl ether acetate. These solvents can be used alone or two or more kinds of them can be used in combination.

When combining 2 or more kinds, for example, the combination of butanol/ethyl acetate/ethanol can be preferably exemplified.

[0052]

The solid content of the organic-inorganic hybrid material of the present invention (organosilicon component, ultraviolet ray-curable compound, silanol condensation catalyst, and photopolymerization initiator) is preferably 1 to 75 mass %, and more preferably 10 to 60 mass %. The ultraviolet ray-curable compound is used preferably by 80% or less, and more preferably 10 to 70 % of~~not particularly limited based on~~ the total mass of the solid content of the organosilicon compound and/or a hydrolysis condensate thereof, silanol condensation catalyst, ultraviolet ray-curable compound, and photopolymerization initiator. ~~It is preferably 80% or less, and more preferably 10 to 70%.~~

When the photosensitive compound is contained as the silanol condensation catalyst, the content of the photosensitive compound depends on the kind thereof. The metal atom in the photosensitive compound is generally 0.01 to 0.5 molar equivalents, and preferably 0.05 to 0.2 molar equivalents, based on Si in the organosilicon compound.

[0053] Tetrafunctional silane or colloidal silica can be added to the organic-inorganic hybrid material in order to enhance hardness of the obtained organic-inorganic hybrid material layer. Examples of the tetrafuntioncal silane include: tetraaminosilane, tetrachlorosilane, tetraacetoxysilane, tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, tetrabenzyloxysilane, tetraphenoxysilane, tetra(meth)acryloxysilane, tetrakis[2-(meth)acryloxyethoxy]silane, tetrakis(2-vinyloxyethoxy)silane, tetraglycidyloxysilane, tetrakis(2-vinyloxybutoxy)silane, and tetrakis(3-methyl-3-

and depressed pattern obtained in the fourth step as a fifth step. The organic-inorganic hybrid material may contain a material for the mold releasing layer without performing the fifth step.

[0061]

(First Step)

The substrate can be coated with the organic-inorganic hybrid material of the present invention. Various known laminating methods can be used. For example, the organic-inorganic hybrid material can be formed by methods including microgravure coating, comma coating, barcoater coating, air knife coating, spin coating, dip coating, offset printing, flexo printing, screen printing, and spray coating.

[0062]

(Second Step)

The fine raised and depressed pattern is formed on the substrate by coating the substrate with a solution containing an organic-inorganic hybrid material, and semi-curing it by heating and/or irradiating an electromagnetic ray. By this step, condensates of organosilicon compounds in the organic-inorganic hybrid material are crosslinked, and the organic-inorganic hybrid material layer is semi-cured. When an organic solvent is used as a diluent solvent, ~~or the like,~~ the organic solvent is removed by this heating. The heating is usually performed at 40 to 200°C, and preferably 50 to 150°C. A heating time is usually 10 seconds to 60 minutes, and preferably 30 seconds to 10 minutes.

[0063]

being less than the carbon content of the back side part means that the total amount of carbon from the surface to the central part is less than the total amount of carbon from the back side to the central part.

[0067]

(Fifth Step)

After the fourth step, the mold releasing layer can be applied onto the surface of the fine raised and depressed pattern. Although the mold releasing layer can be applied by coating the surface of the fine raised and depressed pattern with the material for the mold releasing layer, various known laminating methods can be used. For example, each layer can be formed by methods including microgravure coating, comma coating, barcoater coating, air knife coating, spin coating, dip coating, offset printing, flexo printing, screen printing, spray coating, a deposition method, and a sputter method.

Examples of the material of the mold releasing layer include a melamine resin, a silicone resin, a fluorocarbon resin, a cellulose derivative, a urea resin, a polyolefin resin, a paraffine resin, and a known release agents. One or two or more thereof can be used.

As described in WO2008-059840 pamphlet ~~or the like~~, separately from the above conventional method, the replica mold is brought into contact with an organic solvent solution containing a metal-based surface-active agent having at least one or more hydrolyzable groups, a compound which can interact with the metal-based surface-active agent, and water. Thereby, an organic thin film,

coexist, and (iii) a method for blowing gas containing moisture.

[0084]

The organic solvent solution can be prepared by the method described in WO 2008/059840 pamphlet ~~and the like~~. An organic thin film can be provided on a surface of a cured sheet for fine raised and depressed pattern formation, by bringing the organic solvent solution into contact with the sheet for fine raised and depressed pattern formation by means of dipping methods, spin coating methods, spray methods, roller coating methods, Meyer bar methods, screen printing methods, and brush coating methods, and preferably, dipping methods.

[0085]

In the following, the present invention will be described by referring to Examples, while the technical scope of the present invention will not be limited thereto.

Example 1

[0086]

1 Preparation of Organic-Inorganic Hybrid Material for Producing Replica Mold

103.39 g of titanium diisopropoxybisacetylacetonate (manufactured by Nippon Soda Co., Ltd.; T-50; solid content in terms of titanium oxide: 16.5% by weight) was dissolved into 199.32 g of a mixed solvent of ethanol/ethyl acetate (= 50/50: % by weight). 38.47 g of ion-exchange water (10-fold mol/mol of titanium oxide) was then slowly dropped by stirring. Then, a solution [A-1] was obtained by stirring for 24 hours.

photograph obtained by the digital microscope is shown in Figure 4.

[0090]

4-2 Optical Imprint

PAK-01 (nanoimprint resin manufactured by Toyo Gosei Co., Ltd.; a mixture of radically curing acrylic resins~~, or the like~~) was cast on the PET film. The replica molds (two types of the 5 μm L/S silicon mold and the 5 μm dot silicon mold) made of the slide glass with the organic-inorganic hybrid material to which the mold releasing layer was applied were pressed against it, and were irradiated with black light for 20 seconds.

Then, the replica mold was peeled, and the film surface was observed by the digital microscope. Excellent transfer of 5 μm L/S and dot could be confirmed. The photograph obtained by the digital microscope is shown in Figure 5.

The transfer rate of the pattern in the replica mold made of the slide glass with the organic-inorganic hybrid material to which the mold releasing layer was applied was higher than that in the slide glass with the organic-inorganic hybrid material to which the mold releasing layer was not applied after UV-curing in the item 3, and thereby the replica mold was easily peeled.

Example 2

[0091]

1 Preparation of Organic-Inorganic Hybrid Material for Producing Replica Mold