

DESCRIPTION

TITLE OF THE INVENTION:

METHOD OF FORMING PATTERN, PATTERN, METHOD OF PRODUCING FORMED PRODUCT WITH PATTERN, AND FORMED PRODUCT WITH PATTERN

TECHNICAL FIELD

[0001]

The present invention relates to a method of forming a pattern, the pattern, a method of producing a formed product with the pattern, and the formed product with the pattern.

BACKGROUND ART

[0002]

Examples of a method of forming a pattern includes a method in which a photoresist is exposed using a photomask that passes light only through a desired position and cured, and the unexposed part is removed by washing to form a desired pattern. The method is used, for example, for a method of producing a printing plate or a method of producing a semiconductor device (for example, see Patent Document 1).

[0003]

Furthermore, examples of a method of forming a pattern using phase separation and the pattern thereof include a method in which an ultraviolet-curable resin material is mixed with an incompatible material therewith to produce a coating film having a phase-separated structure, and the incompatible material is removed from the cured film to form a formed body having a concavo-convex structure on its surface. The method is used, for example, as an embossing process method in various industrial fields (for example, see Patent Document 2).

[0004]

Other examples of a method of forming a pattern using phase separation and the pattern thereof include a mold release film produced by curing a coating film including at least an energy ray-curable compound, a resin, and a mold release component. The resin is incompatible with the energy ray-curable compound and is an island component in the case where the energy

ray-curable compound is a sea component. The mold release film continuously forms low protrusions having a certain shape and is used as a film that has excellent mold releasability in various industrial fields (for example, see Patent Document 3).

[0005]

Other examples of a method of forming a pattern using phase separation and the pattern thereof include a method in which a coating composition including a first component and a second component is applied on a substrate, and thereafter the first component is phase-separated from the second component based on the difference in SP value between the first component and the second component to form a resin layer having random concavities and convexities on its surface, and the resin layer is used as an anti-glare coating (for example, see Patent Document 4).

Citation List

Patent Document

[0006]

Patent Document 1: Japanese Patent Publication No. 616790

Patent Document 2: Japanese Unexamined Patent Publication No. 2007-271756

Patent Document 3: Japanese Patent Publication No. 6822549

Patent Document 4: Japanese Unexamined Patent Publication No. 2009-120817

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0007]

However, as described in Patent Document 1, in a method of forming a pattern by exposing a desired portion using a photoresist and washing the unexposed portion, when the pattern is fine, the aspect ratio is high, or the pattern is made of a flexible material, the pattern moves while receiving the vibrations of the process or being washed. Thus, the method has a problem that the shape of the pattern deforms. Furthermore, the reaction in the exposed part propagates and the photoreaction progresses also in the unexposed part, and thus the method also has a problem that the phase boundary is blurred. In other words, a clear pattern may not be obtained.

[0008]

On the other hand, as described in Patent Documents 2 to 4, in a method in which the patterning is carried out using a phase-separated structure, the movement of the pattern is suppressed by the phase-separated materials mutually. Thus, the problem that the pattern moves and deforms is solved. Meanwhile, patterning into an arbitrary shape cannot be carried out. For a patterning method, however, forming an arbitrary pattern is required.

[0009]

The present invention provides a method of forming a pattern by which a clear pattern can arbitrarily be formed, a pattern formed with the method of forming a pattern, and a method of producing a formed product with a pattern including the pattern.

MEANS FOR SOLVING THE PROBLEM

[0010]

The present invention [1] includes a method of forming a pattern, wherein the pattern is formed by incompatibilizing at least a portion of a compatible material in an arbitrary part in a composition containing a flowable material and the compatible material compatibilized with the flowable material.

[0011]

The present invention [2] includes the method of forming a pattern described in the above-described [1], wherein the flowable material contains a flowable resin, and wherein the flowable resin is polymerized to incompatibilize at least a portion of the compatible material.

[0012]

The present invention [3] includes the method of forming a pattern described in the above-described [2], wherein the flowable resin contains an active energy ray-curable resin.

[0013]

The present invention [4] includes the method of forming a pattern described in any one of the above-described [1] to [3], wherein the compatible material contains a removable material, and wherein the removable material is removed after being incompatibilized.

[0014]

The present invention [5] includes the method of forming a pattern described in the above-described [4], wherein the flowable material contains an active energy ray-curable resin, wherein the method includes: a step of preparing the composition containing the active energy ray-curable resin and the removable material; a step of irradiating the composition with active energy rays to cure the active energy ray-curable resin and incompatibilize the removable material; and a step of removing the incompatibilized removable material.

[0015]

The present invention [6] includes the method of forming a pattern described in the above-described [4] or [5], wherein in the removal of the removable material, the removable material is substituted with a non-removable material.

[0016]

The present invention [7] includes the method of forming a pattern described in the above-described [6], wherein the non-removable material contains a non-removable resin.

[0017]

The present invention [8] includes the method of forming a pattern described in any one of the above-described [1] to [7], wherein one of the flowable material and the compatible material has a hydrogen-bondable substituent group value of 0.0001 to 0.1111 mol/g, and wherein a hydrogen-bondable functional group value of the other with respect to the one is less than or equal to $\frac{2}{3}$ of the hydrogen-bondable substituent group value of the one.

[0018]

The present invention [9] includes the method of forming a pattern described in any one of the above-described [1] to [8], wherein the compatible material contains a compatible resin.

[0019]

The present invention [10] includes the method of forming a pattern described in any one of the above-described [1] to [9], wherein the compatible material contains a metal, and wherein after the incompatibilization of the compatible material, the metal is subjected to a plating process.

[0020]

The present invention [11] includes a pattern formed by the method of forming a pattern described in any one of the above-described [1] to [10].

[0021]

The present invention [12] includes a method of producing a formed product with a pattern, wherein the pattern is formed by incompatibilizing a compatible material in an arbitrary part in a composition containing at least one or more flowable materials and the compatible material compatibilized with the flowable material(s).

[0022]

The present invention [13] includes a formed product with a pattern produced by forming the pattern by incompatibilizing a compatible material in an arbitrary part in a composition containing at least one or more flowable materials and the compatible material compatibilized with the flowable material(s).

[0023]

The present invention [14] includes the formed product with the pattern described in the above-described [13], wherein the flowable material contains an active energy ray-curable resin, wherein the composition containing the active energy ray-curable resin and the compatible material is prepared, wherein the composition is irradiated with active energy rays through a photomask to cure the active energy ray-curable resin and incompatibilize the compatible material to form the pattern, and wherein the pattern is clearly formed while corresponding to the photomask.

EFFECTS OF THE INVENTION

[0024]

By the method of forming a pattern of the present invention, a clear pattern can arbitrarily be formed. The pattern of the present invention is a clear pattern that is arbitrarily formed. By the method of a formed product with the pattern of the present invention, a clear pattern can arbitrarily be formed.

[0025]

In other words, in the method of forming a pattern, pattern, and method of producing a formed product with the pattern of the present invention, at least a portion of a compatible material in a composition including a flowable material and the compatible material is incompatibilized in an arbitrary part to form a pattern. In other word, the incompatibilized portion can be formed into an arbitrary pattern. Furthermore, the above-described incompatibilized portion suppresses the movements of the flowable material and the compatible material in the composition, and thus the deformation of the pattern is suppressed, and a high-precision, clear pattern can be obtained.

[0026]

Furthermore, the formed product with the pattern of the present invention includes a clear pattern.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027]

FIG. 1 is an optical photomicrograph of a surface of the formed product with the pattern produced in Example 1.

DESCRIPTION OF THE EMBODIMENTS

[0028]

1. Composition

In the method of forming a pattern of the present invention, a composition including a flowable material and a compatible material compatibilized with the flowable material is used.

[0029]

The flowable material and the compatible material are different materials from each other. More specifically, the flowable material and the compatible material are, as detailed below, compatible materials with each other. Furthermore, for the incompatibilization (described below) of the compatible material, the flowable material and the compatible material are each appropriately selected.

[0030]

Each material described below is provided as an example. In other words, each material is not limited to the examples described below. As long as a material exhibits the operations and effects of the present invention, the material can be used as the flowable material and the compatible material.

[0031]

2. Flowable Material

As long as being a material having flowability, the flowable material is not especially limited. Examples of the flowable material include a liquid, a granular material, and a powder. The liquid may not be a material in a liquid state at room temperatures. For example, a material in a solid state at room temperatures may be used as the flowable material by liquefying the material by heating.

[0032]

More specifically, examples of the flowable material include a material having a melting point, a solution, and a flowable resin.

[0033]

For example, a material having a melting point has flowability under the conditions at a temperature of its melting point or higher. Examples of the material having a melting point include a solvent, a non-metal simple substance, a metal, a glass, a natural material, a polymer, and a composite material thereof.

[0034]

Examples of the solvent include water, acetone, ethyl acetate, ethanol, toluene, hexafluorophosphate 1-butyl-3-methylimidazolium, isophorone, n-octadecane, and n-eicosane. Furthermore, examples of the solvent also include an olefin monomer described below. Examples of the non-metal simple substance include gallium, silicon, sulfur, and carbon. Examples of the metal include iron, cobalt, nickel, aluminum, gold, silver, copper, tin, zinc, and an alloy thereof. Examples of the glass include alkali glass and borosilicate glass. Examples of the natural material include pine resin, gelatin, natural rubber, sugar, chitosan, and protein. Examples of the polymer include polyethylene, polypropylene, nylon, thermoplastic urethane,

polyvinyl alcohol, cellulose acetate, and polyester. These may be used alone or in combination of two or more.

[0035]

Examples of the solution include a solution obtained by dissolving a known salt in the above-described solvent. More specifically, examples of the solution include a saline solution, a silver nitrate aqueous solution, a palladium chloride aqueous solution, and a glucose aqueous solution. These may be used alone or in combination of two or more.

[0036]

Examples of the flowable resin include an active energy ray-curable resin, a thermosetting resin, a two-component curable resin, a moisture-curable resin, and a polymerizable plasticizer. In terms of pattern formation, an active energy ray-curable resin is preferably used. Examples of the active energy rays include an electromagnetic wave having an arbitrary wavelength and an electron beam. Examples of the active energy rays specifically include ultraviolet rays, visible light, and infrared rays.

[0037]

Examples of the active energy ray-curable resin include an active energy ray-curable polyurethane resin (photo-radical-curable polyurethane resin), an active energy ray-curable acrylic resin (photo-radical-curable acrylic resin), an active energy ray-curable epoxy resin (photo-cation curable epoxy resin), an active energy ray-curable oxetane resin (photo-cation curable oxetane resin), and a mixture thereof. An active energy ray-curable polyurethane resin is preferably used. The active energy ray-curable polyurethane resin is not especially limited, and a known active energy ray-curable polyurethane resin is used. The active energy ray-curable polyurethane resin can be produced, for example, in accordance with paragraphs [0016] to [0106] of Japanese Unexamined Patent Publication No. 2021-161136.

[0038]

These flowable materials may be used alone or in combination of two or more. In terms of easily forming the pattern, as the flowable material, a flowable resin is preferably used, an

active energy ray-curable resin is more preferably used, and an active energy ray-curable resin is even more preferably used.

[0039]

When the flowable material contains an active energy ray-curable resin, the flowable material is preferably a flowable composition. The flowable composition contains an active energy ray-curable resin, a known reactive diluent, and a known polymerization initiator. Furthermore, in such a case, the flowable composition may contain an additive as necessary. Examples of the additive include an antioxidant, a plasticizer, and a mold release agent.

[0040]

3. Compatible Material

The compatible material is a material compatible with the above-described flowable material. Compatibilization is defined as that materials are approximately homogeneously mixed each other, and as a state in which separation, flotation, and sedimentation do not occur until one of the materials or the other forms a pattern.

[0041]

The compatible material is not especially limited. However, the compatible material is selected depending on the flowable material so as to be incompatible in the composition containing the flowable material and the compatible material.

[0042]

More specifically, examples of the compatible material include the above-described materials having a melting point, the above-described solutions, and compatible resins.

[0043]

As the compatible material, the above-described solvent is preferably used. Preferably, an olefin monomer is used. Examples of the olefin monomer include an olefin monomer having 2 to 30 carbon atoms. More specifically, examples of the olefin monomer include ethylene, propylene, butene, pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosene.

[0044]

Furthermore, as the compatible material, a compatible resin is preferably used. Examples of the compatible resin include an olefin polymer. Examples of the olefin polymer include an olefin polymer and an olefin oligomer. More specifically, examples of the olefin polymer include polyethylene, polypropylene, and an ethylene- α olefin copolymer. As the olefin polymer, preferably, ethylene- α olefin copolymer is used.

[0045]

Furthermore, examples of the compatible resin include the above-described active energy ray-curable resins that have different reactive properties from that of the flowable material. When a photo-radically polymerizable acrylic resin having a relatively high ultraviolet curability is used as the flowable material, a photo-cation curable epoxy resin having a relatively low ultraviolet curability can be used as the compatible material. When the composition containing the materials is irradiated with ultraviolet rays, the photo-radically polymerizable acrylic resin can be polymerized first, and thus the photo-cation curable epoxy resin can be phase-separated in an arbitrary pattern. Thereafter, the photo-cation curable epoxy resin is cured, and an arbitrary cured pattern can be produced. As long as a phase-separated pattern can be formed using the difference in reactive property, the compatible resin is not limited to the above, and may be, for example, a thermosetting resin, a two-component curable resin and/or a moisture-curable resin.

[0046]

These compatible materials may be used alone or in combination of two or more. As the compatible material, an olefin monomer and an olefin polymer are preferably used, an olefin monomer is more preferably used, an olefin monomer having 6 to 20 carbon atoms is even more preferably used, 1-hexene and 1-dodecene are even more preferably used, and 1-dodecene is particularly preferably used.

[0047]

Furthermore, as the compatible material, a material containing a metal (a metal-containing material) is preferably used. As the material containing a metal, the above-described solutions and metals are used, the above-described solutions are preferably used. More

specifically, examples of the solution include a saline solution, a silver nitrate aqueous solution, and a palladium chloride aqueous solution. As the material containing a metal, a silver nitrate aqueous solution and a palladium chloride aqueous solution are more preferably used, and a palladium chloride aqueous solution is even more preferably used.

[0048]

Furthermore, as the compatible material, a removable material is preferably used. The removable material is a material that can be removed after the compatible material is incompatibilized. The method of the removal is not especially limited, and examples thereof include volatilization, elution, melting, and machine processing, and preferably volatilization is used. In other words, as the compatible material, a volatile material is preferably used. Among the above-described compatible materials, as the volatile material (a material that can be volatilized after being incompatibilized), for example, 1-hexene is used.

[0049]

4. Method of Forming Pattern

In this method, first, a composition containing a flowable material and a compatible material is prepared.

[0050]

The composition containing a flowable material and a compatible material is not especially limited, and is prepared by selecting the flowable material and the compatible material and then mixing them in a known method.

[0051]

In the selection of the flowable material and the compatible material, as described above, materials that are compatible with each other are selected. Furthermore, each of the flowable material and the compatible material is appropriately selected so that the compatible material can be incompatibilized (described below).

[0052]

In terms of adjusting the compatibility using hydrogen bonding, preferably, the flowable material and the compatible material can be selected based on the hydrogen-bondable substituent

group value. The hydrogen-bondable substituent group is a group that can form a hydrogen bonding, and examples thereof include a hydroxyl group, a mercapto group, and an amino group.
[0053]

The hydrogen-bondable functional group value can arbitrarily adjust the compatibility using the hydrogen bonding. For example, by setting the hydrogen-bondable substituent group value of the flowable material close to that of the compatible material, a phase separation before the pattern formation can be suppressed. Contrarily, by setting the hydrogen-bondable substituent group value of the flowable material away from that of the compatible material, the phase separation during the pattern formation can be accelerated.

[0054]

More specifically, for example, the hydrogen-bondable substituent group value of one of the flowable material and the compatible material is, for example, 0.0001 mol/g or more, preferably 0.0005 mol/g or more. Furthermore, the hydrogen-bondable substituent group value of one of the materials is, for example, 0.1111 mol/g or less, preferably 0.1000 mol/g or less.
[0055]

Furthermore, relative to the hydrogen-bondable substituent group value of the above-described one, the hydrogen-bondable functional group value of the other relative to the above-described one is, for example, 1% (1/100) or more, preferably 5% (1/20) or more. Furthermore, relative to the hydrogen-bondable substituent group value of the above-described one, the hydrogen-bondable functional group value of the other relative to the above-described one is, for example, 67% (2/3) or less, preferably 55% (1/2) or less.

[0056]

More specifically, the hydrogen-bondable functional group value of the other is, for example, 0.000001 mol/g or more, preferably 0.000005 mol/g or more. Furthermore, the hydrogen-bondable substituent group value of the other is, for example, 0.0741 mol/g or less, preferably 0.0667 mol/g or less.

[0057]

When the hydrogen-bondable functional group value is in the above-described range, the compatibility can be improved using the hydrogen bonding. The hydrogen-bondable substituent group value can be calculated according to the following formula (1) based on the number of the hydrogen-bondable substituent group values included in one molecule.

[0058]

Hydrogen-bondable Substituent Group Value (mol/g)

= Number of Hydrogen-bondable Substituent Group Values Included in One Molecule
 $\div$ Molecular Weight (1)

[0059]

The mixing ratio of the flowable material to the compatible material is appropriately selected depending on the purpose and use. The size of the phase-separated pattern can be adjusted depending on the volume ratio of the flowable material to the compatible material. For example, when a pattern is formed using a photomask having a 100 μm -diameter opening portion, the dot size of the pattern to be formed can be adjusted to approximately 100 μm by setting the volume ratio of the compatible material at 50 volume%, or the dot size of the pattern to be formed can be adjusted to approximately 10 μm by setting the volume ratio of the compatible material at 10 volume%.

[0060]

Hence, the mixing ratio of the flowable material to the compatible material varies depending on the desired size of the pattern. For example, relative to 100 parts by mass of the flowable material, the compatible material is, for example, 1×10^{-7} parts by mass or more.

[0061]

Next, in this method, in the composition containing a flowable material and a compatible material, at least a portion of the compatible material is incompatibilized at an arbitrary part. In this manner, the flowable material and the compatible material are phase-separated to form a pattern.

[0062]

The method of incompatibilizing the compatible material is not especially limited, and various methods are employed.

[0063]

For example, by changing the temperature(s) of the flowable material and/or the compatible material, the compatibility of the compatible material with the flowable material is reduced, and thus the compatible material can be incompatibilized (deposited).

[0064]

Furthermore, for example, by changing (gasifying or solidifying) the state(s) of the flowable material and/or the compatible material, the compatibility of the compatible material with the flowable material is reduced, and thus the compatible material can be incompatibilized (deposited).

[0065]

Furthermore, for example, by changing the flowable material and/or the compatible material by a chemical reaction, the compatibility of the compatible material with the flowable material is reduced, and thus the compatible material can be incompatibilized (deposited). Examples of the chemical reaction include polymerization, cross-linkage, neutralization, ion substitution, and change in polarization.

[0066]

More specifically, when the flowable material is a flowable resin (preferably, an active energy ray-curable resin and/or a thermosetting resin), the flowable resin is, for example, active energy ray-cured and/or thermally cured to be polymerized. In this manner, the compatibility of the compatible material with the flowable material can be reduced. As a result, the compatible material can be incompatibilized (deposited).

[0067]

Furthermore, in this method, the compatible material is incompatibilized at an arbitrary position in the above-described composition.

[0068]

More specifically, for example, when the flowable material contains a thermosetting resin (a flowable resin), an arbitrary position of the flowable resin is preferably heated in the composition containing the flowable resin and the compatible material. In this manner, a cured product of the flowable resin is produced and simultaneously the compatibility of the compatible material at the arbitrary position is reduced. This can incompatibilize the compatible material. In such a case, to heat the arbitrary position, for example, an infrared-ray laser, a heat mask, and a hot-air nozzle are appropriately used.

[0069]

Furthermore, for example, when the flowable material contains an active energy ray-curable resin (a flowable resin), an arbitrary position of the flowable resin is preferably irradiated with active energy rays in the composition containing the flowable resin and the compatible material. In this manner, a cured product of the flowable resin is produced, and simultaneously the compatibility of the compatible material at the arbitrary position is reduced and thus the compatible material can be incompatibilized.

[0070]

In such a case, to irradiate the arbitrary position with active energy rays, for example, a laser emission device and a photomask are appropriately used. Preferably, a photomask is used.

[0071]

When a photomask is used, the composition containing a flowable material and a compatible material is preferably covered with a photomask having a predetermined pattern (covering step). Then, the part that is not covered with the photomask is irradiated with active energy rays to cure the flowable material (exposing step). In this manner, a cured product of the flowable resin is produced, and simultaneously the compatibility of the compatible material at the arbitrary position is reduced and thus the compatible material can be incompatibilized.

[0072]

In this manner, a pattern consisting of the flowable material (including its cured product) and the incompatibilized compatible material is formed.

[0073]

In particular, when a resin (flowable resin) is used as the flowable material, a cured resin product (formed product) having a pattern on its surface is produced by the above-described method. In other words, a formed product with a pattern is produced by the above-described method.

[0074]

More specifically, when the flowable material includes an active energy ray-curable resin, first, a composition containing the active energy ray-curable resin and a compatible material is prepared. Next, the composition is irradiated with active energy rays through a photomask to cure the active energy ray-curable resin. In this manner, a cured product of the active energy ray-curable resin is produced, and simultaneously the compatible material is incompatibilized.

[0075]

In this manner, a pattern consisting of the cured product of the active energy ray-curable resin and the incompatibilized compatible material is formed. Such a pattern is clearly formed, corresponding to the above-described photomask.

[0076]

The pattern is specific marks that are repeatedly uniformly formed. Examples of the pattern include a dotted pattern, a lattice pattern, a linear pattern, a check pattern, a fish scale pattern, and a letter pattern. The pattern allows the strength of the cured resin product (formed product) to be uniform.

[0077]

Furthermore, the method of forming a pattern can, for example, be used as a photoresist for producing semiconductors. For example, by the method of forming a pattern, a semiconductor pattern can be formed. Examples of the semiconductor pattern include a wire, an insulating film, an etching pattern, a doping pattern, and a solder resist pattern. Furthermore, the above-described method of forming a pattern can preferably be used in MEMS manufacturing, various types of semiconductor manufacturing, and metamaterial manufacturing.

[0078]

5. Removal Process and Substitution Process

When the compatible material includes a removable material, the compatible material (removable material) can be removed after the compatible material (removable material) is incompatibilized by the above-described method. Examples of the removal method include, as described above, volatilization, elution, melting, and machine processing, and volatilization is preferably used.

[0079]

By removing the compatible material (removable material), the part where the compatible material (removable material) existed can be hollowed and/or recessed.

[0080]

More specifically, for example, when the flowable material contains an active energy ray-curable resin (flowable resin) and the compatible material contains a removable material, preferably, a composition containing the active energy ray-curable resin and the removable material is first prepared. Then, the composition is irradiated with active energy rays to cure the active energy ray-curable resin. In this manner, the removable material is incompatibilized. Thereafter, the incompatibilized removable material is removed.

[0081]

In this manner, a pattern consisting of the flowable material (including its cured product) and a hollow and/or a recessed portion is formed.

[0082]

Furthermore, in this method, the incompatibilized compatible material (removable material) can be substituted with a non-removable material. More specifically, after the compatible material (removable material) is incompatibilized by the above-described method, the compatible material (the removable material) is removed by the above-described method, and furthermore the part where the compatible material (removable material) existed can be filled with an incompatible material.

[0083]

The non-removable material is a different material from the flowable material and the compatible material. Examples of the non-removable material are not especially limited, and include a non-removable resin. Examples of the non-removable resin include a known thermosetting resin and a known active energy ray-curable resin. A thermosetting resin is preferably used. A thermosetting epoxy resin and a thermosetting oxetane resin are more preferably used.

[0084]

The method of substituting the compatible material (removable material) with a non-removable material is not especially limited. For example, after the compatible material (removable material) is incompatibilized by the above-described method, the compatible material (removable material) is removed in the non-removable material.

[0085]

In this manner, the part where the compatible material (removable material) existed is hollowed and/or recessed, and simultaneously the hollow and/or recessed portion are/is filled with a non-removable material. Furthermore, when the non-removable material is a thermosetting resin and/or an active energy ray-curable resin, the non-removable material is cured as necessary.

[0086]

In this manner, a pattern consisting of the flowable material (including its cured product) and the non-removable material is formed.

[0087]

6. Metal Plating

When the compatible material contains a metal, the metal is subjected to a plating process. The plating method is not especially limited, and examples thereof include electrolytic plating and non-electrolytic plating.

[0088]

More specifically, in this method, the compatible material (material containing a metal) is incompatibilized by the above-described method, thereby forming a pattern consisting of the

flowable material (including its cured product) and the incompatibilized compatible material (material containing a metal).

[0089]

Thereafter, the pattern (the formed product with the pattern) is immersed in a plating solution to subject the metal in the compatible material to a plating process. Examples of the plating solution include a non-electrolytic plating solution and an electrolytic plating solution. Examples of the non-electrolytic plating solution include a non-electrolytic nickel phosphorus plating solution, a non-electrolytic nickel boron plating solution, and a non-electrolytic silver plating solution. Examples of the electrolytic plating solution include a gold plating solution, a silver plating solution, a copper plating solution, a nickel plating solution, and a gold-cobalt alloy plating solution.

[0090]

In this manner, in the above-described pattern, the plating metal is deposited on the part where the compatible material (material containing a metal) is incompatibilized. In other words, a pattern consisting of the flowable material (including its cured product) and the plating metal is formed.

[0091]

7. Operations and Effects

In the above-described method of forming a pattern, the pattern, and the method of producing the formed product with the pattern, at least a portion of the compatible material is incompatibilized in an arbitrary part in the composition containing the flowable material and the compatible material to form a pattern. In other words, the incompatibilized portion can be formed into an arbitrary pattern. Furthermore, the above-described incompatibilized portion suppresses the movements of the flowable material and the compatible material in the composition, and thus the deformation of the pattern is suppressed and a high-precision clear pattern can be obtained.

[0092]

In other words, by the above-described method of forming a pattern, a clear pattern is arbitrarily formed. The above-described pattern is a clear pattern that is arbitrarily formed. By the above-described method of producing the formed product with the pattern, a clear pattern can arbitrarily be formed.

[0093]

Furthermore, the above-described formed product with the pattern has a clear pattern.

[0094]

Furthermore, decreasing the composition ratio of the incompatibilized portion can decrease the size of the pattern in proportion to the approximate volume ratio, and a finer pattern can also be formed. For example, when photolithography is carried out using a photomask, a finer pattern than that of the photomask can be formed.

[0095]

Furthermore, the above-described pattern can be formed not only on a surface of the composition containing a flowable material and a compatible material but also at an inside of the composition. For example, when the flowable material is a thermosetting resin and/or an active energy ray-curable resin, a lens and/or a mirror is used to collect the infrared rays and/or the ultraviolet rays at an inside of the composition, and the ray-collecting portion is heated. In this manner, the flowable material in the ray-collecting portion is polymerized to increase its molecular weight. As a result, a pattern using the incompatibilized portion can be formed at an inside of the composition. Furthermore, for example, the above-described composition is irradiated with infrared rays and/or ultraviolet rays from 2 or more directions. At the position where the infrared rays and/or ultraviolet rays from 2 or more direction intersect, the flowable material is polymerized and thus its molecular weight can be increased. As a result, a pattern using the incompatibilized portion can be formed at an inside of the composition.

[0096]

Furthermore, on a layer having the above-described pattern (hereinafter a first layer), another layer having a pattern (hereinafter a second layer) can be laminated and formed. In particular, when the compatible material (removable material) is not removed after being

incompatibilized, a high-precision laminated pattern can be formed. In other words, when the second layer is laminated on the first layer in a conventional method, the second layer falls into the recessed portion of the pattern of the first layer. This causes disarrangement of the pattern of the second layer. However, by the above-described method, the pattern of the first layer is formed from the flowable material having an increased molecular weight and the incompatibilized portion and thus a recessed portion is not formed. Hence, the disarrangement of the pattern due to the fall of the second layer can be suppressed, and thus a high-precision laminated pattern can be formed.

Examples

[0097]

Next, the present invention is described based on Examples and Comparative Examples. The present invention is, however, not limited to Examples below. The "parts" and "%" are based on mass unless otherwise specified. The specific numeral values used in the description below, such as mixing ratios (content ratios), physical property values, and parameters, can be replaced with the corresponding mixing ratios (content ratios), physical property values, and parameters in the above-described "DESCRIPTION OF THE EMBODIMENTS", including the upper limit values (numeral values defined with "or less", and "less than") or the lower limit values (numeral values defined with "or more", and "more than").

[0098]

Example 1

(1) Synthesis of Isocyanate Group-terminated Prepolymer

Under nitrogen atmosphere, a glass separable flask was charged with 100 parts of a polyoxypropylene polyol (manufactured by Mitsui Chemicals & SKC Polyurethanes Inc.; DL 10000, an average functionality of 2, a number average molecular weight of 10000) as a polyol component. Next, the separable flask was charged with 1,3-bis(isocyanatomethyl) cyclohexane (manufactured by Mitsui Chemicals, Inc.; 1,3-H₆XDI) as a polyisocyanate component in a ratio in which the equivalent ratio (NCO/OH) became 8.0. Thereafter, the temperature of the mixture was increased to 80°C. Thereafter, STANOCT (tin ethylhexanoate (II)) was charged as a

urethane-formation catalyst into the mixture in a ratio of 10 ppm relative to the mixture.

Thereafter, the mixture was reacted for four hours. In this manner, a crude product containing the isocyanate group-terminated prepolymer and an unreacted polyisocyanate component was produced.

[0099]

(2) Purification of Isocyanate Group-terminated Prepolymer

The crude product containing the isocyanate group-terminated prepolymer was set in a Smith film-forming and wiping distillation apparatus to separate the isocyanate group-terminated prepolymer from the unreacted polyisocyanate component under the conditions below. In this manner, the isocyanate group-terminated prepolymer was purified.

Temperature condition: 160 to 170°C

Pressure condition: 70 to 100 Pa

Supply Flow Rate: 3.5 to 4 g/min

[0100]

(3) Synthesis of Active Energy Ray-curable Polyurethane Resin

Under an atmosphere (under dry air), a separable flask was charged with 100 parts of the purified isocyanate group-terminated prepolymer (a purified product of the prepolymer). Next, the separable flask was charged with 2 hydroxyethyl acrylate as a hydroxy group-containing unsaturated compound in a ratio in which the equivalent ratio (NCO/OH) of the isocyanate group of the isocyanate group-terminated prepolymer to the hydroxy group of the hydroxy group-containing unsaturated compound became 1.0. Next, the temperature of the mixture was heated to 70°C.

[0101]

Thereafter, the separable flask was charged with STANOCT (tin ethylhexanoate (II)) as a urethane-formation catalyst in a ratio of 200 ppm to the isocyanate group-terminated prepolymer, and the mixture was reacted for four hours until the isocyanate group concentration became 0.01% or less. In this manner, the active energy ray-curable polyurethane resin was synthesized.

[0102]

(4) Preparation of Composition Containing Flowable Material and Compatible Material

The following components were mixed at 60°C to produce a flowable material containing an active energy ray-curable polyurethane resin and simultaneously produce a mixture of the flowable material and a compatible material.

Flowable Material (Flowable Composition)

Active Energy Ray-curable Polyurethane Resin 100 parts

Plasticizer (trade name Benzoflex manufactured by CBC Co., Ltd.) 350 parts

Reactive Diluent (4-hydroxybutyl acrylate) 10 parts

Reactive Diluent (trade name AO-MA manufactured by NIPPON SHOKUBAI CO., LTD.) 50 parts

Polymerization Initiator (diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide) 3 parts

Antioxidant (bis[3-(3-methyl-4-hydroxy-5-tert-butylphenyl) propionate] ethylene bis oxy bis ethylene) 0.1 parts

Compatible Material

Olefin Monomer (1-dodecene (trade name LINEALENE 12 manufactured by Idemitsu Kosan Co.,Ltd.)) 30 parts

[0103]

(5) Formation of Pattern

By the method described below, a pattern was formed using the above-described composition.

[0104]

Using a doctor blade, a film of the above-described composition was formed on a glass plate to form a coating film having a thickness of 5 μm . Next, a photomask (Toppan TEST CHART No. 1 negative type pattern, Toppan Printing CO., LTD.) was used to irradiate the above-described coating film with active energy rays.

[0105]

The output of the active energy rays was 0.6 mW/cm^2 (measured with an illuminometer (manufactured by HIOKI E.E. CORPORATION 3664 OPTICAL POWER METER (measurement wavelength 405 nm)), and the irradiation was carried out so that its accumulated light intensity became 20 mJ/cm^2 .

[0106]

In this manner, the active energy ray-curable polyurethane resin was cured (polymerized) to produce a cured resin product. By carrying out the above-described operation, the compatibility of the olefin monomer (1-dodecene) in the active energy ray-curable polyurethane resin was reduced. In other words, the compatible material was incompatibilized on a surface of the cured resin product.

[0107]

By carrying out the above-described operation, a pattern consisting of the cured product of the active energy ray-curable polyurethane resin and the incompatibilized olefin monomer (1-dodecene) was formed. In other words, a formed product with the pattern was produced by the above-described method.

[0108]

Example 2 (volatilization)

1-hexene was used as the compatible material in place of 1-dodecene. Except for that, a formed product with the pattern was produced in the same manner as Example 1.

[0109]

Thereafter, the formed product with the pattern was heated in an 80°C oven for one hour. In this manner, the compatible material was volatilized. In this manner, the part where 1-hexene had existed was recessed.

[0110]

By carrying out the above-described operation, a pattern consisting of the cured product of the active energy ray-curable polyurethane resin and the recessed portion was formed.

[0111]

Example 3 (substitution)

1-hexene was used as the compatible material in place of 1-dodecene. Except for that, a formed product with the pattern was produced in the same manner as Example 1.

[0112]

Thereafter, the formed product with the pattern was immersed in a thermosetting epoxy resin composition for one hour. A mixture of 100 parts by mass of 3',4'-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate and 5 parts of a thermal cationic curing catalyst (manufactured by Sanshin Chemical Industry co., ltd., SAN AID SI-110L) was used as the thermosetting epoxy resin composition.

[0113]

In this manner, 1-hexene was substituted with the thermosetting epoxy resin composition. Thereafter, the formed product with the pattern was heated at 150°C for two hours to thermally cure the thermosetting epoxy resin composition.

[0114]

By carrying out the above-described operation, a pattern consisting of the cured product of the active energy ray-curable polyurethane resin and the cured product of the thermosetting epoxy resin composition was formed.

[0115]

Example 4 (using the difference in reactivity)

A mixture of 100 parts by mass of 3',4'-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate and 3 parts of a short-wavelength light curing cationic curing catalyst (manufactured by Sanshin Chemical Industry co., ltd., SAN AID SI-300) was used as a compatible material in place of 1-dodecene. Except for that, a formed product with the pattern was produced in the same manner as Example 1.

[0116]

Thereafter, the compatible material of the formed product with the pattern was cured using an ultraviolet rays spot light source L9566-02A (manufactured by HAMAMATSU PHOTONICS K.K.). The output of the active energy rays was 50 mW/cm² (measured using an illuminometer (manufactured by Ushio Inc. Accumulated UV meter UIT-250 (measurement

wavelength 254 nm)), and the irradiation was carried out so that its accumulated light intensity became 500 mJ/cm².

[0117]

Example 5 (plating)

A palladium chloride aqueous solution (a concentration of 0.1% by mass) was used as the compatible material in place of 1-dodecene. Except for that, a formed product with the pattern was produced in the same manner as Example 1.

[0118]

In this manner, a pattern consisting of the cured product of the active energy ray-curable polyurethane resin and the incompatibilized palladium chloride was formed.

[0119]

Next, the formed product with the pattern was washed with pure water and dried in a 40°C oven for 24 hours.

[0120]

Next, the formed product with the pattern was immersed in an electroless nickel plating solution (trade name TOP NICORON KMP-LF, OKUNO Chemical Industries Co., Ltd.) at 60°C for five minutes. In this manner, nickel was deposited on a palladium chloride surface of the formed product with the pattern. Thereafter, the formed product with the pattern was washed with pure water and dried in a 40°C oven for 24 hours.

[0121]

By carrying out the above-described operation, a pattern consisting of the cured product of the active energy ray-curable polyurethane resin and the plating metal was formed.

[0122]

Comparative Example 1 (without a compatible material)

1-dodecene was not added. Except for that, a cured product of the active energy ray-curable polyurethane resin was produced in the same manner as Example 1. Thereafter, the cured product of the active energy ray-curable polyurethane resin was washed with ethyl acetate and dried in a 40°C oven for 24 hours.

[0123]

Comparative Example 2 (without a photomask)

A photomask was not used. Except for that, a cured product of the active energy ray-curable polyurethane resin was produced in the same manner as Example 1.

[0124]

<Evaluations>

The appearance of the cured resin product was observed by optical microscope. The results are shown below.

[0125]

Example 1: It was confirmed that 1-dodecene was phase-separated and gathered on the part irradiated with light while the cured product of the active energy ray-curable polyurethane resin was patterned along the shape of the mask on the other part. A mere soft touch did not deform the film, but instead the 1-dodecene that had seeped into the pattern exuded and thus the surface of the film had a slimy slippery texture.

[0126]

The optical microscopic image of the surface of the formed product with the pattern produced in Example 1 is shown in FIG. 1.

[0127]

Example 2: It was confirmed that the pattern was formed in the shape of the shade of the mask while no pattern existed on the part irradiated with light. A mere soft touch did not deform the film.

[0128]

Example 3: It was confirmed that epoxy resin was patterned along the shape of the mask on the part irradiated with light while the cured product of the active energy ray-curable polyurethane resin was patterned along the shape of the mask on the other part. A mere soft touch did not deform the film.

[0129]

Example 4: It was confirmed that epoxy resin was phase-separated and gathered on the part irradiated with light while the cured product of the active energy ray-curable polyurethane resin was patterned along the shape of the mask on the other part. A mere soft touch did not deform the film.

[0130]

Example 5: It was confirmed that nickel plating was patterned along the shape of the mask on the part irradiated with light while the cured product of the active energy ray-curable polyurethane resin was patterned along the shape of the mask on the other part. A mere soft touch did not deform the film.

[0131]

Comparative Example 1: Adhesion of the patterns of the cured product of the active energy ray-curable polyurethane resin occurred and thus a pattern was not confirmed. A mere soft touch did not deform the film.

[0132]

Comparative Example 2; 1-dodecene was randomly phase-separated, and thus a mere soft touch caused the film to fall apart. The random phase-separation of the 1-dodecene decreased the strength of the film.

[0133]

While the illustrative embodiments of the present invention are provided in the above description, such is for illustrative purpose only and it is not to be construed as limiting in any manner. Modification and variation of the present invention that will be obvious to those skilled in the art is to be covered by the following claims.

Industrial Applicability

[0134]

The method of forming a pattern, the pattern, method of producing a formed product with the pattern, and the formed product with the pattern of the present invention are suitably used in various industrial fields where pattern formation is required.

CLAIMS

[Claim 1]

A method of forming a pattern, wherein the pattern is formed by incompatibilizing at least a portion of a compatible material in an arbitrary part in a composition containing a flowable material and the compatible material compatibilized with the flowable material.

[Claim 2]

The method of forming a pattern according to claim 1,
wherein the flowable material contains a flowable resin, and
wherein the flowable resin is polymerized to incompatibilize at least a portion of the compatible material.

[Claim 3]

The method of forming a pattern according to claim 2,
wherein the flowable resin contains an active energy ray-curable resin.

[Claim 4]

The method of forming a pattern according to claim 1,
wherein the compatible material contains a removable material, and
wherein the removable material is removed after being incompatibilized.

5 [Claim 5]

The method of forming a pattern according to claim 4,
wherein the flowable material contains an active energy ray-curable resin,
wherein the method comprises:

a step of preparing the composition containing the active energy ray-curable resin and the removable material;

a step of irradiating the composition with active energy rays to cure the active energy ray-curable resin and incompatibilize the removable material; and

a step of removing the incompatibilized removable material.

[Claim 6]

The method of forming a pattern according to claim 4,
wherein in the removal of the removable material,
the removable material is substituted with a non-removable material.

[Claim 7]

The method of forming a pattern according to claim 6,
wherein the non-removable material contains a non-removable resin.

[Claim 8]

The method of forming a pattern according to claim 1,
wherein one of the flowable material and the compatible material has a hydrogen-bondable
substituent group value of 0.0001 to 0.1111 mol/g, and
wherein a hydrogen-bondable functional group value of the other with respect to the one is
less than or equal to $2/3$ of the hydrogen-bondable substituent group value of the one.

[Claim 9]

The method of forming a pattern according to claim 1,
wherein the compatible material contains a compatible resin.

5 [Claim 10]

The method of forming a pattern according to claim 1,
wherein the compatible material contains a metal, and
wherein after the incompatibilization of the compatible material, the metal is subjected to a
plating process.

[Claim 11]

A pattern formed by the method of forming a pattern according to claim 1.

[Claim 12]

A method of producing a formed product with a pattern, wherein the pattern is formed by incompatibilizing a compatible material in an arbitrary part in a composition containing at least one or more flowable materials and the compatible material compatibilized with the flowable material(s).

[Claim 13]

A formed product with a pattern produced by forming the pattern by incompatibilizing a compatible material in an arbitrary part in a composition containing at least one or more flowable materials and the compatible material compatibilized with the flowable material(s).

[Claim 14]

The formed product with the pattern according to claim 13,
wherein the flowable material contains an active energy ray-curable resin,
wherein the composition containing the active energy ray-curable resin and the compatible material is prepared,
wherein the composition is irradiated with active energy rays through a photomask to cure the active energy ray-curable resin and incompatibilize the compatible material to form the pattern,
and
wherein the pattern is clearly formed while corresponding to the photomask.