

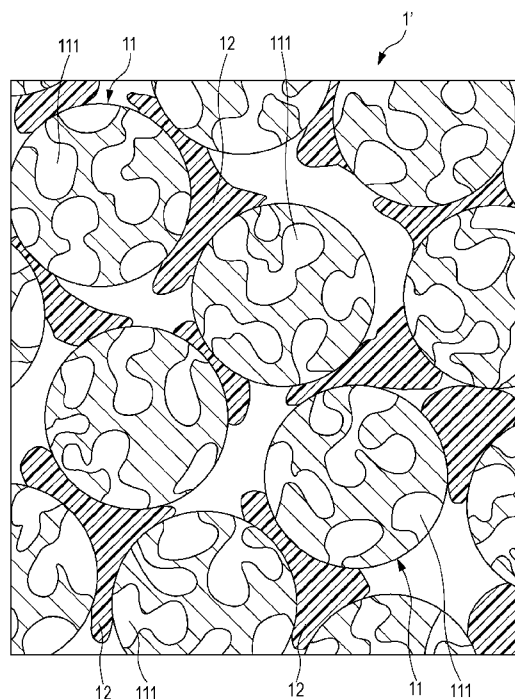


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[Continued on next page]

(54) Title: THREE-DIMENSIONAL STRUCTURE FORMING POWDER, THREE-DIMENSIONAL STRUCTURE FORMING COMPOSITION, MANUFACTURING METHOD OF THREE-DIMENSIONAL STRUCTURE, AND THREE-DIMENSIONAL STRUCTURE

[Fig. 3]



(57) Abstract: An object of the present invention is to provide a three-dimensional structure forming composition which is able to be preferably used for manufacturing a three-dimensional structure with excellent mechanical strength. The present invention relates to a three-dimensional structure forming composition. The three-dimensional structure forming composition includes a three-dimensional structure forming powder configured of a plurality of particles, and a water soluble resin, in which the particles are porous and are subjected to a hydrophobization treatment. It is preferable that a hydrocarbon group be introduced into the particle. It is preferable that the three-dimensional structure forming composition further include water.

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Description

Title of Invention: THREE-DIMENSIONAL STRUCTURE FORMING POWDER, THREE-DIMENSIONAL STRUCTURE FORMING COMPOSITION, MANUFACTURING METHOD OF THREE-DIMENSIONAL STRUCTURE, AND THREE-DIMENSIONAL STRUCTURE

Technical Field

[0001] The present invention relates to a three-dimensional structure forming powder, a three-dimensional structure forming composition, a manufacturing method of a three-dimensional structure, and a three-dimensional structure.

Background Art

[0002] A technology for forming a three-dimensional object while solidifying powders with binding liquid (for example, refer to PTL 1) is known. In this technology, the three-dimensional object is formed by repeating the following manipulation. First, a powder layer is formed by thinly spreading out the powder with a uniform thickness, and the binding liquid is discharged onto a desired portion of the powder layer, and thus the powder is bound. As a result, only the portion onto which the binding liquid is discharged in the powder layer is bound, and thus a thin plate-like member (hereinafter, referred to as a "cross-sectional member") is formed. Subsequently, a thin powder layer is further formed on the powder layer, and binding liquid is discharged onto a desired portion. As a result, a new cross-sectional member is formed in the portion onto which the binding liquid of the newly formed powder layer is discharged. At this time, the binding liquid discharged onto the powder layer permeates through the layer to reach the cross-sectional member which is previously formed, and thus the newly formed cross-sectional member is bound to the cross-sectional member which is previously formed. By repeating such a manipulation, the thin plate-like cross-sectional members are laminated one by one, and thus it is possible to form the three-dimensional object.

[0003] Such a three-dimensional structure technology is able to directly form the object by binding the powder when there is three-dimensional shape data of the object to be formed, and it is not necessary to prepare a mold before forming the three-dimensional structure or the like, and thus it is possible to rapidly and inexpensively form the three-dimensional object. In addition, the object is formed by laminating the thin plate-like cross-sectional members one by one, and for example, even when a complicated object having an inner structure is formed, it is possible to form the object as an integrated

structure without being divided into a plurality of parts.

- [0004] However, in the related art, it is not possible to sufficiently increase binding force by the binding liquid, and thus it is not possible to sufficiently increase strength of the three-dimensional structure.

Citation List

Patent Literature

- [0005] PTL 1: JP-A-6-218712

Summary of Invention

Technical Problem

- [0006] An object of the invention is to provide a three-dimensional structure with excellent mechanical strength, to provide a manufacturing method of a three-dimensional structure which is able to efficiently manufacture the three-dimensional structure with excellent mechanical strength, and to provide a three-dimensional structure forming powder and a three-dimensional structure forming composition which are able to be preferably used for manufacturing the three-dimensional structure with excellent mechanical strength.

Solution to Problem

- [0007] The object is attained by the invention described below.
- [0008] According to an aspect of the invention, there is provided a three-dimensional structure forming powder including a plurality of particles, in which the particles are porous, and are subjected to a hydrophobization treatment.
- [0009] Accordingly, it is possible to provide the three-dimensional structure forming powder which is able to be preferably used for manufacturing a three-dimensional structure with excellent mechanical strength.
- [0010] In the three-dimensional structure forming powder according to this aspect, the hydrophobization treatment may introduce a hydrocarbon group.
- [0011] Accordingly, it is possible to further improve hydrophobicity of the particle. In addition, it is possible to more easily and reliably increase uniformity of the degree of the hydrophobization treatment in each portion (including a surface inside a pore) of each particle or particle surface.
- [0012] In the three-dimensional structure forming powder according to this aspect, porosity of the particle may be greater than or equal to 50%.
- [0013] Accordingly, it is possible to sufficiently include a space (a pore) into which the binding agent penetrates, and it is possible to make mechanical strength of the particle itself excellent, and as a result, it is possible to make mechanical strength of the three-dimensional structure which is formed by allowing the binding agent to enter inside the pore especially excellent.

- [0014] In the three-dimensional structure forming powder according to this aspect, an average pore diameter of the particles may be greater than or equal to 10 nm.
- [0015] Accordingly, it is possible to make mechanical strength of the finally obtained three-dimensional structure especially excellent. In addition, when a coloring ink including a pigment is used for manufacturing the three-dimensional structure, the pigment preferably being kept in the pores of the particle is possible. For this reason, it is possible to prevent unintended diffusion of the pigment, and thus it is possible to more reliably form a high-definition image.
- [0016] In the three-dimensional structure forming powder according to this aspect, an average particle diameter of the particles may be greater than or equal to 1 micrometer and less than or equal to 25 micrometers.
- [0017] Accordingly, it is possible to make mechanical strength of the three-dimensional structure especially excellent, and it is possible to make dimensional accuracy of the three-dimensional structure especially excellent by more effectively preventing occurrence of unintended concavities and convexities in the three-dimensional structure to be manufactured. In addition, it is possible to make productivity of the three-dimensional structure especially excellent by making fluidity of the three-dimensional structure forming powder and fluidity of a three-dimensional structure forming composition including the three-dimensional structure forming powder especially excellent.
- [0018] In the three-dimensional structure forming powder according to this aspect, the particles may be configured of silica.
- [0019] Accordingly, it is possible to make properties such as mechanical strength and light resistance of the three-dimensional structure especially excellent. In addition, the silica has excellent fluidity, and thus it is advantageous for forming a layer having higher uniformity in thickness, and it is possible to make productivity and dimensional accuracy of the three-dimensional structure especially excellent.
- [0020] According to another aspect of the invention, there is provided a three-dimensional structure forming composition including the three-dimensional structure forming powder according to the invention; and a water soluble resin.
- [0021] Accordingly, it is possible to provide the three-dimensional structure forming composition which is able to be preferably used for manufacturing the three-dimensional structure with excellent mechanical strength.
- [0022] In the three-dimensional structure forming composition according to this aspect, the three-dimensional structure forming composition may further include water.
- [0023] Accordingly, it is possible to more reliably dissolve the water soluble resin, and thus it is possible to make fluidity of the three-dimensional structure forming composition and uniformity of a composition of a layer which is formed by using the three-

dimensional structure forming composition especially excellent. In addition, the water is easily removed after the layer is formed by the three-dimensional structure forming composition, and even when the water remains in the three-dimensional structure, it is difficult for the water to exert a negative effect. In addition, it is advantageous from a viewpoint of safety with respect to the human body, and environmental concerns.

[0024] In the three-dimensional structure forming composition according to this aspect, a content ratio of the water in the three-dimensional structure forming composition may be greater than or equal to 20 mass% and less than or equal to 73 mass%.

[0025] Accordingly, it is possible to make productivity of the three-dimensional structure especially excellent by making fluidity of the three-dimensional structure forming composition especially excellent. In addition, it is possible to easily remove a solvent (the water) in a manufacturing process of the three-dimensional structure in a short period of time, and thus it is advantageous from a viewpoint of further improving productivity of the three-dimensional structure.

[0026] In the three-dimensional structure forming composition according to this aspect, the water soluble resin may be polyvinyl alcohol.

[0027] Accordingly, it is possible to make mechanical strength of the three-dimensional structure especially excellent. In addition, by adjusting a saponification degree or polymerization degree, it is possible to more preferably control properties (for example, water solubility, water resistance, or the like) of the water soluble resin, or properties (for example, viscosity, fixing force of the particles, wettability, or the like) of the three-dimensional structure forming composition. For this reason, it is possible to more preferably support various manufacture of the three-dimensional structure. In addition, among various water soluble resins, polyvinyl alcohol is inexpensive and there is a stable supply thereof. For this reason, it is possible to reduce the production cost, and to stably manufacture the three-dimensional structure.

[0028] In the three-dimensional structure forming composition according to this aspect, the water soluble resin may be polyvinyl pyrrolidone.

[0029] Polyvinyl pyrrolidone has excellent adhesiveness with respect to various materials such as glass, metal, and plastic, and thus it is possible to make dimensional accuracy of the finally obtained three-dimensional structure especially excellent by making strength and shape stability of a portion onto which the ink is not applied in the layer formed by using the three-dimensional structure forming composition especially excellent. In addition, polyvinyl pyrrolidone exhibits high solubility with respect to various organic solvents, and thus when the three-dimensional structure forming composition includes the organic solvent, it is possible to make fluidity of the three-dimensional structure forming composition especially excellent. In addition, it is possible to preferably form a layer in which an unintended variation in a thickness is

more effectively prevented, and thus it is possible to make dimensional accuracy of the finally obtained three-dimensional structure especially excellent. In addition, polyvinyl pyrrolidone exhibits high solubility with respect to water, and thus it is possible to easily and reliably remove particles which are not bound by the binding agent among the particles configuring each layer after the formation is ended. In addition, polyvinyl pyrrolidone has suitable affinity with the three-dimensional structure forming powder, and thus it is difficult to sufficiently cause polyvinyl pyrrolidone to penetrate into the pores of the particles configuring the three-dimensional structure forming composition. On the other hand, polyvinyl pyrrolidone has relatively high wettability with respect to the surface of the particles. For this reason, it is possible to more effectively realize a function of temporary fixing that the water soluble resin should have. In addition, polyvinyl pyrrolidone has excellent affinity with various colorants, and thus when an ink including the colorant is used in an ink applying process, it is possible to effectively prevent the colorant from unintentionally diffusing. In addition, polyvinyl pyrrolidone has an antistatic function, and thus when a powder which is not fixed is used as the three-dimensional structure forming composition at the time of forming the layer by using the three-dimensional structure forming composition, it is possible to effectively prevent the powder from being scattered. In addition, when a powder which is fixed is used as the three-dimensional structure forming composition at the time of forming the layer by using the three-dimensional structure forming composition, it is possible to effectively prevent bubbles from being entrained into the three-dimensional structure forming composition when the paste-like three-dimensional structure forming composition includes polyvinyl pyrrolidone, and it is possible to more effectively prevent occurrence of a defect due to the entrained bubbles.

[0030] In the three-dimensional structure forming composition according to this aspect, the water soluble resin may be polycaprolactam diol.

[0031] Accordingly, it is possible to preferably form the three-dimensional structure forming composition in a pellet-state, and it is possible to effectively prevent unintended scattering of the particles or the like, and thus handleability (easiness of handling) of the three-dimensional structure forming composition is improved. Therefore, it is possible to improve safety of an operator and dimensional accuracy of the three-dimensional structure to be manufactured. In addition, the three-dimensional structure forming composition is able to be melted at a relatively low temperature, and thus it is possible to reduce energy required and cost incurred for producing the three-dimensional structure, and it is possible to make productivity of the three-dimensional structure sufficiently excellent.

[0032] According to still another aspect of the invention, there is provided a manufacturing method of a three-dimensional structure, including a layer forming process of forming

a layer of a predetermined thickness by using the three-dimensional structure forming composition according to the invention; and an ink applying process of applying an ink which includes a hydrophobic binding agent onto the layer, in which the processes are repeated in sequence.

[0033] Accordingly, it is possible to provide the manufacturing method of the three-dimensional structure which is able to efficiently manufacture the three-dimensional structure with excellent mechanical strength.

[0034] In the manufacturing method of the three-dimensional structure according to this aspect, the ink applying process may be performed by an ink jet method.

[0035] Accordingly, it is possible to apply the ink with high reproducibility even when an ink applying pattern is a fine pattern. As a result, together with the effect due to penetration of the binding agent into the pores of the particle, it is possible to especially increase dimensional accuracy of the finally obtained three-dimensional structure.

[0036] According to still yet another aspect of the invention, there is provided a three-dimensional structure which is manufactured by using the three-dimensional structure forming composition according to the invention.

[0037] Accordingly, it is possible to provide the three-dimensional structure with excellent mechanical strength.

Brief Description of Drawings

[0038] [fig.1A]Fig. 1A is a schematic view illustrating each process with respect to a preferred embodiment of a manufacturing method of a three-dimensional structure according to the invention.

[fig.1B]Fig. 1B is a schematic view illustrating each process with respect to a preferred embodiment of a manufacturing method of a three-dimensional structure according to the invention.

[fig.1C]Fig. 1C is a schematic view illustrating each process with respect to a preferred embodiment of a manufacturing method of a three-dimensional structure according to the invention.

[fig.1D]Fig. 1D is a schematic view illustrating each process with respect to a preferred embodiment of a manufacturing method of a three-dimensional structure according to the invention.

[fig.2E]Fig. 2E is a schematic view illustrating each process with respect to the preferred embodiment of the manufacturing method of the three-dimensional structure according to the invention.

[fig.2F]Fig. 2F is a schematic view illustrating each process with respect to the preferred embodiment of the manufacturing method of the three-dimensional structure according to the invention.

[fig.2G]Fig. 2G is a schematic view illustrating each process with respect to the preferred embodiment of the manufacturing method of the three-dimensional structure according to the invention.

[fig.2H]Fig. 2H is a schematic view illustrating each process with respect to the preferred embodiment of the manufacturing method of the three-dimensional structure according to the invention.

[fig.3]Fig. 3 is a cross-sectional view schematically illustrating a state of a layer (a three-dimensional structure forming composition) immediately before an ink applying process.

[fig.4]Fig. 4 is a cross-sectional view schematically illustrating a state where particles are bound by a hydrophobic binding agent.

[fig.5]Fig. 5 is a perspective view illustrating a shape of a three-dimensional structure (a three-dimensional structure A) manufactured in each Example and each Comparative Example.

[fig.6]Fig. 6 is a perspective view illustrating a shape of a three-dimensional structure (a three-dimensional structure B) manufactured in each Example and each Comparative Example.

Description of Embodiments

[0039] Hereinafter, a preferred embodiment of the invention will be described in detail with reference to the drawings.

[0040] First, a manufacturing method of a three-dimensional structure according to the invention will be described.

[0041] <Manufacturing Method of Three-dimensional structure>

Figs. 1A to 1D and Figs. 2E to 2H are schematic views illustrating each process with respect to the preferred embodiment of the manufacturing method of the three-dimensional structure according to the invention, Fig. 3 is a cross-sectional view schematically illustrating a state of a layer (a three-dimensional structure forming composition) immediately before an ink applying process, and Fig. 4 is a cross-sectional view schematically illustrating a state where particles are bound by a hydrophobic binding agent.

[0042] As illustrated in Figs. 1A to 1D and Figs. 2E to 2H, the manufacturing method of this embodiment includes a layer forming process (Figs. 1A and 1D) for forming a layer 1 of a predetermined thickness by using a three-dimensional structure forming composition 1' (described in detail later) of the invention, an ink applying process (Fig. 1B and Fig. 2E) for applying an ink 2 including a hydrophobic binding agent 21 onto the layer 1 by an ink jet method, and a curing process (Fig. 1C and Fig. 2F) for curing the binding agent 21 included in the ink 2 which is applied onto the layer 1, and repeats the

processes in sequence, and then further includes an unbound particle removing process (Fig. 2H) for removing particles which are not bound by the binding agent 21 among particles 11 configuring each layer 1.

[0043] <Layer Forming Process>

First, the layer 1 of a predetermined thickness is formed on a support (a stage) 9 by using the three-dimensional structure forming composition 1' (Fig. 1A).

[0044] The support 9 has a flat surface (a portion onto which the three-dimensional structure forming composition 1' is applied). Accordingly, it is possible to easily and reliably form the layer 1 with high uniformity in thickness.

[0045] It is preferable that the support 9 be configured of a high strength material. As a constituent material of the support 9, for example, various metal materials such as stainless steel and the like are included.

[0046] In addition, the surface (the portion onto which the three-dimensional structure forming composition 1' is applied) of the support 9 may be subjected to a surface treatment. Accordingly, for example, it is possible to promote stable production of a three-dimensional structure 100 for a longer period of time by more effectively preventing the constituent materials of the three-dimensional structure forming composition 1' or a constituent material of the ink 2 from being attached to the support 9, or by making durability of the support 9 especially excellent. As a material used for the surface treatment of the surface of the support 9, for example, a fluorine-based resin such as polytetrafluoroethylene, and the like are included.

[0047] As described in detail later, the three-dimensional structure forming composition 1' includes a plurality of particles 11 and a water soluble resin 12. By including the water soluble resin 12, it is possible to effectively prevent the particles 11 from being bound (temporarily fixed) (refer to Fig. 3), and to effectively prevent the unintended scattering of the particles or the like. Accordingly, it is possible to improve safety of the operator and dimensional accuracy of the three-dimensional structure 100 to be manufactured.

[0048] This process, for example, is able to be implemented by using a method such as a squeegee method, a screen printing method, a doctor blade method, and a spin coat method.

[0049] The thickness of the layer 1 formed in this process is not particularly limited, but the thickness is, preferably greater than or equal to 30 micrometers and less than or equal to 500 micrometers, and more preferably greater than or equal to 70 micrometers and less than or equal to 150 micrometers. Accordingly, it is possible to make productivity of the three-dimensional structure 100 sufficiently excellent, and it is possible to make dimensional accuracy of the three-dimensional structure 100 especially excellent by more effectively preventing the occurrence of the unintended concavities and con-

vexities of the three-dimensional structure 100 to be manufactured or the like.

[0050] Furthermore, for example, when the three-dimensional structure forming composition 1' is in a solid-state (a pellet-state) (for example, when the three-dimensional structure forming composition 1' includes the water soluble resin (a thermoplastic resin) 12 which is in the solid-state at a temperature near a storage temperature (for example, room temperature (25 degrees Celsius)), and the plurality of particles 11 is in a state of being bound by the water soluble resin), the three-dimensional structure forming composition 1' may be heated to be melted, and thus may be brought into a state where the three-dimensional structure forming composition 1' has fluidity before forming the layer described above. Accordingly, by a simple method as described above, it is possible to efficiently form the layer, and thus it is possible to more effectively prevent an unintended variation in the thickness of the layer 1 to be formed. As a result, it is possible to manufacture the three-dimensional structure 100 having higher dimensional accuracy with higher productivity.

[0051] <Ink Applying Process>

Subsequently, the ink 2 including the hydrophobic binding agent 21 is applied onto the layer 1 by the ink jet method (Fig. 1B).

[0052] In this process, the ink is selectively applied onto only a portion corresponding to a real portion (a substantive portion) of the three-dimensional structure 100 in the layer 1.

[0053] Accordingly, it is possible to more solidly bind the particles 11 configuring the layer 1 by the binding agent 21, and thus it is possible to make mechanical strength of the finally obtained three-dimensional structure 100 excellent. More specifically, in the invention, as described in detail later, the three-dimensional structure forming composition 1' configuring the layer 1 is porous, and includes the plurality of particles 11 subjected to a hydrophobization treatment (a lipophilic treatment), and thus the hydrophobic (lipophilic) binding agent 21 has high affinity with the particles 11 subjected to the hydrophobization treatment (the lipophilic treatment). For this reason, the binding agent 21 penetrates into a pore 111 of the particle 11, and thus an anchor effect is realized. As a result, it is possible to make binding force between the particles 11 (binding force through the binding agent 21) excellent, and thus it is possible to make mechanical strength of the finally obtained three-dimensional structure 100 excellent (refer to Fig. 4). In addition, the binding agent 21 configuring the ink 2 which is applied in this process penetrates the pores 111 of the particles 11, and thus it is possible to effectively prevent unintended wet spreading of the ink. As a result, it is possible to increase dimensional accuracy of the finally obtained three-dimensional structure 100.

[0054] In this process, the ink 2 is applied by the ink jet method, and thus it is possible to

apply the ink 2 with high reproducibility even when an applying pattern of the ink 2 is a fine pattern. As a result, together with the effect due to the penetration of the binding agent 21 into the pores 111 of the particles 11, it is possible to especially increase dimensional accuracy of the finally obtained three-dimensional structure 100.

[0055] Furthermore, the ink 2 will be described in detail later.

[0056] <Curing Process>

Subsequently, the binding agent 21 applied onto the layer 1 is cured, and a cured portion 3 is formed (Fig. 1C). Accordingly, it is possible to make binding strength between the binding agent 21 and the particle 11 especially excellent. As a result, it is possible to make mechanical strength of the finally obtained three-dimensional structure 100 especially excellent.

[0057] This process is different according to a type of binding agent 21, and for example, when the binding agent 21 is a thermosetting resin, the process is able to be performed by being heated, and when the binding agent 21 is a photocurable resin, the process is able to be performed by being irradiated with corresponding light (for example, when the binding agent 21 is an ultraviolet ray curable resin, the process is able to be performed by being irradiated with ultraviolet rays).

[0058] Furthermore, the ink applying process and the curing process may be simultaneously progressively performed. That is, before forming the entire pattern of one entire layer 1, a curing reaction may be allowed to sequentially progress from the portion onto which the ink 2 is applied.

[0059] In addition, for example, when the binding agent 21 is not a curable component, this process is able to be omitted.

[0060] Subsequently, serial processes described above are repeated (refer to Fig. 1D, and Figs. 2E and 2F). Accordingly, among each of the layers 1, the particles 11 of the portion onto which the ink 2 is applied are in the state of being bound, and thus the three-dimensional structure 100 as a laminated body in which a plurality of layers 1 in such a state is laminated is obtained (refer to Fig. 2G).

[0061] In addition, the ink 2 applied onto the layer 1 by the ink applying process after a second ink applying process (refer to Fig. 1D) is used for binding the particles 11 configuring the layer 1, and a part of the applied ink 2 seeps through the layer 1 which is lower than that of the applied ink 2. For this reason, the ink 2 binds not only the particles 11 in each of the layers 1, but also the particles 11 between adjacent layers. As a result, the entire finally obtained three-dimensional structure 100 has excellent mechanical strength.

[0062] <Unbound Particle Removing Process>

Then, as a post-processing process after repeating the serial processes described above, the unbound particle removing process (Fig. 2H) for removing the particles

(unbound particles) which are not bound by the binding agent 21 among the particles 11 configuring each of the layers 1 is performed. Accordingly, the three-dimensional structure 100 is taken out.

[0063] As a specific method of this process, for example, a method for cleaning away the unbound particles by a brush or the like, a method for removing the unbound particles by suction, a method for spraying gas such as air, a method for applying liquid such as water (for example, a method for immersing the laminated body obtained as described above in the liquid, a method for spraying the liquid, or the like), a method for applying vibration such as ultrasonic vibration, and the like are included. In addition, this process is able to be performed by combining two or more methods selected therefrom. More specifically, a method for immersing the laminated body in the liquid such as water after spraying the gas such as air, a method for applying the ultrasonic vibration in a state where the laminated body is immersed in the liquid such as water, and the like are included. Among them, a method for applying the liquid including water onto the laminated body obtained as described above (in particular, a method for immersing the laminated body in the liquid including water) is preferably adopted. Accordingly, the particles which are not bound by the binding agent 21 among the particles 11 configuring each of the layers 1 are temporarily fixed by the water soluble resin 12, but the temporary fixing is released by dissolving the water soluble resin 12 with the liquid including the water, and thus it is possible to more easily and more reliably remove the unbound particles from the three-dimensional structure 100. In addition, it is possible to more reliably prevent occurrence of a defect such as damage to the three-dimensional structure 100 at the time of removing the unbound particles. In addition, by adopting such a method, it is also possible to perform cleaning of the three-dimensional structure 100.

[0064] <Ink>

Next, the ink used for manufacturing the three-dimensional structure according to the invention will be described in detail.

[0065] The ink 2 includes at least the binding agent 21.

[0066] <Binding Agent>

The binding agent 21 has hydrophobicity (lipophilicity). Accordingly, it is possible to increase affinity between the ink 2 and the particles 11 subjected to the hydrophobization treatment, and the ink 2 is able to preferably enter the pores 111 of the particles 11 subjected to the hydrophobization treatment by applying the ink 2 onto the layer 1. As a result, the anchor effect is preferably realized by the binding agent 21, and thus it is possible to make mechanical strength of the finally obtained three-dimensional structure 100 excellent. Furthermore, in the invention, the hydrophobic binding agent may have sufficiently low affinity with the water, and for example, it is

preferable that solubility of the hydrophobic binding agent with respect to water at 25 degrees Celsius be less than or equal to 1 g/100 g of water.

[0067] As the binding agent 21, for example, a thermoplastic resin; a thermosetting resin; various photocurable resins such as a visible light curable resin (in the narrow sense, a photocurable resin) which is cured by light in a visible light region, an ultraviolet ray curable resin, and an infrared ray curable resin; an X-ray curable resin, and the like are included, and a combination of at least one selected therefrom is able to be used. Among them, from a viewpoint of mechanical strength of the three-dimensional structure 100 to be obtained, productivity of the three-dimensional structure 100, or the like, it is preferable that the binding agent 21 be a curable resin. In addition, among the various curable resins, from a viewpoint of mechanical strength of the three-dimensional structure 100 to be obtained, productivity of the three-dimensional structure 100, storage stability of the ink 2, or the like, the ultraviolet ray curable resin (a polymerizable compound) is especially preferable.

[0068] As the ultraviolet ray curable resin (the polymerizable compound), a material in which addition polymerization or ring-opening polymerization is started by radical species, cationic species, and the like which are generated from a photopolymerization initiator by irradiation of ultraviolet rays, and thus a polymer is generated, is preferably used. As a polymerization method of the addition polymerization, radicals, cations, anions, metathesis, and coordination polymerization are used. In addition, as a polymerization method of the ring-opening polymerization, cations, anions, radicals, metathesis, and coordination polymerization are used.

[0069] As an addition polymerizable compound, for example, a compound having at least one ethylenically unsaturated double bond and the like are included. As the addition polymerizable compound, a compound having at least one, preferably at least two terminal ethylenically unsaturated bonds is able to be preferably used.

[0070] An ethylenically unsaturated polymerizable compound has a chemical form of a monofunctional polymerizable compound and a multifunctional polymerizable compound, or a mixture thereof. As the monofunctional polymerizable compound, for example, an unsaturated carboxylic acid (for example, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, maleic acid, or the like), esters thereof, amides thereof, and the like are included. As the multifunctional polymerizable compound, esters of an unsaturated carboxylic acid and an aliphatic polyhydric alcohol compound, and amides of an unsaturated carboxylic acid and an aliphatic polyvalent amine compound are used.

[0071] In addition, an addition reaction product of unsaturated carboxylic acid esters or amides having a nucleophilic substituent such as a hydroxyl group, an amino group, and a mercapto group with isocyanates and epoxies, a product of a dehydration con-

densation reaction with a carboxylic acid, and the like are able to be used. In addition, an addition reaction product of unsaturated carboxylic acid esters or amides having an electrophilic substituent such as an isocyanate group or an epoxy group with alcohols, amines, and thiols, and a substitution reaction product with unsaturated carboxylic acid esters or amides having a releasing substituent such as a halogen group or a tosyloxy group with alcohols, and amines or thiols are able to be used.

- [0072] As a specific example of a radical polymerizable compound which is an ester of an unsaturated carboxylic acid and an aliphatic polyhydric alcohol compound, for example, (meth)acrylic ester is representative, and either monofunctional (meth)acrylic ester or multifunctional (meth)acrylic ester is able to be used.
- [0073] As a specific example of a monofunctional (meth)acrylate, for example, tolyloxyethyl (meth)acrylate, phenyloxyethyl (meth)acrylate, cyclohexyl (meth)acrylate, ethyl (meth)acrylate, methyl (meth)acrylate, isobornyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, and the like are included.
- [0074] As a specific example of a bifunctional (meth)acrylate, for example, ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, tetramethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, hexanediol di(meth)acrylate, 1,4-cyclohexanediol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, pentaerythritol di(meth)acrylate, dipentaerythritol di(meth)acrylate, and the like are included.
- [0075] As a specific example of a trifunctional (meth)acrylate, for example, trimethylolpropane tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, alkylene oxide-modified tri(meth)acrylate of trimethylolpropane, pentaerythritol tri(meth)acrylate, dipentaerythritol tri(meth)acrylate, trimethylolpropane tri((meth)acryloyloxy propyl) ether, isocyanuric acid alkylene oxide-modified tri(meth)acrylate, propionic acid dipentaerythritol tri(meth)acrylate, tri((meth)acryloyloxyethyl) isocyanurate, hydroxypivalaldehyde-modified dimethylolpropane tri(meth)acrylate, sorbitol tri(meth)acrylate, and the like are included.
- [0076] As a specific example of a tetrafunctional (meth)acrylate, for example, pentaerythritol tetra(meth)acrylate, sorbitol tetra(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, propionic acid dipentaerythritol tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, and the like are included.
- [0077] As a specific example of a pentafunctional (meth)acrylate, for example, sorbitol penta(meth)acrylate, dipentaerythritol penta(meth)acrylate, and the like are included.
- [0078] As a specific example of a hexafunctional (meth)acrylate, for example, dipentaerythritol hexa(meth)acrylate, sorbitol hexa(meth)acrylate, alkylene oxide-modified hexa(meth)acrylate of phosphazene, caprolactone-modified dipentaerythritol hexa(meth)acrylate, and the like are included.

- [0079] As a polymerizable compound in addition to a (meth)acrylate, for example, itaconic acid ester, crotonic acid ester, isocrotonic acid ester, maleic acid ester, and the like are included.
- [0080] As an itaconic acid ester, for example, ethylene glycol diitaconate, propylene glycol diitaconate, 1,3-butanediol diitaconate, 1,4-butanediol diitaconate, tetramethylene glycol diitaconate, pentaerythritol diitaconate, sorbitol tetraitaconate, and the like are included.
- [0081] As a crotonic acid ester, for example, ethylene glycol dicrotonate, tetramethylene glycol dicrotonate, pentaerythritol dicrotonate, sorbitol tetradicrotonate, and the like are included.
- [0082] As an isocrotonic acid ester, for example, ethylene glycol diisocrotonate, pentaerythritol diisocrotonate, sorbitol tetraisocrotonate, and the like are included.
- [0083] As a maleic acid ester, for example, ethylene glycol dimaleate, triethylene glycol dimaleate, pentaerythritol dimaleate, sorbitol tetramaleate, and the like are included.
- [0084] As an example of other esters, for example, aliphatic alcohol-based esters disclosed in JP-B-46-27926, JP-B-51-47334, and JP-A-57-196231, esters having an aromatic skeleton disclosed in JP-A-59-5240, JP-A-59-5241, and JP-A-2-226149, esters containing an amino group disclosed in JP-A-1-165613 and the like are able to be used.
- [0085] In addition, as a specific example of a monomer of an amide from an unsaturated carboxylic acid and an aliphatic polyvalent amine compound, for example, methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, 1,6-hexamethylene bis-methacrylamide, diethylenetriamine tris-acrylamide, xylylene bis-acrylamide, xylylene bis-methacrylamide, and the like are included.
- [0086] As other preferred amide-based monomers, for example, an amide-based monomer having a cyclohexylene structure disclosed in JP-B-54-21726, and the like are included.
- [0087] In addition, a urethane-based addition polymerizable compound manufactured by using an addition reaction between isocyanate and a hydroxyl group is also preferable, and as a specific example thereof, for example, a vinylurethane compound containing two or more polymerizable vinyl groups in one molecule in which a vinyl monomer containing a hydroxyl group shown in the following Formula (1) is added to a polyisocyanate compound having two or more isocyanate groups in one molecule disclosed in JP-B-48-41708, and the like are included.

<Formula 1>



(Where, in Formula (1), R^1 and R^2 independently indicate H or CH_3 , respectively.)

- [0088] In the invention, a cationic ring-opening polymerizable compound having one or

more cyclic ether groups such as an epoxy group, and an oxetane group in the molecule is able to be preferably used as the ultraviolet ray curable resin (the polymerizable compound).

[0089] As a cationically polymerizable compound, for example, a curable compound containing a ring-opening polymerizable group, and the like are included, and among them, a curable compound containing a heterocyclic group is especially preferable. As the curable compound, for example, cyclic imino ethers such as an epoxy derivative, an oxetane derivative, a tetrahydrofuran derivative, a cyclic lactone derivative, a cyclic carbonate derivative, and an oxazoline derivative, vinyl ethers, and the like are included, and among them, an epoxy derivative, an oxetane derivative, and vinyl ethers are preferable.

[0090] As an example of the preferred epoxy derivative, for example, monofunctional glycidyl ethers, multifunctional glycidyl ethers, monofunctional alicyclic epoxies, multifunctional alicyclic epoxies, and the like are included.

[0091] Examples of specific glycidyl ether compounds include, for example, diglycidyl ethers (for example, ethylene glycol diglycidyl ether, bisphenol A diglycidyl ether, or the like), trifunctional or higher glycidyl ethers (for example, trimethylolethane triglycidyl ether, trimethylolpropane triglycidyl ether, glycerol triglycidyl ether, triglycidyl tris-hydroxyethyl isocyanurate, or the like), tetrafunctional or higher glycidyl ethers (for example, sorbitol tetraglycidyl ether, pentaerythritol tetraglycidyl ether, a polyglycidyl ether of a cresol novolac resin, polyglycidyl ethers of a phenol novolac resin, or the like), alicyclic epoxies (for example, Celloxide 2021P, Celloxide 2081, Epolead GT-301, and Epolead GT-401 (manufactured by Daicel Co., Ltd.), EHPE (manufactured by Daicel Co., Ltd.), polycyclohexyl epoxy methyl ether of a phenol novolac resin, or the like), oxetanes (for example, OX-SQ, PNOX-1009 (manufactured by Toa Gosei Co., Ltd.), or the like), and the like.

[0092] As the polymerizable compound, an alicyclic epoxy derivative is able to be preferably used. The "alicyclic epoxy group" indicates a structure of a portion in which a double bond of a cycloalkene ring such as a cyclopentene group, and cyclohexene group is epoxidized by a suitable oxidizing agent such as hydrogen peroxide, and a peracid.

[0093] As the alicyclic epoxy compound, multifunctional alicyclic epoxies having two or more cyclopentene oxide groups or cyclohexene oxide groups in one molecule is preferable. As a specific example of the alicyclic epoxy compound, for example, 4-vinylcyclohexene dioxide, (3,4-epoxycyclohexyl)methyl-3,4-epoxycyclohexylcarboxylate, di(3,4-epoxycyclohexyl) adipate, di(3,4-epoxycyclohexylmethyl) adipate, bis(2,3-epoxycyclopentyl) ether, di(2,3-epoxy-6-methylcyclohexylmethyl) adipate, di-

cyclopentadiene dioxide, and the like are included.

[0094] A glycidyl compound having a general epoxy group which does not have an alicyclic structure in the molecule is able to be independently used, or is able to be used together with the alicyclic epoxy compound.

[0095] As a general glycidyl compound, for example, a glycidyl ether compound, a glycidyl ester compound, and the like are able to be included, and a combination including a glycidyl ether compound is preferable.

[0096] As a specific example of the glycidyl ether compound, for example, an aromatic glycidyl ether compound such as 1,3-bis(2,3-epoxypropyloxy)benzene, a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, a phenol novolac type epoxy resin, a cresol novolac type epoxy resin, and a trisphenolmethane type epoxy resin, an aliphatic glycidyl ether compound such as 1,4-butanediol glycidyl ether, glycerol triglycidyl ether, propylene glycol diglycidyl ether, and trimethylolpropane triglycidyl ether, and the like are included. As a glycidyl ester, for example, a glycidyl ester of a linoleic acid dimer and the like are able to be included.

[0097] As the polymerizable compound, a compound (hereinafter, simply referred to as an "oxetane compound") having an oxetanyl group which is a cyclic ether of a four-membered ring is able to be used. A compound containing an oxetanyl group is a compound having one or more oxetanyl groups in one molecule.

[0098] A content ratio of the binding agent in the ink 2 is, preferably greater than or equal to 80 mass%, and more preferably greater than or equal to 85 mass%. Accordingly, it is possible to make mechanical strength of the finally obtained three-dimensional structure 100 especially excellent.

[0099] <Other Components>

In addition, the ink 2 may include other components in addition to the components described above. As the other component, for example, various colorants such as a pigment, and a dye; a dispersant; a surfactant agent; a polymerization initiator; a polymerization accelerator; a solvent; a penetration enhancer; a wetting agent (a moisturizing agent); a fixing agent; an antifungal agent; an antiseptic agent; an antioxidantizing agent; an ultraviolet ray absorber; a chelating agent; a pH adjuster; a thickener; a filler; an aggregation prevention agent; an antifoaming agent, and the like are included.

[0100] In particular, by including the colorant in the ink 2, it is possible to obtain the three-dimensional structure 100 which is colored with a color corresponding to a color of the colorant.

[0101] In particular, by including a pigment as the colorant, it is possible to make light resistance of the ink 2 and the three-dimensional structure 100 excellent. As the pigment, either an inorganic pigment or an organic pigment is able to be used.

- [0102] As the inorganic pigment, for example, carbon blacks (C.I. Pigment Black 7) such as furnace black, lamp black, acetylene black, and channel black, iron oxide, titanium oxide, and the like are included, and a combination of at least one selected therefrom is able to be used.
- [0103] Among the inorganic pigments, in order to exhibit a preferred white color, titanium oxide is preferable.
- [0104] As the organic pigment, for example, an azo pigment such as an insoluble azo pigment, a condensed azo pigment, an azo lake, and an azo chelate pigment, a polycyclic pigment such as a phthalocyanine pigment, a perylene or perynone pigment, an anthraquinone pigment, a quinacridone pigment, a dioxane pigment, a thioindigo pigment, an isoindolinone pigment, and a quinophthalone pigment, a dye chelate (for example, basic dye-type chelate, acid dye-type chelate, or the like), a dyeing lake (basic dye-type lake, or acid dye-type lake), a nitro pigment, a nitroso pigment, aniline black, a daylight fluorescent pigment, and the like are included, and a combination of at least one selected therefrom is able to be used.
- [0105] More specifically, as the carbon black used as a black-colored (black) pigment, for example, No. 2300, No. 900, MCF 88, No. 33, No. 40, No. 45, No. 52, MA 7, MA 8, MA 100, No. 2200B, or the like (manufactured by Mitsubishi Chemical Corporation), Raven 5750, Raven 5250, Raven 5000, Raven 3500, Raven 1255, Raven 700, or the like (manufactured by Carbon Columbia), Regal 400R, Regal 330R, Regal 660R, Mogul L, Monarch 700, Monarch 800, Monarch 880, Monarch 900, Monarch 1000, Monarch 1100, Monarch 1300, Monarch 1400, or the like (manufactured by CABOT JAPAN K.K.), Color Black FW1, Color Black FW2, Color Black FW2V, Color Black FW18, Color Black FW200, Color Black S150, Color Black S160, Color Black S170, Printex 35, Printex U, Printex V, Printex 140U, Special Black 6, Special Black 5, Special Black 4A, Special Black 4 (manufactured by Degussa), and the like are included.
- [0106] As a white-colored (white) pigment, for example, C.I. Pigment White 6, 18, and 21, and the like are included.
- [0107] As a yellow-colored (yellow) pigment, for example, C.I. Pigment Yellow 1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 13, 14, 16, 17, 24, 34, 35, 37, 53, 55, 65, 73, 74, 75, 81, 83, 93, 94, 95, 97, 98, 99, 108, 109, 110, 113, 114, 117, 120, 124, 128, 129, 133, 138, 139, 147, 151, 153, 154, 167, 172, and 180, and the like are included.
- [0108] As a magenta-colored (magenta) pigment, for example, C.I. Pigment Red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18, 19, 21, 22, 23, 30, 31, 32, 37, 38, 40, 41, 42, 48(Ca), 48(Mn), 57(Ca), 57:1, 88, 112, 114, 122, 123, 144, 146, 149, 150, 166, 168, 170, 171, 175, 176, 177, 178, 179, 184, 185, 187, 202, 209, 219, 224, and 245, or C.I. Pigment Violet 19, 23, 32, 33, 36, 38, 43, and 50, and the like are included.

- [0109] As a cyan-colored (cyan) pigment, for example, C.I. Pigment Blue 1, 2, 3, 15, 15:1, 15:2, 15:3, 15:34, 15:4, 16, 18, 22, 25, 60, 65, and 66, C.I. Pigment Cobalt Blue 4, and 60, and the like are included.
- [0110] In addition, as other pigments, for example, C.I. Pigment Green 7, and 10, C.I. Pigment Brown 3, 5, 25, and 26, C.I. Pigment Orange 1, 2, 5, 7, 13, 14, 15, 16, 24, 34, 36, 38, 40, 43, and 63, and the like are included.
- [0111] When the ink 2 includes a pigment, an average particle diameter of the pigment is, preferably less than or equal to 300 nm, and more preferably greater than or equal to 50 nm and less than or equal to 250 nm. Accordingly, it is possible to make discharge stability of the ink 2 or dispersion stability of the pigment in the ink 2 especially excellent, and it is possible to form an image with more excellent image quality.
- [0112] In addition, as the dye, for example, an acid dye, a direct dye, a reactive dye, a basic dye, and the like are included, and a combination of at least one selected therefrom is able to be used.
- [0113] As a specific example of the dye, for example, C.I. Acid Yellow 17, 23, 42, 44, 79, and 142, C.I. Acid Red 52, 80, 82, 249, 254, and 289, C.I. Acid Blue 9, 45, and 249, C.I. Acid Black 1, 2, 24, and 94, C.I. Food Black 1, and 2, C.I. Direct Yellow 1, 12, 24, 33, 50, 55, 58, 86, 132, 142, 144, and 173, C.I. Direct Red 1, 4, 9, 80, 81, 225, and 227, C.I. Direct Blue 1, 2, 15, 71, 86, 87, 98, 165, 199, and 202, C.I. Direct Black 19, 38, 51, 71, 154, 168, 171, and 195, C.I. Reactive Red 14, 32, 55, 79, and 249, C.I. Reactive Black 3, 4, and 35, and the like are included.
- [0114] When the ink 2 includes the colorant, a content ratio of the colorant in the ink 2 is, preferably greater than or equal to 1 mass% and less than or equal to 20 mass%. Accordingly, it is possible to obtain especially excellent shielding properties and color reproducibility.
- [0115] In particular, when the ink 2 includes titanium oxide as the colorant, a content ratio of titanium oxide in the ink 2 is, preferably greater than or equal to 12 mass% and less than or equal to 18 mass%, and more preferably greater than or equal to 14 mass% and less than or equal to 16 mass%. Accordingly, it is possible to obtain especially excellent shielding properties.
- [0116] When the ink 2 includes a pigment, it is possible to make dispersibility of the pigment more excellent at the time of further including a dispersant. The dispersant is not particularly limited, but for example, includes a dispersant which is commonly used for manufacturing a pigment dispersion liquid such as a polymeric dispersant. As a specific example of the polymeric dispersant, for example, a polymeric dispersant containing at least one of polyoxyalkylene polyalkylene polyamine, a vinyl-based polymer and copolymer, an acryl-based polymer and copolymer, polyester, polyamide, polyimide, polyurethane, an amino-based polymer, a silicon-containing polymer, a

sulfur-containing polymer, a fluorine-containing polymer, and an epoxy resin as a main component is included. As a commercialized product of the polymeric dispersant, for example, Ajisper series manufactured by Ajinomoto Fine-Techno Co., Inc., Solsperser series (Solsperser 36000 or the like) manufactured by Noveon Company, Disperbyk series manufactured by BYK company, Disparon series manufactured by Kusumoto Chemicals, Ltd., and the like are included.

[0117] When the ink 2 includes a surfactant agent, it is possible to make scratch resistance of the three-dimensional structure 100 more excellent. The surfactant agent is not particularly limited, but for example, polyester-modified silicone or polyether-modified silicone as a silicone-based surfactant agent is able to be used, and among them, it is preferable that polyether-modified polydimethylsiloxane or polyester-modified polydimethylsiloxane be used. As a specific example of the surfactant agent, for example, BYK-347, BYK-348, BYK-UV 3500, 3510, 3530, and 3570 (trade names of BYK company), and the like are included.

[0118] In addition, the ink 2 may include a solvent. Accordingly, it is possible to preferably perform viscosity adjustment of the ink 2, and thus when the ink 2 includes a component of high viscosity, it is possible to make discharge stability of the ink 2 with the ink jet method especially excellent.

[0119] As the solvent, for example, (poly)alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monomethyl ether, and propylene glycol monoethyl ether; ester acetates such as ethyl acetate, n-propyl acetate, iso-propyl acetate, n-butyl acetate, and iso-butyl acetate; aromatic hydrocarbons such as benzene, toluene, and xylene; ketones such as methyl ethyl ketone, acetone, methyl isobutyl ketone, ethyl-n-butyl ketone, diisopropyl ketone, and acetylacetone; alcohols such as ethanol, propanol, and butanol, and the like are included, and a combination of at least one selected therefrom is able to be used.

[0120] In addition, viscosity of the ink 2 is, preferably greater than or equal to 10 mPa·s and less than or equal to 25 mPa·s, and more preferably greater than or equal to 15 mPa·s and less than or equal to 20 mPa·s. Accordingly, it is possible to make discharge stability of the ink with the ink jet method especially excellent. Furthermore, herein, "viscosity" indicates a value measured at 25 degrees Celsius by using an E-type viscometer (VISCONIC ELD manufactured by Tokyo Keiki INC).

[0121] In addition, a plurality of types of ink 2 may be used for manufacturing the three-dimensional structure 100.

[0122] For example, an ink 2 (a color ink) which includes a colorant, and an ink 2 (a clear ink) which does not include a colorant may be used. Accordingly, for example, in appearance of the three-dimensional structure 100, the ink 2 which includes the colorant may be used as the ink 2 applied onto a region affecting a color tone, and in ap-

pearance of the three-dimensional structure 100, the ink 2 which does not include the colorant may be used as the ink 2 applied onto a region not affecting the color tone. In addition, in the finally obtained three-dimensional structure 100, a plurality of types of ink 2 may be used together such that a region (a coat layer) is disposed on an outer surface of the region formed by the ink 2 which includes the colorant by using the ink 2 which does not include the colorant.

[0123] In addition, for example, a plurality of types of ink 2 including colorants of different compositions may be used. Accordingly, it is possible to broaden a color reproduction region which is able to be shown according to a combination of the inks 2.

[0124] When a plurality of types of ink 2 is used, it is preferable that at least a cyan-colored (cyan) ink 2, a magenta-colored (magenta) ink 2 and a yellow-colored (yellow) ink 2 be used. Accordingly, it is possible to broaden the color reproduction region which is able to be shown according to the combination of the inks 2.

[0125] In addition, by using a white-colored (white) ink 2 together with another colored ink 2, for example, the following effects are obtained. That is, it is possible to form the finally obtained three-dimensional structure 100 to include a first region onto which the white-colored (white) ink 2 is applied, and a region (a second region) disposed on an outer surface side of the first region, onto which the colored ink 2 other than the white-colored ink is applied. Accordingly, it is possible to realize shielding properties of the first region onto which the white-colored (white) ink 2 is applied, and thus it is possible to further increase chromaticness of the three-dimensional structure 100.

[0126] <Three-dimensional structure forming powder>

Next, the three-dimensional structure forming powder of the invention will be described.

[0127] The three-dimensional structure forming powder of the invention is configured of a plurality of particles, and the particles are porous, and are subjected to the hydrophobization treatment. According to this configuration, as described above, when the three-dimensional structure is manufactured, it is possible to allow the hydrophobic binding agent to preferably enter the pores. As a result, the three-dimensional structure forming powder is able to be preferably used for manufacturing the three-dimensional structure with excellent mechanical strength. In addition, the three-dimensional structure forming powder of the invention is able to be preferably reused. In more specific description, since the particles configuring the three-dimensional structure forming powder are subjected to the hydrophobization treatment in order to prevent the water soluble resin described later from penetrating into the pores, in the manufacturing of the three-dimensional structure, the particles in a region onto which the ink is not applied are cleaned by water or the like, and thus it is possible to collect the particles at high purity with a low content ratio of impurities. For this reason, by

mixing again the collected three-dimensional structure forming powder with the water soluble resin or the like at a predetermined ratio, it is possible to obtain the three-dimensional structure forming composition of which the composition is reliably controlled to be a desired composition.

[0128] It is preferable that the particles configuring the three-dimensional structure forming powder be porous and be subjected to the hydrophobization treatment, and as a constituent material of the particles (base particles subjected to the hydrophobization treatment), for example, an inorganic material, an organic material, a complex thereof, and the like are included.

[0129] As the inorganic material configuring the particles, for example, various metals, a metallic compound, and the like are included. As the metallic compound, for example, various metal oxides such as silica, alumina, titanium oxide, zinc oxide, zirconium oxide, tin oxide, magnesium oxide, and potassium titanate; various metal hydroxides such as magnesium hydroxide, aluminum hydroxide, and calcium hydroxide; various metal nitrides such as silicon nitride, titanium nitride, and aluminum nitride; various metal carbides such as silicon carbide, and titanium carbide; various metal sulfides such as zinc sulfide; various metal carbonates such as calcium carbonate, and magnesium carbonate; various metal sulfates such as calcium sulfate, and magnesium sulfate; various metal silicates such as calcium silicate, and magnesium silicate; various metal phosphates such as calcium phosphate; various metal borates such as aluminum borate, and magnesium borate; a complex compound thereof, and the like are included.

[0130] As the organic material configuring the particles, for example, a synthetic resin, a natural polymer, and the like are included, and more specifically, a polyethylene resin; polypropylene; polyethylene oxide; polypropylene oxide; polyethylene imine; polystyrene; polyurethane; polyurea; polyester; a silicone resin; an acrylic silicone resin; a polymer such as polymethyl methacrylate having (meth)acrylic ester as a constituent monomer; a cross polymer (an ethylene acrylic acid copolymer resin or the like) such as methyl methacrylate cross polymer having (meth)acrylic ester as a constituent monomer; a polyamide resin such as nylon 12, nylon 6, and copolymer nylon; polyimide; carboxymethyl cellulose; gelatin; a starch; chitin; chitosan, and the like are included.

[0131] Among them, the particles are, preferably configured of an inorganic material, more preferably configured of a metal oxide, and further preferably configured of silica. Accordingly, it is possible to make properties such as mechanical strength, and light resistance of the three-dimensional structure especially excellent. In addition, particularly, when the particles are configured of silica, the effects described above are more remarkably realized. In addition, since silica has excellent fluidity, it is ad-

vantageous for forming a layer with high uniformity in thickness, and thus it is possible to make productivity and dimensional accuracy of the three-dimensional structure especially excellent.

- [0132] As the hydrophobization treatment performed with respect to the particles configuring the three-dimensional structure forming powder, any treatment may be used insofar as hydrophobicity of the particle (the base particle) increases, and a treatment which introduces a hydrocarbon group is preferable. Accordingly, it is possible to further increase hydrophobicity of the particle. In addition, it is possible to more easily and reliably increase uniformity of the degree of the hydrophobization treatment in each portion (including a surface inside the pore) of each particle or particle surface.
- [0133] As a compound used for the hydrophobization treatment, a silane compound having a silyl group is preferable. As a specific example of the compound which is able to be used for the hydrophobization treatment, for example, hexamethyl disilazane, dimethyl dimethoxysilane, diethyl diethoxysilane, 1-propenyl methyl dichlorosilane, propyl dimethyl chlorosilane, propyl methyl dichlorosilane, propyl trichlorosilane, propyl triethoxysilane, propyl trimethoxysilane, styryl ethyl trimethoxysilane, tetradecyl trichlorosilane, 3-thiocyanate propyl triethoxysilane, p-tolyl dimethyl chlorosilane, p-tolyl methyl dichlorosilane, p-tolyl trichlorosilane, p-tolyl trimethoxysilane, p-tolyl triethoxysilane, di-n-propyl-di-n-propoxysilane, diisopropyl diisopropoxysilane, di-n-butyl-di-n-butyloxysilane, di-sec-butyl-di-sec-butyloxysilane, di-t-butyl-di-t-butyloxysilane, octadecyl trichlorosilane, octadecyl methyl diethoxysilane, octadecyl triethoxysilane, octadecyl trimethoxysilane, octadecyl dimethyl chlorosilane, octadecyl methyl dichlorosilane, octadecyl methoxy dichlorosilane, 7-octenyl dimethyl chlorosilane, 7-octenyl trichlorosilane, 7-octenyl trimethoxysilane, octyl methyl dichlorosilane, octyl dimethyl chlorosilane, octyl trichlorosilane, 10-undecenyl dimethyl chlorosilane, undecyl trichlorosilane, vinyl dimethyl chlorosilane, methyl octadecyl dimethoxysilane, methyl dodecyl diethoxysilane, methyl octadecyl dimethoxysilane, methyl octadecyl diethoxysilane, n-octyl methyl dimethoxysilane, n-octyl methyl diethoxysilane, triacontyl dimethyl chlorosilane, triacontyl trichlorosilane, methyl trimethoxysilane, methyl triethoxysilane, methyl tri-n-propoxysilane, methyl isopropoxysilane, methyl-n-butyloxysilane, methyl tri-sec-butyloxysilane, methyl tri-t-butyloxysilane, ethyl trimethoxysilane, ethyl triethoxysilane, ethyl tri-n-propoxysilane, ethyl isopropoxysilane, ethyl-n-butyloxysilane, ethyl tri-sec-butyloxysilane, ethyl tri-t-butyloxysilane, n-propyl trimethoxysilane, isobutyl trimethoxysilane, n-hexyl trimethoxysilane, hexadecyl trimethoxysilane, n-octyl trimethoxysilane, n-dodecyl trimethoxysilane, n-octadecyl trimethoxysilane, n-propyl triethoxysilane, isobutyl triethoxysilane, n-hexyl triethoxysilane, hexadecyl triethoxysilane, n-octyl triethoxysilane, n-dodecyl trimethoxysilane, n-octadecyl tri-

ethoxysilane, 2-[2-(trichlorosilyl)ethyl] pyridine, 4-[2-(trichlorosilyl)ethyl] pyridine, diphenyl dimethoxysilane, diphenyl diethoxysilane, 1,3-(trichlorosilyl methyl) heptacosane, dibenzyl dimethoxysilane, dibenzyl ethoxysilane, phenyl trimethoxysilane, phenyl methyl dimethoxysilane, phenyl dimethyl methoxysilane, phenyl dimethoxysilane, phenyl diethoxysilane, phenyl methyl diethoxysilane, phenyl dimethyl ethoxysilane, benzyl triethoxysilane, benzyl trimethoxysilane, benzyl methyl dimethoxysilane, benzyl dimethyl methoxysilane, benzyl dimethoxysilane, benzyl diethoxysilane, benzyl methyl diethoxysilane, benzyl dimethyl ethoxysilane, benzyl triethoxysilane, dibenzyl dimethoxysilane, dibenzyl diethoxysilane, 3-acetoxy propyl trimethoxysilane, 3-acryloxy propyl trimethoxysilane, allyl trimethoxysilane, allyl triethoxysilane, 4-aminobutyl triethoxysilane, (aminoethyl aminomethyl) phenethyl trimethoxysilane, N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, 6-(aminohexyl aminopropyl) trimethoxysilane, p-aminophenyl trimethoxysilane, p-aminophenyl ethoxysilane, m-aminophenyl trimethoxysilane, m-aminophenyl ethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, omega-aminoundecyl trimethoxysilane, amyl triethoxysilane, benzoxasilepin dimethyl ester, 5-(bicycloheptenyl) triethoxysilane, bis(2-hydroxyethyl)-3-aminopropyl triethoxysilane, 8-bromooctyl trimethoxysilane, bromophenyl trimethoxysilane, 3-bromopropyl trimethoxysilane, n-butyl trimethoxysilane, 2-chloromethyl triethoxysilane, chloromethyl methyl diethoxysilane, chloromethyl methyl diisopropoxysilane, p-(chloromethyl) phenyl trimethoxysilane, chloromethyl triethoxysilane, chlorophenyl triethoxysilane, 3-chloropropyl methyl dimethoxysilane, 3-chloropropyl triethoxysilane, 3-chloropropyl trimethoxysilane, 2-(4-chlorosulfonyl phenyl) ethyl trimethoxysilane, 2-cyanoethyl triethoxysilane, 2-cyanoethyl trimethoxysilane, cyanomethyl phenethyl triethoxysilane, 3-cyanopropyl triethoxysilane, 2-(3-cyclohexenyl) ethyl trimethoxysilane, 2-(3-cyclohexenyl) ethyl triethoxysilane, 3-cyclohexenyl trichlorosilane, 2-(3-cyclohexenyl) ethyl trichlorosilane, 2-(3-cyclohexenyl) ethyl dimethyl chlorosilane, 2-(3-cyclohexenyl) ethyl methyl dichlorosilane, cyclohexyl dimethyl chlorosilane, cyclohexyl ethyl dimethoxysilane, cyclohexyl methyl dichlorosilane, cyclohexyl methyl dimethoxysilane, (cyclohexyl methyl) trichlorosilane, cyclohexyl trichlorosilane, cyclohexyl trimethoxysilane, cyclooctyl trichlorosilane, (4-cyclooctenyl) trichlorosilane, cyclopentyl trichlorosilane, cyclopentyl trimethoxysilane, 1,1-diethoxy-1-silacyclopenta-3-ene, 3-(2,4-dinitrophenylamino) propyl triethoxysilane, (dimethylchlorosilyl) methyl-7,7-dimethylnorpinane, (cyclohexylaminomethyl) methyl diethoxysilane, (3-cyclopentadienyl) triethoxysilane, N,N-diethyl-3-aminopropyl trimethoxysilane, 2-(3,4-epoxy cyclohexyl) ethyl trimethoxysilane, 2-(3,4-epoxy cyclohexyl) ethyl tri-

ethoxysilane, (furfuryloxymethyl) triethoxysilane, 2-hydroxy-4-(3-triethoxypropoxy) diphenyl ketone, 3-(p-methoxyphenyl) propyl methyl dichlorosilane, 3-(p-methoxyphenyl) propyl trichlorosilane, p-(methyl phenethyl) methyl dichlorosilane, p-(methyl phenethyl) trichlorosilane, p-(methyl phenethyl) dimethyl chlorosilane, 3-morpholinopropyl trimethoxysilane, (3-glycidoxy propyl) methyl diethoxysilane, 3-glycidoxy propyl trimethoxysilane, 1,2,3,4,7,7-hexachloro-6-methyl diethoxysilyl-2-norbornene, 1,2,3,4,7,7-hexachloro-6-triethoxysilyl-2-norbornene, 3-iodopropyl trimethoxysilane, 3-isocyanate propyl triethoxysilane, (mercaptomethyl) methyl diethoxysilane, 3-mercaptopropyl methyl dimethoxysilane, 3-mercaptopropyl dimethoxysilane, 3-mercaptopropyl triethoxysilane, 3-methacryloxy propyl methyl diethoxysilane, 3-methacryloxy propyl trimethoxysilane, methyl {2-(3-trimethoxysilyl propylamino)ethylamino}-3-propionate, 7-octenyl trimethoxysilane, R-N-alpha-phenethyl-N'-triethoxysilyl propyl urea, S-N-alpha-phenethyl-N'-triethoxysilyl propyl urea, phenethyl trimethoxysilane, phenethyl methyl dimethoxysilane, phenethyl dimethyl methoxysilane, phenethyl dimethoxysilane, phenethyl diethoxysilane, phenethyl methyl diethoxysilane, phenethyl dimethyl ethoxysilane, phenethyl triethoxysilane, (3-phenylpropyl) dimethyl chlorosilane, (3-phenylpropyl) methyl dichlorosilane, N-phenylamino propyl trimethoxysilane, N-(triethoxysilyl propyl) dansylamide, N-(3-triethoxysilyl propyl)-4,5-dihydroimidazole, 2-(triethoxysilyl ethyl)-5-(chloroacetoxy) bicycloheptane, (S)-N-triethoxysilyl propyl-O-menthocarbamate, 3-(triethoxysilyl propyl)-p-nitro benzamide, 3-(triethoxysilyl) propyl succinic anhydride, N-[5-(trimethoxysilyl)-2-aza-1-oxo-pentyl] caprolactam, 2-(trimethoxysilyl ethyl) pyridine, N-(trimethoxysilyl ethyl) benzyl-N,N,N-trimethyl ammonium chloride, phenyl vinyl diethoxysilane, 3-thiocyanate propyl triethoxysilane, (tridecafluoro-1,1,2,2-tetrahydrooctyl) triethoxysilane, N-{3-(triethoxysilyl) propyl} phthalamide acid, (3,3,3-trifluoropropyl) methyl dimethoxysilane, (3,3,3-trifluoropropyl) trimethoxysilane, 1-trimethoxysilyl-2-(chloromethyl) phenyl ethane, 2-(trimethoxysilyl) ethyl phenyl sulfonyl azide, beta-trimethoxysilyl ethyl-2-pyridine, trimethoxysilyl propyl diethylene triamine, N-(3-trimethoxysilyl propyl) pyrrole, N-trimethoxysilyl propyl-N,N,N-tributyl ammonium bromide, N-trimethoxysilyl propyl-N,N,N-tributyl ammonium chloride, N-trimethoxysilyl propyl-N,N,N-trimethyl ammonium chloride, vinyl methyl diethoxysilane, vinyl triethoxysilane, vinyl trimethoxysilane, vinyl methyl dimethoxysilane, vinyl dimethyl methoxysilane, vinyl dimethyl ethoxysilane, vinyl methyl dichlorosilane, vinyl phenyl dichlorosilane, vinyl phenyl diethoxysilane, vinyl phenyl dimethyl silane, vinyl phenyl methyl chlorosilane, vinyl triphenoxysilane, vinyl tris-t-butoxysilane, adamantyl ethyl trichlorosilane, allyl phenyl trichlorosilane, (aminoethyl aminomethyl) phenethyl

trimethoxysilane, 3-aminophenoxy dimethyl vinyl silane, phenyl trichlorosilane, phenyl dimethyl chlorosilane, phenyl methyl dichlorosilane, benzyl trichlorosilane, benzyl dimethyl chlorosilane, benzyl dimethyl dichlorosilane, phenethyl diisopropyl chlorosilane, phenethyl trichlorosilane, phenethyl dimethyl chlorosilane, phenethyl methyl dichlorosilane, 5-(bicycloheptenyl) trichlorosilane, 5-(bicycloheptenyl) triethoxysilane, 2-(bicycloheptyl) dimethyl chlorosilane, 2-(bicycloheptyl) trichlorosilane, 1,4-bis(trimethoxysilyl ethyl) benzene, bromophenyl trichlorosilane, 3-phenoxy propyl dimethyl chlorosilane, 3-phenoxy propyl trichlorosilane, t-butyl phenyl chlorosilane, t-butyl phenyl methoxysilane, t-butyl phenyl dichlorosilane, p-(t-butyl) phenethyl dimethyl chlorosilane, p-(t-butyl) phenethyl trichlorosilane, 1,3-(chlorodimethylsilyl methyl) heptacosane, ((chloromethyl) phenyl ethyl) dimethyl chlorosilane, ((chloromethyl) phenyl ethyl) methyl dichlorosilane, ((chloromethyl) phenyl ethyl) trichlorosilane, ((chloromethyl) phenyl ethyl) trimethoxysilane, chlorophenyl trichlorosilane, 2-cyanoethyl trichlorosilane, 2-cyanoethyl methyl dichlorosilane, 3-cyanopropyl methyl diethoxysilane, 3-cyanopropyl methyl dichlorosilane, 3-cyanopropyl methyl dichlorosilane, 3-cyanopropyl dimethyl ethoxysilane, 3-cyanopropyl methyl dichlorosilane, 3-cyanopropyl trichlorosilane, fluorinated alkylsilane, and the like are able to be included, and a combination of at least one selected therefrom is able to be used.

- [0134] Among them, it is preferable that hexamethyl disilazane be used for the hydrophobization treatment. Accordingly, it is possible to further increase hydrophobicity of the particles. In addition, it is possible to more easily and reliably increase uniformity of the degree of the hydrophobization treatment in each of the portions (including the surface inside the pores) of each of the particles or the particle surfaces.
- [0135] When the hydrophobization treatment using the silane compound is performed in a liquid phase, the particles (the base particles) to be subjected to the hydrophobization treatment are immersed in liquid including the silane compound, and thus it is possible to preferably allow a desired reaction to be proceeded, and it is possible to form a chemical adsorption film of the silane compound.
- [0136] In addition, when the hydrophobization treatment using the silane compound is performed in a vapor phase, the particles (the base particles) to be subjected to the hydrophobization treatment are exposed to vapor of the silane compound, and it is possible to preferably allow a desired reaction to proceed, and it is possible to form the chemical adsorption film of the silane compound.
- [0137] An average particle diameter of the particles configuring the three-dimensional structure forming powder is not particularly limited, but is preferably greater than or equal to 1 micrometer and less than or equal to 25 micrometers, and more preferably greater than or equal to 1 micrometer and less than or equal to 15 micrometers. Ac-

Accordingly, it is possible to make mechanical strength of the three-dimensional structure 100 especially excellent, and it is possible to make dimensional accuracy of the three-dimensional structure 100 especially excellent by more effectively preventing the occurrence of the unintended concavities and convexities of the three-dimensional structure 100 to be manufactured. In addition, it is possible to make fluidity of the three-dimensional structure forming powder and fluidity of the three-dimensional structure forming composition including the three-dimensional structure forming powder especially excellent, and thus it is possible to make productivity of the three-dimensional structure especially excellent. Furthermore, in the invention, the average particle diameter is a volume-based average particle diameter, and for example, the average particle diameter is able to be obtained by adding a sample to methanol, and by analyzing a dispersion liquid dispersed by an ultrasonic dispersion instrument for 3 minutes using an aperture of 50 micrometers in a particle size distribution measuring instrument (TA-II Type manufactured by COULTER ELECTRONICS INS) using a Coulter counter method.

[0138] Dmax of the particles configuring the three-dimensional structure forming powder is, preferably greater than or equal to 3 micrometers and less than or equal to 40 micrometers, and more preferably greater than or equal to 5 micrometers and less than or equal to 30 micrometers. Accordingly, it is possible to make mechanical strength of the three-dimensional structure 100 especially excellent, and it is possible to make dimensional accuracy of the three-dimensional structure 100 especially excellent by more effectively preventing the occurrence of the unintended concavities and convexities of the three-dimensional structure 100 to be manufactured. In addition, it is possible to make fluidity of the three-dimensional structure forming powder and fluidity of the three-dimensional structure forming composition including the three-dimensional structure forming powder especially excellent, and thus it is possible to make productivity of the three-dimensional structure especially excellent.

[0139] Porosity of the particle configuring the three-dimensional structure forming powder is, preferably greater than or equal to 50%, and more preferably greater than or equal to 55% and less than or equal to 90%. Accordingly, the binding agent has sufficient penetrating space (the pores), and thus it is possible to make mechanical strength of the particle itself excellent. As a result, it is possible to make mechanical strength of the three-dimensional structure which is formed by allowing the binding agent to enter inside the pores especially excellent. Furthermore, in the invention, the porosity of the particle indicates a ratio (a volume fraction) of the pores existing in the particle with respect to an apparent volume of the particle, and when density of the particle is ρ [g/cm³], and real density of the constituent material of the particle is ρ_0 [g/cm³], the porosity is a value shown by $\{(\rho_0 - \rho) / \rho_0\} \times 100$.

- [0140] An average pore diameter (a fine pore diameter) of the particle is, preferably greater than or equal to 10 nm, and more preferably greater than or equal to 50 nm and less than or equal to 300 nm. Accordingly, it is possible to make mechanical strength of the finally obtained three-dimensional structure especially excellent. In addition, when a coloring ink including a pigment is used for manufacturing the three-dimensional structure, the pigment preferably being kept in the pores of the particle is possible. For this reason, it is possible to prevent unintended diffusion of the pigment, and thus it is possible to more reliably form a high-definition image.
- [0141] The particle configuring the three-dimensional structure forming powder may have any shape, and it is preferable that the particle be in the shape of a sphere. Accordingly, it is possible to make fluidity of the three-dimensional structure forming powder and fluidity of the three-dimensional structure forming composition including the three-dimensional structure forming powder especially excellent, and thus it is possible to make productivity of the three-dimensional structure especially excellent, and it is possible to make dimensional accuracy of the three-dimensional structure especially excellent by more effectively preventing the occurrence of the unintended concavities and convexities of the three-dimensional structure to be manufactured.
- [0142] The three-dimensional structure forming powder of the invention may include a plurality of types of particles of which conditions (for example, a constituent material of the particles, a type of hydrophobization treatment, or the like) as described above are different from each other.
- [0143] Voidage of the three-dimensional structure forming powder is, preferably greater than or equal to 70% and less than or equal to 98%, and more preferably greater than or equal to 75% and less than or equal to 97.7%. Accordingly, it is possible to make mechanical strength of the three-dimensional structure especially excellent. In addition, it is possible to make fluidity of the three-dimensional structure forming powder and fluidity of the three-dimensional structure forming composition including the three-dimensional structure forming powder especially excellent, and thus it is possible to make productivity of the three-dimensional structure especially excellent, and it is possible to make dimensional accuracy of the three-dimensional structure especially excellent by more effectively preventing the occurrence of the unintended concavities and convexities of the three-dimensional structure to be manufactured. Furthermore, in the invention, the voidage of the three-dimensional structure forming powder indicates a ratio of a sum of a volume of the pores of the entire particles configuring the three-dimensional structure forming powder and a volume of voids existing between the particles when a container with a predetermined capacity (for example, 100 mL) is filled with the three-dimensional structure forming powder to a capacity of a container, and when bulk density of the three-dimensional structure

forming powder is P [g/cm³], and real density of a constituent material of the three-dimensional structure forming powder is P_0 [g/cm³], the voidage is a value shown by $\{(P_0 - P) / P_0\} \times 100$.

[0144] <Three-dimensional structure forming composition>

Next, the three-dimensional structure forming composition of the invention will be described.

[0145] The three-dimensional structure forming composition of the invention includes at least the three-dimensional structure forming powder of the invention described above, and the water soluble resin. Accordingly, when the three-dimensional structure is manufactured, it is possible to allow the hydrophobic binding agent to preferably enter inside the pores of the particles configuring the three-dimensional structure forming powder, and thus it is possible to make mechanical strength of the three-dimensional structure to be manufactured excellent. In addition, before the binding agent is applied to the three-dimensional structure forming composition, the water soluble resin is effectively prevented from penetrating into the pores of the particles (the particles subjected to the hydrophobization treatment) configuring the three-dimensional structure forming powder in the three-dimensional structure forming composition. For this reason, a function of the water soluble resin for temporary fixing the particles is reliably realized, and it is possible to reliably prevent occurrence of a problem in which the water soluble resin penetrates into the pores of the particles in advance, and thus the penetrating space of the binding agent is not able to be secured.

[0146] <Water soluble Resin>

The three-dimensional structure forming composition 1' includes the water soluble resin 12 together with a plurality of particles 11. By including the water soluble resin 12, the particles 11 are bound (temporarily fixed) (refer to Fig. 3), and thus it is possible to effectively prevent the unintended scattering of the particles 11 or the like. Accordingly, it is possible to improve safety of the operator and dimensional accuracy of the three-dimensional structure 100 to be manufactured.

[0147] In the invention, at least a part of the water soluble resin may be soluble in water, and for example, solubility with respect to water (mass dissolvable in 100 g of water) at 25 degrees Celsius is preferably greater than or equal to 5 [g/100 g of water], and is more preferably greater than or equal to 10 [g/100 g of water].

[0148] As the water soluble resin 12, for example, a synthetic polymer such as polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), polycaprolactam diol, sodium polyacrylate, polyacrylamide, modified polyamide, polyethylene imine, polyethylene oxide, and a random copolymer of ethylene oxide and propylene oxide, a natural polymer such as corn starch, mannan, pectin, agar, alginic acid, dextran, glue, and gelatin, a semi-synthetic polymer such as carboxymethyl cellulose, hydroxyethyl

cellulose, oxidized starch, and modified starch, and the like are included, and a combination of at least one selected therefrom is able to be used.

[0149] As a specific example of the water soluble resin product, for example, methyl cellulose (manufactured by Shin-Etsu Chemical Co., Ltd., Metolose SM-15), hydroxyethyl cellulose (manufactured by Fuji Chemical Co., AL-15), hydroxy propyl cellulose (manufactured by Nippon Soda Co., Ltd., HPC-M), carboxymethyl cellulose (manufactured by Nichirin Chemical Co., Ltd., CMC-30), starch phosphate ester sodium (I) (manufactured by Matsutani Chemical Co., Hosta 5100), polyvinyl pyrrolidone (manufactured by Tokyo Chemical Co., PVP K-90), methyl vinyl ether/a maleic acid copolymer (manufactured by GAF Gauntlet Inc. AN-139), polyacrylamide (manufactured by Wako Pure Chemical Industries, Ltd.), modified polyamide (modified nylon) (manufactured by Toray Industries, Inc., Ltd., AQ nylon), polyethylene oxide (manufactured by Steel Chemical Co., Ltd., PEO-1, manufactured by Meisei Chemical Works, Ltd., Alkox), a random copolymer of ethylene oxide and propylene oxide (manufactured by Meisei Chemical Works, Ltd., Alkox EP), sodium polyacrylate (manufactured by Wako Pure Chemical Industries, Ltd.), a carboxy vinyl polymer/a cross-linked acryl-based water soluble resin (manufactured by Sumitomo Seika Chemicals Co., Ltd., Aqupec), and the like are included.

[0150] Among them, when the water soluble resin 12 is polyvinyl alcohol, it is possible to make mechanical strength of the three-dimensional structure 100 especially excellent. In addition, by adjusting a saponification degree or polymerization degree, it is possible to more preferably control properties (for example, water solubility, water resistance, or the like) of the water soluble resin 12 or properties (for example, viscosity, fixing force of the particles 11, wettability, or the like) of the three-dimensional structure forming composition 1'. For this reason, it is possible to more preferably support manufacturing of various three-dimensional structures 100. In addition, among various water soluble resins, polyvinyl alcohol is inexpensive, and there is a stable supply thereof. For this reason, it is possible to reduce the production cost and to perform stable manufacturing of the three-dimensional structure 100.

[0151] When the water soluble resin 12 includes polyvinyl alcohol, the saponification degree of polyvinyl alcohol is, preferably greater than or equal to 85 and less than or equal to 90. Accordingly, it is possible to inhibit solubility of polyvinyl alcohol with respect to water from being decreased. For this reason, when the three-dimensional structure forming composition 1' includes water, it is possible to more effectively inhibit adhesiveness between adjacent layers 1 from being decreased.

[0152] When the water soluble resin 12 includes polyvinyl alcohol, the polymerization degree of polyvinyl alcohol is, preferably greater than or equal to 300 and less than or equal to 1000. Accordingly, when the three-dimensional structure forming composition

1' includes water, it is possible to make mechanical strength of each layer 1 or adhesiveness between adjacent layers 1 especially excellent.

[0153] In addition, when the water soluble resin 12 is polyvinyl pyrrolidone (PVP), the following effects are obtained. That is, polyvinyl pyrrolidone has excellent adhesiveness with respect to various materials such as glass, metal, and plastic, and thus it is possible to make strength and shape stability of a portion onto which the ink is applied in the layer 1 especially excellent, and it is possible to make dimensional accuracy of the finally obtained three-dimensional structure 100 especially excellent. In addition, polyvinyl pyrrolidone exhibits high solubility with respect to various organic solvents, and thus when the three-dimensional structure forming composition 1' includes an organic solvent, it is possible to make fluidity of the three-dimensional structure forming composition 1' especially excellent. In addition, it is possible to preferably form the layer 1 in which an unintended variation in a thickness is more effectively prevented, and thus it is possible to make dimensional accuracy of the finally obtained three-dimensional structure 100 especially excellent. In addition, polyvinyl pyrrolidone exhibits high solubility with respect to water, and thus it is possible to easily and reliably remove the particles which are not bound by the binding agent 21 among the particles 11 configuring each layer 1 in the unbound particle removing process (after the formation is ended). In addition, polyvinyl pyrrolidone has suitable affinity with the three-dimensional structure forming powder, and thus it is difficult to sufficiently cause polyvinyl pyrrolidone to penetrate into the pores 111 as described above. On the other hand, polyvinyl pyrrolidone has relatively high wettability with respect to the surface of the particles 11. For this reason, it is possible to more effectively realize a function of temporary fixing as described above. In addition, polyvinyl pyrrolidone has excellent affinity with various colorants, and thus when the ink 2 including the colorant is used in the ink applying process, it is possible to effectively prevent the colorant from unintentionally diffusing. In addition, polyvinyl pyrrolidone has an antistatic function, and thus when a powder which is not fixed is used as the three-dimensional structure forming composition 1' in the layer forming process, it is possible to effectively prevent the powder from being scattered. In addition, when a powder which is fixed is used as the three-dimensional structure forming composition 1' in the layer forming process, it is possible to effectively prevent bubbles from being entrained into the three-dimensional structure forming composition 1' when the paste-like three-dimensional structure forming composition 1' includes polyvinyl pyrrolidone, and it is possible to more effectively prevent occurrence of a defect due to the entrained bubbles in the layer forming process.

[0154] When the water soluble resin 12 includes polyvinyl pyrrolidone, a weight average molecular weight of the polyvinyl pyrrolidone is, preferably greater than or equal to

10000 and less than or equal to 1700000, and more preferably greater than or equal to 30000 and less than or equal to 1500000. Accordingly, it is possible to more effectively realize the functions described above.

[0155] In addition, when the water soluble resin 12 includes polycaprolactam diol, it is possible to preferably form the three-dimensional structure forming composition 1' in a pellet-state, and it is possible to effectively prevent unintended scattering of the particles 11 or the like, and thus handleability (easiness of handling) of the three-dimensional structure forming composition 1' is improved. Therefore, it is possible to improve safety of the operator and dimensional accuracy of the three-dimensional structure 100 to be manufactured. In addition, the three-dimensional structure forming composition is able to be melted at a relatively low temperature, and thus it is possible to reduce energy and cost required for producing the three-dimensional structure 100, and it is possible to make productivity of the three-dimensional structure 100 sufficiently excellent.

[0156] When the water soluble resin 12 includes polycaprolactam diol, a weight average molecular weight of the polycaprolactam diol is, preferably greater than or equal to 10000 and less than or equal to 1700000, and more preferably greater than or equal to 30000 and less than or equal to 1500000. Accordingly, it is possible to more effectively realize the functions described above.

[0157] In the three-dimensional structure forming composition 1', it is preferable that the water soluble resin 12 be in a liquid state (for example, a dissolved state, a melted state, or the like) at least in the layer forming process. Accordingly, it is possible to more easily and reliably increase uniformity in thickness of the layer 1 formed by using the three-dimensional structure forming composition 1'.

[0158] <Three-dimensional structure forming powder>

The three-dimensional structure forming composition of the invention includes the three-dimensional structure forming powder as described above.

[0159] A content ratio of the three-dimensional structure forming powder in the three-dimensional structure forming composition 1' is, preferably greater than or equal to 10 mass% and less than or equal to 90 mass%, and more preferably greater than or equal to 15 mass% and less than or equal to 65 mass%. Accordingly, it is possible to make fluidity of the three-dimensional structure forming composition 1' sufficiently excellent, and it is possible to make mechanical strength of the finally obtained three-dimensional structure 100 especially excellent.

[0160] <Solvent>

The three-dimensional structure forming composition 1' may include the solvent in addition to the water soluble resin 12 and the three-dimensional structure forming powder as described above, accordingly, it is possible to make fluidity of the three-

dimensional structure forming composition 1' especially excellent, and it is possible to make productivity of the three-dimensional structure 100 especially excellent.

[0161] It is preferable that the solvent dissolve the water soluble resin 12. Accordingly, it is possible to make fluidity of the three-dimensional structure forming composition 1' excellent, and it is possible to more effectively prevent the unintended variation in the thickness of the layer 1 formed by using the three-dimensional structure forming composition 1'. In addition, at the time of forming the layer 1 in a state where the solvent is removed, it is possible to attach the water soluble resin 12 to the particles 11 with higher uniformity over the entire layer 1, and it is possible to more effectively prevent occurrence of unintended unevenness in a composition. For this reason, it is possible to more effectively prevent occurrence of an unintended variation in mechanical strength of each portion of the finally obtained three-dimensional structure 100, and it is possible to further increase reliability of the three-dimensional structure 100.

[0162] As the solvent configuring the three-dimensional structure forming composition 1', for example, water; an alcoholic solvent such as methanol, ethanol, and isopropanol; a ketone-based solvent such as methyl ethyl ketone, and acetone; a glycol ether-based solvent such as ethylene glycol monoethyl ether, and ethylene glycol monobutyl ether; a glycol ether acetate-based solvent such as propylene glycol-1-monomethylether-2-acetate, and propylene glycol-1-monoethylether-2-acetate; polyethylene glycol, poly propylene glycol, and the like are included, and a combination of at least one selected therefrom is able to be used.

[0163] Among them, it is preferable that the three-dimensional structure forming composition 1' include water. Accordingly, it is possible to more reliably dissolve the water soluble resin 12, and it is possible to make fluidity of the three-dimensional structure forming composition 1' and uniformity of the composition of the layer 1 formed by using the three-dimensional structure forming composition 1' especially excellent. In addition, the water is easily removed after forming the layer 1, and even when the water remains in the three-dimensional structure 100, it is difficult for the water to exert a negative effect. In addition, it is advantageous from a viewpoint of safety with respect to the human body, and environmental concerns.

[0164] When the three-dimensional structure forming composition 1' includes the solvent, a content ratio of the solvent in the three-dimensional structure forming composition 1' is, preferably greater than or equal to 5 mass% and less than or equal to 75 mass%, and more preferably greater than or equal to 35 mass% and less than or equal to 70 mass%. Accordingly, it is possible to more remarkably realize an effect which is obtained by including the solvent described above, and it is possible to easily remove the solvent in the manufacturing process of the three-dimensional structure 100 in a short period of time, and thus it is advantageous from a viewpoint of further improving productivity of

the three-dimensional structure 100.

[0165] In particular, when the three-dimensional structure forming composition 1' includes water as the solvent, a content ratio of the water in the three-dimensional structure forming composition 1' is, preferably greater than or equal to 20 mass% and less than or equal to 73 mass%, and more preferably greater than or equal to 50 mass% and less than or equal to 70 mass%. Accordingly, it is possible to more remarkably realize the effect as described above.

<Other Components>

[0166] In addition, the three-dimensional structure forming composition 1' may include a component in addition to the components described above. As the component, for example, a polymerization initiator; a polymerization accelerator; a penetration enhancer; a wetting agent (a moisturizing agent); a fixing agent; an antifungal agent; an antiseptic agent; an antioxidizing agent; an ultraviolet ray absorber; a chelating agent; a pH adjuster, and the like are included.

[0167] <Three-dimensional structure>

The three-dimensional structure of the invention is manufactured by using the three-dimensional structure forming composition as described above. Accordingly, it is possible to provide the three-dimensional structure with excellent mechanical strength.

[0168] An intended purpose of the three-dimensional structure according to the invention is not particularly limited, but for example, an aesthetic object and an exhibit such as a doll, or a figure; a medical instrument such as an implant, and the like are included.

[0169] In addition, the three-dimensional structure of the invention may be applied to any one of a prototype, a mass-produced product, and a tailor-made product.

[0170] As described above, the preferred embodiment of the invention has been described, but the invention is not limited thereto.

[0171] For example, the three-dimensional structure of the invention may be manufactured by using the three-dimensional structure forming composition described above, but is not limited to being manufactured by using the method described above.

[0172] More specifically, for example, in the embodiment described above, a case where the curing process, in addition to the layer forming process and the ink applying process, is also repeated along with the layer forming process and the ink applying process is described, but the curing process may not be repeated. For example, after a laminated body including a plurality of layers which is not cured is formed, the laminated body may be collectively cured. In addition, when the binding agent is not a curable component, the curing process is able to be omitted.

[0173] In addition, in the manufacturing method of the invention, as necessary, a pre-processing process, an intermediate-processing process, and a post-processing process may be performed.

- [0174] As the pre-processing process, for example, a sweeping process of the support (the stage) and the like are included.
- [0175] As the intermediate-processing process, for example, when the three-dimensional structure forming composition is formed in a pellet-state, a process (a water soluble resin solidifying process) for stopping heating or the like may be included between the layer forming process and the ink applying process. Accordingly, the water soluble resin is able to be in a solid state, and thus it is possible to obtain the layer in which binding force between the particles is stronger. In addition, for example, when the three-dimensional structure forming composition includes a solvent component (a dispersion medium) such as water, a solvent component removing process of removing the solvent component may be included between the layer forming process and the ink applying process. Accordingly, it is possible to more smoothly perform the layer forming process, and thus it is possible to more effectively prevent the unintended variation in the thickness of the layer to be formed. As a result, it is possible to manufacture the three-dimensional structure with higher dimensional accuracy at higher productivity.
- [0176] As the post-processing process, for example, a cleaning process, a shape adjusting process of performing deburring or the like, a coloring process, a covering layer forming process, a binding agent curing completion process of performing light irradiation processing which reliably cures uncured binding agent or heat processing, and the like are included.
- [0177] In addition, in the embodiment described above, a case where the ink is applied onto all the layers is described, but there may be a layer onto which the ink is not applied. For example, the ink may not be applied onto a layer formed immediately on the support (the stage), and this layer may function as a sacrificial layer.
- [0178] In addition, in the embodiment described above, a case where the ink applying process is performed by the ink jet method is mainly described, but the ink applying process may be performed by using other methods (for example, other printing methods).

Examples

- [0179] The invention will be more described in detail with reference to the following specific examples, but the invention is not limited to the examples. Furthermore, in the following description, processing which does not particularly indicate a temperature condition is performed at room temperature (25 degrees Celsius). In addition, various measurement conditions which do not particularly indicate a temperature condition are values at room temperature (25 degrees Celsius).
- [0180] <1 Manufacturing of Three-dimensional structure forming composition>

Example 1

- [0181] First, a synthetic amorphous silica powder including a plurality of porous particles was prepared.
- [0182] The hydrophobization treatment was performed by stirring the silica powder in hexamethyl disilazane vapor at 40 degrees Celsius. By the hydrophobization treatment, the three-dimensional structure forming powder in which a methyl group was introduced into a surface including insides of the pores was obtained.
- [0183] The average particle diameter of the particles configuring the obtained three-dimensional structure forming powder was 2.6 micrometers, Dmax was 10 micrometers, the porosity was 80%, and the average pore diameter was 60 nm. In addition, the voidage of the three-dimensional structure forming powder was 93%. Furthermore, the average particle diameter and Dmax were obtained by adding a sample to methanol, and by analyzing a dispersion liquid dispersed by an ultrasonic dispersion instrument for 3 minutes using an aperture of 50 micrometers in a particle size distribution measuring instrument (TA-II Type manufactured by COULTER ELECTRONICS INS) using a Coulter counter method. In addition, the porosity and the average pore diameter were obtained by a mercury measuring method using a Porosimeter 2000 (manufactured by Amco Inc.).
- [0184] Next, the three-dimensional structure forming powder obtained therefrom: 100 parts by mass, water: 325 parts by mass, and polyvinyl pyrrolidone (weight average molecular weight: 50000): 50 parts by mass were mixed, and thus the three-dimensional structure forming composition was obtained.

Examples 2 to 11

- [0185] The three-dimensional structure forming composition was manufactured by the same method as described in Example 1 except that a configuration of the three-dimensional structure forming composition was changed as shown in Table 1 by changing types of raw material used for manufacturing the three-dimensional structure forming composition, and a mixing ratio of each component.
- [0186] <Comparative Example 1>
- The three-dimensional structure forming composition was manufactured by the same method as described in Examples except that a powder including particles which had no pores was used as the three-dimensional structure forming powder.
- [0187] <Comparative Example 2>
- The three-dimensional structure forming composition was manufactured by the same method as described in Example 1 except that a synthetic amorphous silica powder including a plurality of porous particles which was not subjected to the hydrophobization treatment was used as the three-dimensional structure forming powder.

[0188] <Comparative Example 3>

The three-dimensional structure forming composition was manufactured by the same method as described in Example 1 except that the synthetic amorphous silica powder including the plurality of porous particles which was not subjected to the hydrophobization treatment was used as the three-dimensional structure forming powder, and a mixing ratio of the three-dimensional structure forming powder and water was changed without using the water soluble resin.

[0189] Configurations of the three-dimensional structure forming compositions of the respective Examples and Comparative Examples are collectively shown in Table 1. Furthermore, in Table 1, polymethyl methacrylate is shown by "PMMA", polyvinyl pyrrolidone is shown by "PVP", polyvinyl alcohol is shown by "PVA", polycaprolactam diol is shown by "PCDO", poly(ethylene oxide) is shown by "P(EO)", an ethylene oxide/propylene oxide copolymer is shown by "P(EPO)", hexamethyl disilazane is shown by "HMDS", and diethyl diethoxysilane is shown by "DEDES". In addition, the solubility of all of the water soluble resins included in the three-dimensional structure forming compositions of the respective Examples with respect to water at 25 degrees Celsius was greater than or equal to 20 [g/100 g of water].

[0190]

[Table 1]

Three-dimensional structure forming powder															Water Soluble Resin					Solvent	
	Composition of Base Particle	Presence or Absence of Hydrophobization treatment	Functional Group Introduced By Hydrophobization treatment	Hydrophobization treatment Agent	Average Particle Diameter [micrometers]	Presence or Absence of Pores	Porosity [%]	Average Pore Diameter [nm]	Voidage [%]	Content ratio [mass%]	Composition	Mw	Polymerization Degree	Saponification Degree	Content ratio [mass%]	Composition					
Example 1	SiO ₂	Present	Methyl Group	HMDS	2.6	Present	80	60	93	21.1	PVP	50000	-	-	10.5	H ₂ O					
Example 2	SiO ₂	Present	Methyl Group	HMDS	4.4	Present	64	40	86	33.0	PVA	-	500	88	8.8	H ₂ O					
Example 3	TiO ₂	Present	Methyl Group	HMDS	3.7	Present	50	80	75	62.1	PVP	1200000	-	-	5.0	H ₂ O					
Example 4	PMMA	Present	Methyl Group	HMDS	6.2	Present	17	120	66	45.0	PVA	-	500	94	7.2	H ₂ O					
Example 5	SiO ₂	Present	Methyl Group	DEDES	4.4	Present	64	40	86	33.0	PVA	-	1500	93	8.8	H ₂ O					
Example 6	SiO ₂	Present	Methyl Group	HMDS	4.4	Present	64	40	86	33.0	PVA	-	1500	87	8.8	H ₂ O					
Example 7	SiO ₂	Present	Methyl Group	HMDS	4.4	Present	64	40	86	33.0	PVA	-	2400	88	8.8	H ₂ O					
Example 8	SiO ₂	Present	Methyl Group	HMDS	4.4	Present	64	40	86	33.0	PVA	-	500	88	17.7	H ₂ O					
Example 9	SiO ₂	Present	Methyl Group	HMDS	4.4	Present	64	40	86	78.9	PCDO	-	-	-	21.1	-					
Example 10	TiO ₂	Present	Methyl Group	HMDS	3.7	Present	50	80	75	92.6	P(EO)	-	-	-	7.4	-					
Example 11	PMMA	Present	Methyl Group	HMDS	6.2	Present	17	120	66	86.2	PCDO	-	-	-	13.8	-					
Comparative Example 1	SiO ₂	Present	Methyl Group	HMDS	2.6	Absent	-	-	37.9	77.7	PVP	50000	-	-	2.7	H ₂ O					
Comparative Example 2	SiO ₂	Absent	-	-	2.6	Present	80	60	93	21.1	PVP	50000	-	-	10.5	H ₂ O					
Comparative Example 3	SiO ₂	Absent	-	-	2.6	Present	80	60	93	21.1	-	-	-	-	-	H ₂ O					

[0191] <2 Manufacturing of Three-dimensional structure>

By using the three-dimensional structure forming composition of the respective Examples and Comparative Examples, a shape illustrated in Fig. 5, that is, a three-dimensional structure A in which a thickness was 4 mm and a length was 150 mm, a width of regions disposed at both ends (an upper side and a lower side in the drawing) illustrated as a hatched line portion was 20 mm and a length thereof was 35 mm, and a width of a region between the regions was 10 mm and a length thereof was 80 mm, and a shape illustrated in Fig. 6, that is, a three-dimensional structure B in the shape of a cube in which a thickness was 4 mm, a width was 10 mm, and a length was 80 mm

were manufactured as described below.

[0192] First, the manufacturing of the three-dimensional structure using the three-dimensional structure forming compositions of Examples 1 to 8 and Comparative Examples 1 and 2 will be described.

[0193] First, a three-dimensional structure apparatus was prepared, and a layer with a thickness of 100 micrometers was formed on the surface of the support (the stage) by the squeegee method using the three-dimensional structure forming composition (the layer forming process).

[0194] Next, after forming the layer, water included in the three-dimensional structure forming composition was removed by being left at room temperature for 1 minute.

[0195] Next, the ink was applied onto the layer configured of the three-dimensional structure forming composition by the ink jet method in a predetermined pattern (the ink applying process). As the ink, an ink of which the viscosity was 22 mPa·s at 25 degrees Celsius in the following compositions was used.

<Polymerizable Compounds>

[0196] - 2-(2-Vinyloxyethoxy) ethyl acrylate: 32 mass%
 - Polyether-based aliphatic urethane acrylate oligomer: 10 mass%
 - 2-Hydroxy-3-phenoxy propyl acrylate: 13.75 mass%
 - Dipropylene glycol diacrylate: 15 mass%
 - 4-Hydroxy butyl acrylate: 20 mass%

[0197] <Polymerization Initiator>

- Bis(2,4,6-trimethyl benzoyl)-phenyl phosphine oxide: 5 mass%
 - 2,4,6-trimethyl benzoyl-diphenyl-phosphine oxide: 4 mass%

[0198] <Fluorescent Brightening Agent (Sensitizer)>

- 1,4-Bis-(benzoxazol-2-yl) naphthalene: 0.25 mass%

[0199] Next, the layer was irradiated with ultraviolet rays, and thus the binding agent included in the three-dimensional structure forming composition was cured (the curing process).

[0200] Subsequently, the ink applying pattern was changed according to the shape of the three-dimensional structure to be manufactured, and serial processes of the layer forming process to the curing process were repeated such that a plurality of layers was laminated.

[0201] Subsequently, the laminated body obtained therefrom was immersed in water, and the particles (the unbound particles) which were not bound by the binding agent among the particles configuring each of the layers were removed by applying ultrasonic vibration, and thus two three-dimensional structures A and two three-dimensional structures B were obtained, respectively.

[0202] Subsequently, drying processing was performed at 60 degrees Celsius for 20

minutes.

[0203] Next, the manufacturing of the three-dimensional structure using the three-dimensional structure forming compositions of Examples 9 to 11 will be described.

[0204] First, the pellet-like three-dimensional structure forming composition was heated to 70 degrees Celsius, and the water soluble resin was softened, and thus the three-dimensional structure forming composition was brought into a liquid state with fluidity.

[0205] Next, a temperature of the three-dimensional structure forming composition was maintained at 70 degrees Celsius, and a layer with a thickness of 100 micrometers was formed on the surface of the support (the stage) of the three-dimensional structure apparatus by the squeegee method using the three-dimensional structure forming composition (the layer forming process).

[0206] Next, the temperature of the formed layer was chilled (cooled) to lower than or equal to 30 degrees Celsius.

[0207] Next, the ink was applied onto the layer configured of the three-dimensional structure forming composition by the ink jet method in a predetermined pattern (the ink applying process). An ink of which the viscosity was 22 mPa·s at 25 degrees Celsius in the following compositions was used.

[0208] <Polymerizable Compounds>

- 2-(2-Vinyloxyethoxy) ethyl acrylate: 32 mass%
- Polyether-based aliphatic urethane acrylate oligomer: 10 mass%
- 2-Hydroxy-3-phenoxy propyl acrylate: 13.75 mass%
- Dipropylene glycol diacrylate: 15 mass%
- 4-Hydroxy butyl acrylate: 20 mass%

[0209] <Polymerization Initiators>

- Bis(2,4,6-trimethyl benzoyl)-phenyl phosphine oxide: 5 mass%
- 2,4,6-Trimethyl benzoyl-diphenyl-phosphine oxide: 4 mass%

[0210] <Fluorescent Brightening Agent (Sensitizer)>

- 1,4-Bis-(benzoxazolyl-2-yl) naphthalene: 0.25 mass%

[0211] Next, the layer was irradiated with ultraviolet rays, and thus the binding agent included in the three-dimensional structure forming composition was cured (the curing process).

[0212] Subsequently, the ink applying pattern was changed according to the shape of the three-dimensional structure to be manufactured, and serial processes of the layer forming process to the curing process were repeated such that a plurality of layers was laminated.

[0213] Subsequently, the laminated body obtained therefrom was immersed in water, and the particles (the unbound particles) which were not bound by the binding agent among

the particles configuring each of the layers were removed by applying ultrasonic vibration, and thus two three-dimensional structures A and two three-dimensional structures B were obtained, respectively.

[0214] Subsequently, drying processing was performed at 60 degrees Celsius for 20 minutes.

[0215] <3 Evaluation>

<3.1 Scattering of Powder>

A degree of scattering of powder at the time of manufacturing the three-dimensional structures of the respective Examples and Comparative Examples was evaluated according to the following criteria.

- [0216] A: Scattering of powder was not observed.
B: Scattering of powder was hardly observed.
C: Scattering of powder was slightly observed.
D: Scattering of powder was definitely observed.
E: Scattering of powder was remarkably observed.

[0217] <3.2 Tensile Strength and Tensile Modulus of Elasticity>

The three-dimensional structures A of the respective Examples and Comparative Examples were measured based on JIS K 7161: 1994 (ISO 527: 1993) under a condition where tensile yield stress was 50 mm/min and a tensile modulus of elasticity was 1 mm/min, and thus the tensile strength and the tensile modulus of elasticity were evaluated according to the following criteria.

[0218] <Tensile Strength>

- A: Tensile strength was greater than or equal to 35 MPa.
B: Tensile strength was greater than or equal to 30 MPa and less than 35 MPa.
C: Tensile strength was greater than or equal to 20 MPa and less than 30 MPa.
D: Tensile strength was greater than or equal to 10 MPa and less than 20 MPa.
E: Tensile strength was less than 10 MPa.

[0219] <Tensile Modulus of Elasticity>

- A: Tensile modulus of elasticity was greater than or equal to 1.5 GPa.
B: tensile modulus of elasticity was greater than or equal to 1.3 GPa and less than 1.5 GPa.
C: Tensile modulus of elasticity was greater than or equal to 1.1 GPa and less than 1.3 GPa.
D: Tensile modulus of elasticity was greater than or equal to 0.9 GPa and less than 1.1 GPa.
E: Tensile modulus of elasticity was less than 0.9 GPa.

[0220] <3.3 Flexural Strength and Flexural Modulus>

The three-dimensional structures B of the respective Examples and Comparative

Examples were measured based on JIS K 7171: 1994 (ISO 178: 1993) under a condition where a distance between points was 64 mm and a test speed was 2 mm/min, and thus the flexural strength and the flexural modulus were evaluated according to the following criteria.

[0221] <Flexural Strength>

A: Flexural strength was greater than or equal to 65 MPa.

B: Flexural strength was greater than or equal to 60 MPa and less than 65 MPa.

C: Flexural strength was greater than or equal to 45 MPa and less than 60 MPa.

D: Flexural strength was greater than or equal to 30 MPa and less than 45 MPa.

E: Flexural strength was less than 30 MPa.

[0222] <Flexural Modulus>

A: Flexural modulus was greater than or equal to 2.4 GPa.

B: Flexural modulus was greater than or equal to 2.3 GPa and less than 2.4 GPa.

C: Flexural modulus was greater than or equal to 2.2 GPa and less than 2.3 GPa.

D: Flexural modulus was greater than or equal to 2.1 GPa and less than 2.2 GPa.

E: Flexural modulus was less than 2.1 GPa.

[0223] The results are collectively shown in Table 2.

[0224] [Table 2]

	Scattering of Powder	Tensile Strength	Tensile Modulus of Elasticity	Flexural Strength	Flexural Modulus
Example 1	A	A	A	A	A
Example 2	A	A	A	A	A
Example 3	A	A	A	A	A
Example 4	A	C	B	C	B
Example 5	A	B	B	B	B
Example 6	A	B	B	B	B
Example 7	A	C	B	C	B
Example 8	A	C	B	C	B
Example 9	A	A	A	A	A
Example 10	A	A	A	A	A
Example 11	A	B	B	B	B
Comparative Example 1	A	D	D	D	D
Comparative Example 2	A	E	E	E	E
Comparative Example 3	E	E	E	E	E

[0225] As is obvious from Table 2, in the invention, the three-dimensional structure with excellent mechanical strength was obtained. In addition, in the invention, scattering of powder at the time of manufacturing the three-dimensional structure was effectively prevented. In contrast, in Comparative Example, it was not possible to make mechanical strength of the three-dimensional structure sufficiently excellent. In addition, in Comparative Example 3, scattering of powder at the time of manufacturing the

three-dimensional structure was remarkable.

Reference Signs List

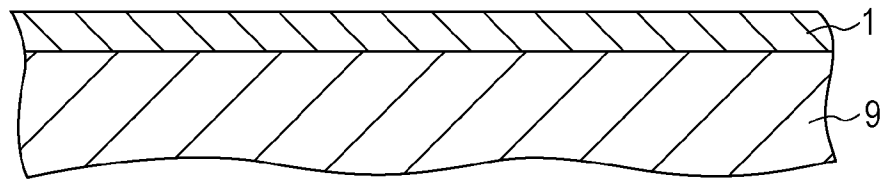
- [0226] 1' Three-dimensional structure forming composition
- 11 Particle
- 111 Pore
- 12 Water soluble resin
- 1 Layer
- 2 Ink
- 21 Binding agent
- 3 Cured portion
- 100 Three-dimensional structure
- 9 Support (Stage)

Claims

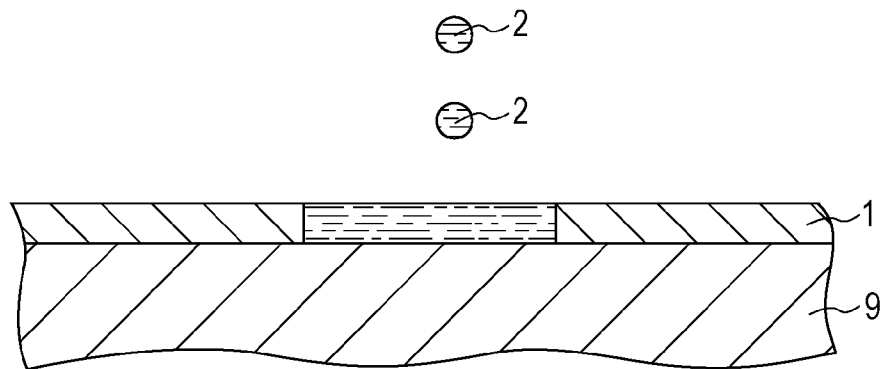
- [Claim 1] 1. A three-dimensional structure forming powder, comprising:
a plurality of particles,
wherein the particles are porous, and are subjected to a hydrophobization treatment.
- [Claim 2] The three-dimensional structure forming powder according to Claim 1,
wherein the hydrophobization treatment introduces a hydrocarbon group.
- [Claim 3] The three-dimensional structure forming powder according to Claim 1 or 2,
wherein porosity of the particle is greater than or equal to 50%.
- [Claim 4] The three-dimensional structure forming powder according to any one of Claims 1 to 3,
wherein an average pore diameter of the particles is greater than or equal to 10 nm.
- [Claim 5] The three-dimensional structure forming powder according to any one of Claims 1 to 4,
wherein an average particle diameter of the particles is greater than or equal to 1 micrometer and less than or equal to 25 micrometers.
- [Claim 6] The three-dimensional structure forming powder according to any one of Claims 1 to 5,
wherein the particle is configured of silica.
- [Claim 7] A three-dimensional structure forming composition, comprising:
the three-dimensional structure forming powder according to any one of Claims 1 to 6; and
a water soluble resin.
- [Claim 8] The three-dimensional structure forming composition according to Claim 7, further comprising water.
- [Claim 9] The three-dimensional structure forming composition according to Claim 7 or 8,
wherein a content ratio of the water in the three-dimensional structure forming composition is greater than or equal to 20 mass% and less than or equal to 73 mass%.
- [Claim 10] The three-dimensional structure forming composition according to any one of Claims 7 to 9,
wherein the water soluble resin is polyvinyl alcohol.
- [Claim 11] The three-dimensional structure forming composition according to any

- one of Claims 7 to 10,
wherein the water soluble resin is polyvinyl pyrrolidone.
- [Claim 12] The three-dimensional structure forming composition according to any one of Claims 7 to 10,
wherein the water soluble resin is polycaprolactam diol.
- [Claim 13] A manufacturing method of a three-dimensional structure, comprising:
a layer forming process of forming a layer of a predetermined thickness
by using the three-dimensional structure forming composition
according to any one of Claims 7 to 12; and
an ink applying process of applying an ink which includes a hydrophobic binding agent onto the layer,
wherein the processes are repeated in sequence.
- [Claim 14] The manufacturing method of the three-dimensional structure
according to Claim 13,
wherein the ink applying process is performed by an ink jet method.
- [Claim 15] A three-dimensional structure which is manufactured by using the
three-dimensional structure forming composition according to any one
of Claims 7 to 12.

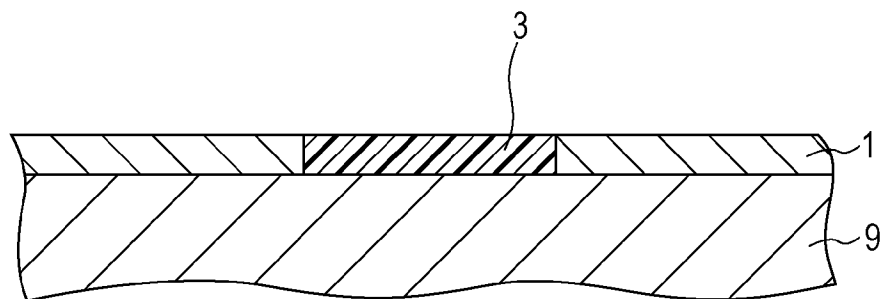
[Fig. 1A]



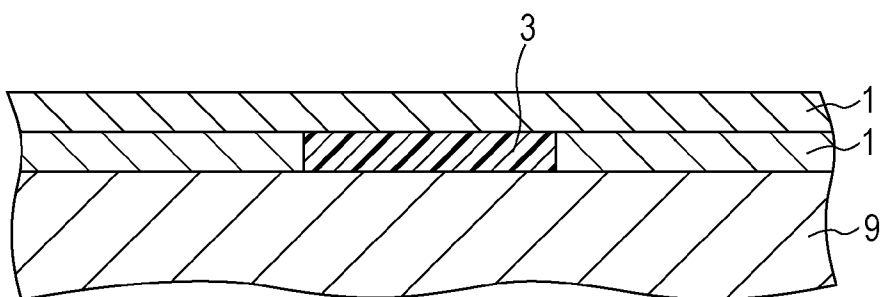
[Fig. 1B]



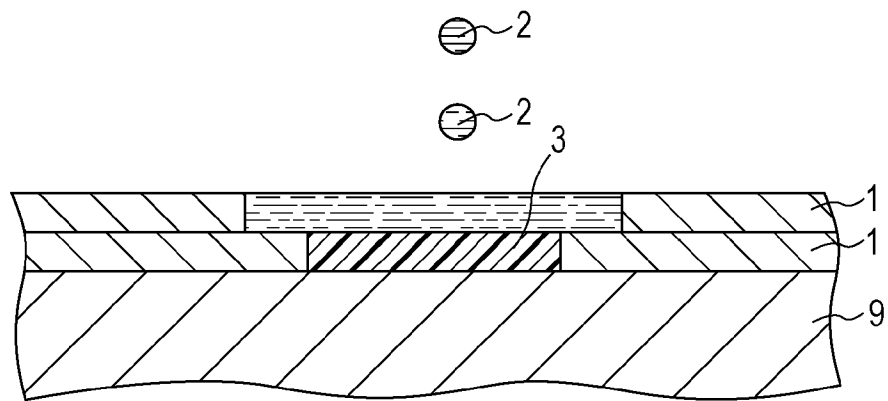
[Fig. 1C]



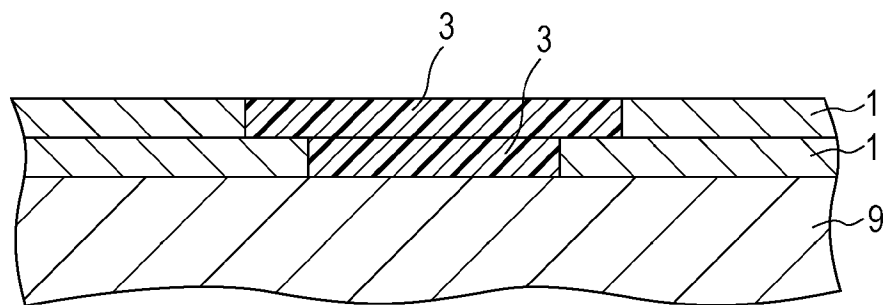
[Fig. 1D]



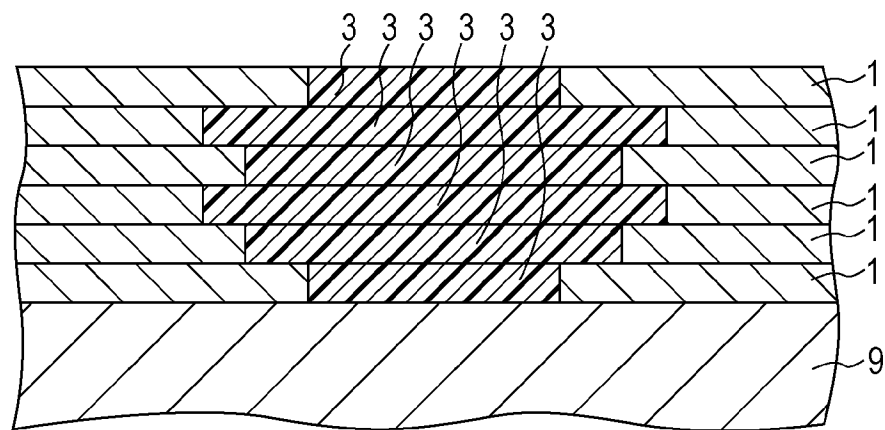
[Fig. 2E]



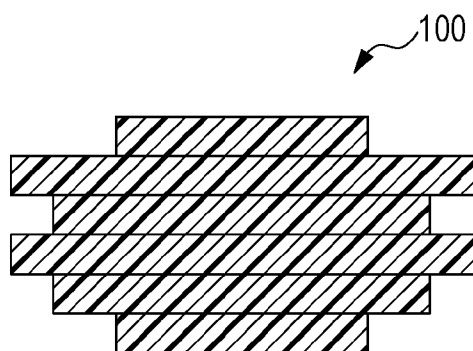
[Fig. 2F]



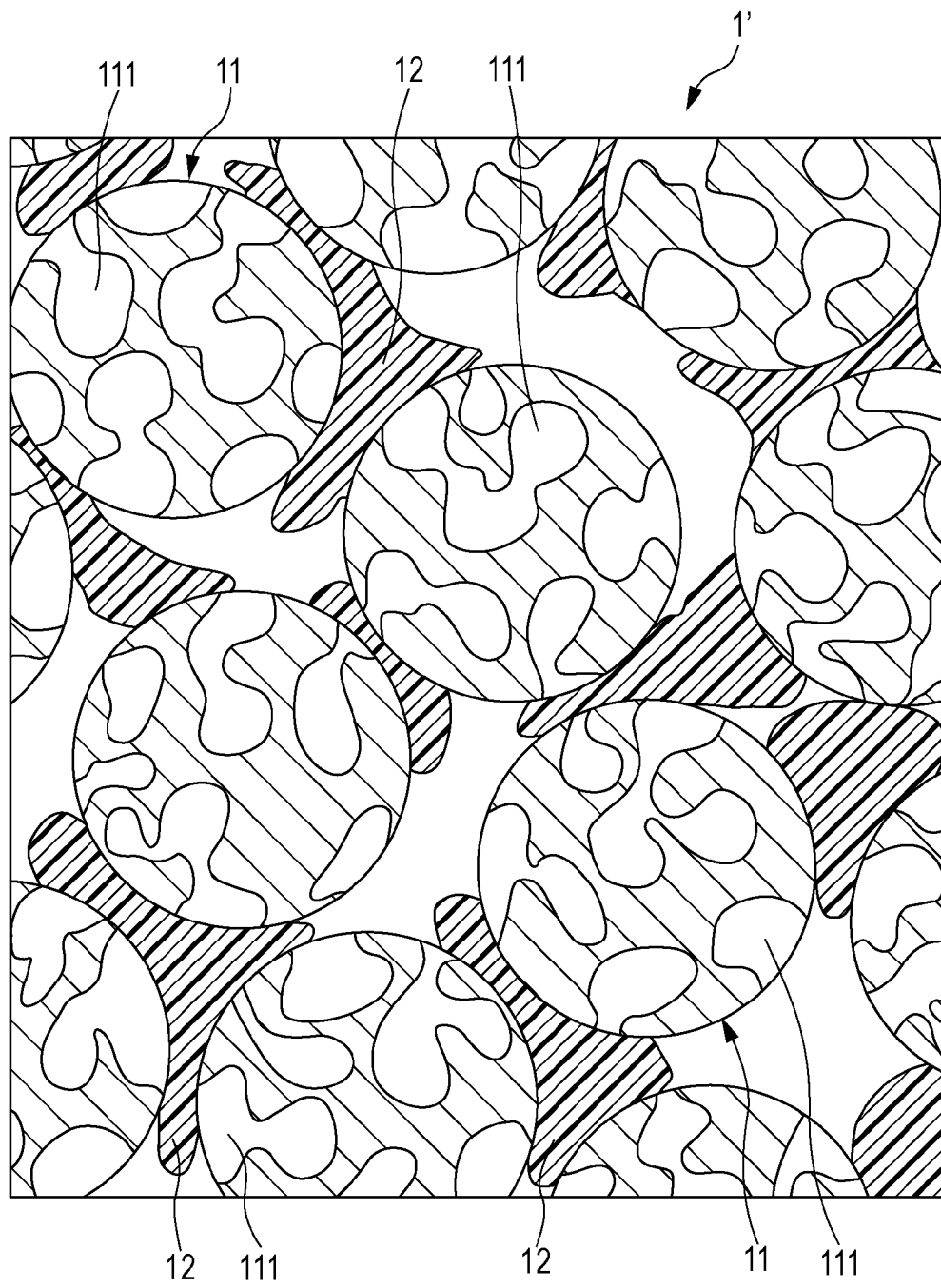
[Fig. 2G]



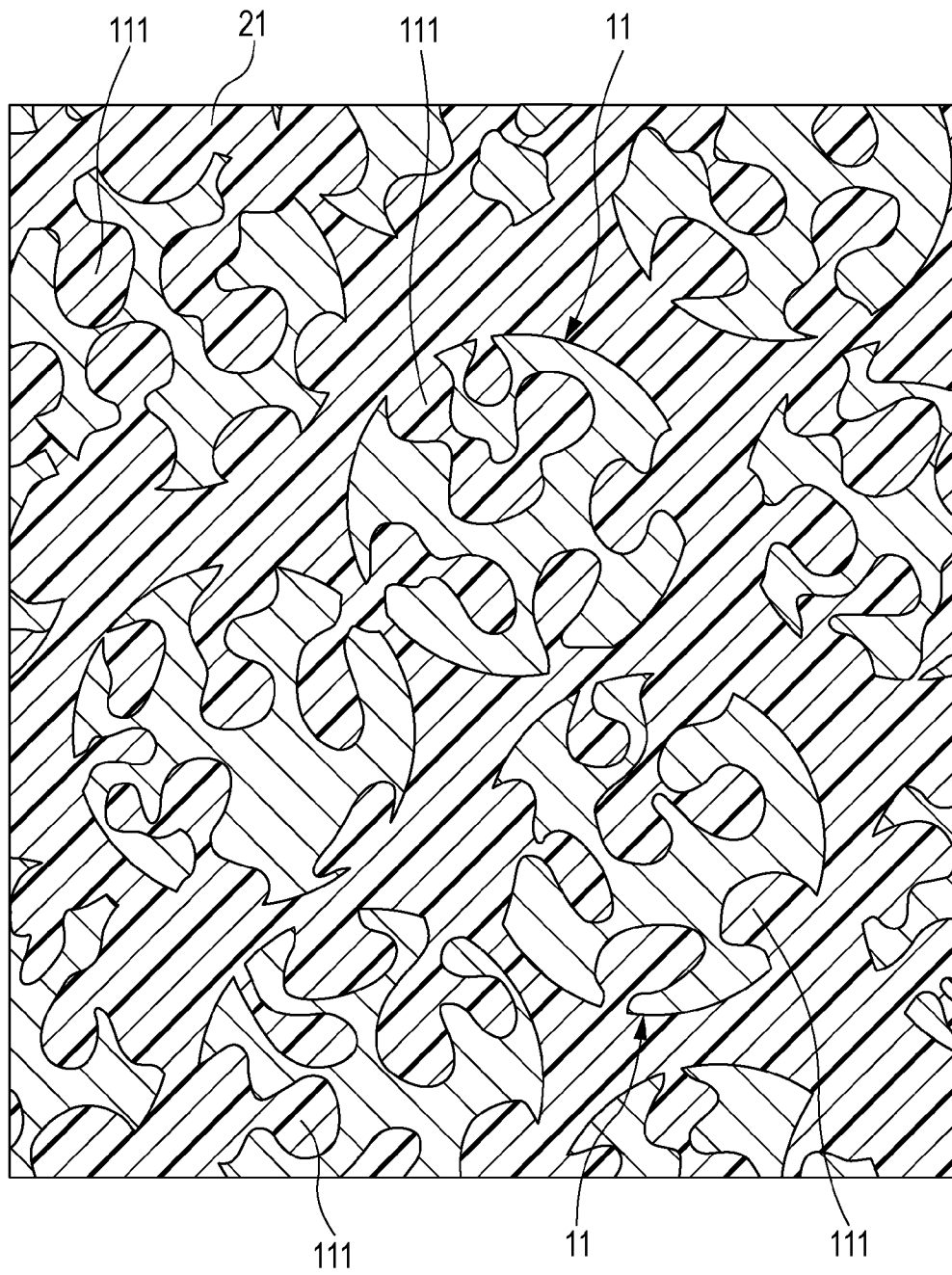
[Fig. 2H]



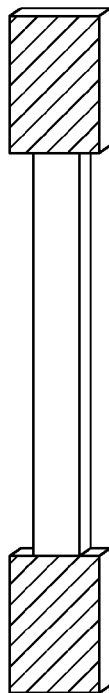
[Fig. 3]



[Fig. 4]



[Fig. 5]



[Fig. 6]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/005720

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B29C67/00 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. B29C67/00, C08J3/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2015
 Registered utility model specifications of Japan 1996-2015
 Published registered utility model applications of Japan 1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2006-515812 A (HEWLETT-PACKARD DEVELOPMENT COMPANY L.P.) 2006.06.08, 【0003】, 【0007】-【0009】, 【0019】-【0025】, 【0028】 & US 2004/0161544 A1 & EP 1594677 A & WO 2004/062891 A1 & DE 602004007359 D & CN 1723118 A & TW 288153 B	1-15
A	JP 2004-330679 A (FUJI PHOTO FILM CO., LTD.) 2004.11.25, 【0011】-【0014】, 【0024】-【0027】 & US 2004/0222548 A1 & EP 1475221 A2	1-15
A	JP 2005-96199 A (FUJI PHOTO FILM CO., LTD.) 2005.04.14, 【0010】, 【0013】-【0016】, 【0036】-【0040】 (Family:None)	1-15



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

15.01.2015

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/005720

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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