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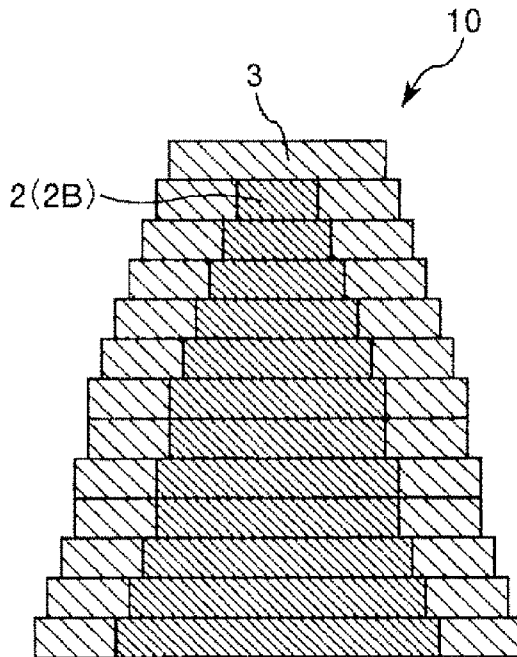
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[Continued on next page]

(54) Title: METHOD FOR MANUFACTURING THREE-DIMENSIONAL STRUCTURE, THREE-DIMENSIONAL STRUCTURE MANUFACTURING APPARATUS, AND THREE-DIMENSIONAL STRUCTURE

[Fig. 2Q]



(57) Abstract: A method for manufacturing a three-dimensional structure by stacking layers, includes: forming a first portion which is a region including at least a part of the outer surface of the three-dimensional structure by discharging a liquid by an ink jet method and then curing the discharged liquid; and forming a second portion which is a region of at least a part of portions other than the first portion of the three-dimensional structure by ejecting a thermoplastic composition including a melted thermoplastic resin from a nozzle and by solidifying the ejected thermoplastic composition.



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## Description

### **Title of Invention: METHOD FOR MANUFACTURING THREE-DIMENSIONAL STRUCTURE, THREE-DIMENSIONAL STRUCTURE MANUFACTURING APPARATUS, AND THREE-DIMENSIONAL STRUCTURE**

#### **Technical Field**

[0001] The present invention relates to a method for manufacturing a three-dimensional structure, a three-dimensional structure manufacturing apparatus, and a three-dimensional structure.

#### **Background Art**

[0002] In the related art, a method for forming a three-dimensional structure is known based on a model of a three-dimensional object, for example, generated by a three-dimensional CAD software or the like.

[0003] As a method for forming a three-dimensional structure, a stacking method (three-dimensional forming method) is known. In the stacking method, in general, after splitting the model of a three-dimensional object into a large number of two-dimensional cross-sectional layers, a three-dimensional structure is formed by sequentially stacking cross-section members while sequentially forming the cross-section members corresponding to each two-dimensional cross-sectional layer.

[0004] By the stacking method, a three-dimensional structure can be formed immediately as long as there is a model of a three-dimensional structure to be formed, and since there is no need to make a die before forming, it is possible to quickly and inexpensively form a three-dimensional structure. In addition, since a three-dimensional structure is formed by stacking cross-section members having a thin plate-shape layer by layer, for example, even in a case where the object has a complex internal structure, it is possible to form a formed object as one piece without being divided into a plurality of parts.

[0005] As such a stacking method, a technology for manufacturing a three-dimensional structure by binding plaster particles by applying water to plaster powder is known (for example, refer to PTL 1).

[0006] However, in such a technology, it is difficult to obtain a three-dimensional structure having a desired color, and as a result, it is difficult to make design of the three-dimensional structure sufficiently excellent. In addition, in such a method, the range of choice in materials capable of being used is relatively narrow, and thus, in the three-dimensional structure to be manufactured, for example, various properties such as specific gravity, hardness, elastic modulus, and flexibility are significantly different

from those to be imagined from the appearance of the three-dimensional structure, and users of the three-dimensional structure feel uneasy.

### **Citation List**

#### **Patent Literature**

[0007] PTL 1: JP-T-2003-531220

#### **Summary of Invention**

##### **Technical Problem**

[0008] An advantage of some aspects of the invention is to provide a method for manufacturing a three-dimensional structure and a three-dimensional structure manufacturing apparatus, capable of manufacturing a three-dimensional structure which has a wide range of choice in color and design and physical properties depending on the appearance, with high productivity, and to provide a three-dimensional structure which is excellent in design and has physical properties depending on the appearance.

##### **Solution to Problem**

[0009] The advantage is achieved by aspects of the invention described below.

An aspect of the invention is directed to a method for manufacturing a three-dimensional structure by stacking layers including: forming a first portion which is a region including at least a part of the outer surface of the three-dimensional structure by discharging a liquid by an ink jet method and then curing the discharged liquid; and forming a second portion which is a region of at least a part of portions other than the first portion of the three-dimensional structure by ejecting a thermoplastic composition including a melted thermoplastic resin from a nozzle and by solidifying the ejected thermoplastic composition.

[0010] With this configuration, it is possible to provide a method for manufacturing a three-dimensional structure capable of manufacturing a three-dimensional structure which has a wide range of choice in color and design and physical properties depending on the appearance, with high productivity.

[0011] In the method for manufacturing a three-dimensional structure according to the aspect of the invention, it is preferable that the first portion is formed by applying the liquid to a layer formed using a particle containing composition including particles by the ink jet method, by penetrating the liquid into gaps between the particles, and by curing the liquid.

[0012] With this configuration, it is possible to form a solidified portion in the inside of a layer, and as a result, it is possible to form a bound portion in which particles are bound by the solidified portion. Since the bound portion formed in this manner includes the particles and the solidified portion (cured portion), the bound portion has particularly excellent hardness and mechanical strength. Therefore, the finally obtained

three-dimensional structure has particularly excellent mechanical strength, unintended deformation thereof is more reliably prevented, and thus, the reliability thereof becomes higher.

- [0013] In the method for manufacturing a three-dimensional structure according to the aspect of the invention, it is preferable that the particle containing composition includes a solvent, and the liquid is applied to the layer in a state of removing the solvent from the layer.
- [0014] With this configuration, it is possible to make the handleability (ease of handling) of the particle containing composition particularly excellent, it is possible to make the productivity of the three-dimensional structure particularly excellent, and the dimensional accuracy, the mechanical strength, and the reliability of the finally obtained three-dimensional structure become particularly excellent.
- [0015] In the method for manufacturing a three-dimensional structure according to the aspect of the invention, it is preferable that the particle containing composition includes an aqueous solvent as a solvent.
- [0016] With this configuration, it is possible to make the fluidity of the particle containing composition and the uniformity of the constitution of the layer formed using the particle containing composition particularly excellent. Water is easily removed after the layer is formed, and does not exercise adverse effects even in a case where water remains in the three-dimensional structure. Water is also advantageous from the viewpoint of safety with respect to human body and environmental issues.
- [0017] In the method for manufacturing a three-dimensional structure according to the aspect of the invention, it is preferable that the particle containing composition further includes a binder.
- [0018] With this configuration, it is possible to further improve safety of a worker at the time of manufacturing a three-dimensional structure and the dimensional accuracy of the three-dimensional structure to be manufactured.
- [0019] In the method for manufacturing a three-dimensional structure according to the aspect of the invention, it is preferable that the layer is formed such that at least a part of the second portion is buried using the particle containing composition after forming the second portion using the thermoplastic composition.
- [0020] With this configuration, the dimensional accuracy of the three-dimensional structure becomes particularly excellent. In addition, it is possible to make productivity of the three-dimensional structure particularly excellent.
- [0021] In the method for manufacturing a three-dimensional structure according to the aspect of the invention, it is preferable that the liquid includes a photocurable resin.
- [0022] With this configuration, it is possible to make the mechanical strength of the obtained three-dimensional structure and the productivity of the three-dimensional structure par-

ticularly excellent, and it is possible to more effectively prevent unintended deformation at the time of manufacturing a three-dimensional structure.

[0023] In the method for manufacturing a three-dimensional structure according to the aspect of the invention, it is preferable that the thermoplastic resin includes polycarbonate, and the liquid includes an acryl-based polymerizable compound.

[0024] With this configuration, it is possible to make the adhesion between a solidified portion formed using a thermoplastic resin and the solidified portion formed using the liquid particularly excellent, and it is possible to make the durability and the reliability of the three-dimensional structure particularly excellent.

[0025] In the method for manufacturing a three-dimensional structure according to the aspect of the invention, it is preferable that the thickness of a first portion is 0.01 mm to 1.0 mm.

[0026] With this configuration, it is possible to more reliably make the three-dimensional structure have physical properties depending on the appearance, and it is possible to make the range of choice in color and design of the three-dimensional structure wider. In addition, it is possible to make the adhesion between the first portion and a second portion particularly excellent, and it is possible to make the durability of the three-dimensional structure particularly excellent.

[0027] In the method for manufacturing a three-dimensional structure according to the aspect of the invention, it is preferable that the thermoplastic composition includes a filler in addition to the thermoplastic resin.

[0028] With this configuration, it is possible to make the mechanical strength and the reliability of the overall three-dimensional structure particularly excellent. It is also possible to suitably adjust the hardness of the finally obtained three-dimensional structure. In addition, it is possible to easily adjust the specific gravity or the like of the second portion, it is possible to manufacture a three-dimensional structure having high specific gravity, and it is possible to more suitably adjust the physical properties of the three-dimensional structure.

[0029] Another aspect of the invention is directed to a three-dimensional structure manufacturing apparatus for manufacturing a three-dimensional structure by stacking layers including: a liquid discharge unit that discharges a liquid used in formation of a cured portion by an ink jet method; and a thermoplastic composition applying unit that applies a thermoplastic composition including a melted thermoplastic resin.

[0030] With this configuration, it is possible to provide a three-dimensional structure manufacturing apparatus capable of manufacturing a three-dimensional structure which has a wide range of choice in color and design, and physical properties depending on the appearance, with high productivity.

[0031] Still another aspect of the invention is directed to a three-dimensional structure man-

ufactured using the method for manufacturing a three-dimensional structure according to the invention.

[0032] With this configuration, it is possible to provide a three-dimensional structure which is excellent in design and has physical properties depending on the appearance.

[0033] Yet another aspect of the invention is directed to a three-dimensional structure manufactured using the three-dimensional structure manufacturing apparatus according to the invention.

[0034] With this configuration, it is possible to provide a three-dimensional structure which is excellent in design and has physical properties depending on the appearance.

[0035] Still yet another aspect of the invention is directed to a three-dimensional structure manufactured using a three-dimensional forming method, in which a first portion which is a region including at least a part of the outer surface is configured of a material including a cured product of a curable resin, and a second portion which is a region of at least a part of portions other than the first portion is configured of a material including a thermoplastic resin.

[0036] With this configuration, it is possible to provide a three-dimensional structure which is excellent in design and has physical properties depending on the appearance.

### **Brief Description of Drawings**

[0037] [fig.1A]Fig. 1A is a cross-sectional view schematically showing a step in a first embodiment of a method for manufacturing a three-dimensional structure according to the invention.

[fig.1B]Fig. 1B is a cross-sectional view schematically showing a step in a first embodiment of a method for manufacturing a three-dimensional structure according to the invention.

[fig.1C]Fig. 1C is a cross-sectional view schematically showing a step in a first embodiment of a method for manufacturing a three-dimensional structure according to the invention.

[fig.1D]Fig. 1D is a cross-sectional view schematically showing a step in a first embodiment of a method for manufacturing a three-dimensional structure according to the invention.

[fig.1E]Fig. 1E is a cross-sectional view schematically showing a step in a first embodiment of a method for manufacturing a three-dimensional structure according to the invention.

[fig.1F]Fig. 1F is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1G]Fig. 1G is a cross-sectional view schematically showing a step in the first em-

bodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1H]Fig. 1H is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1I]Fig. 1I is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1J]Fig. 1J is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1K]Fig. 1K is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1L]Fig. 1L is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1M]Fig. 1M is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1N]Fig. 1N is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1O]Fig. 1O is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1P]Fig. 1P is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.1Q]Fig. 1Q is a cross-sectional view schematically showing a step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2A]Fig. 2A is a cross-sectional view schematically showing a step in a second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2B]Fig. 2B is a cross-sectional view schematically showing a step in a second embodiment of the method for manufacturing a three-dimensional structure according to the invention.



[fig.2C]Fig. 2C is a cross-sectional view schematically showing a step in a second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2D]Fig. 2D is a cross-sectional view schematically showing a step in a second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2E]Fig. 2E is a cross-sectional view schematically showing a step in a second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2F]Fig. 2F is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2G]Fig. 2G is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2H]Fig. 2H is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2I]Fig. 2I is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2J]Fig. 2J is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2K]Fig. 2K is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2L]Fig. 2L is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2M]Fig. 2M is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2N]Fig. 2N is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2O]Fig. 2O is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according

to the invention.

[fig.2P]Fig. 2P is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.2Q]Fig. 2Q is a cross-sectional view schematically showing a step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[fig.3]Fig. 3 is a cross-sectional view schematically showing a preferred embodiment of a three-dimensional structure manufacturing apparatus according to the invention.

### **Description of Embodiments**

[0038] Hereinafter, preferred embodiments of the invention will be described in detail with reference to the accompanying drawings.

#### Method for Manufacturing Three-Dimensional Structure

[0039] First, the method for manufacturing a three-dimensional structure according to the invention will be described.

#### First Embodiment

Fig. 1A to Fig. 1Q are cross-sectional views schematically showing each step in the first embodiment of the method for manufacturing a three-dimensional structure according to the invention.

[0040] As shown in Fig. 1A to Fig. 1Q, the method for manufacturing a three-dimensional structure 10 of the embodiment has a layer forming step (Fig. 1B, Fig. 1C, Fig. 1D, Fig. 1H, Fig. 1I, Fig. 1J, Fig. 1N, and Fig. 1O) of forming a layer 1 using a particle containing composition (layer forming composition) 1' including particles 11 and a solvent 12, a first solidified portion forming step (Fig. 1E, Fig. 1F, Fig. 1K, and Fig. 1L) of forming a solidified portion 2 (first solidified portion 2A) in the layer 1 by penetrating a liquid 2' into the layer 1 and by curing the penetrated liquid 2', and a second solidified portion forming step (Fig. 1A, Fig. 1F, and Fig. 1M) of forming the solidified portion 2 (second solidified portion 2B) by ejecting a thermoplastic composition 2'' including a melted thermoplastic resin from a nozzle M81, and further has a unbound particle removing step (Fig. 1Q) of removing particles which are not bound by the solidified portion 2, of the particles 11 configuring each layer 1 after the above steps are sequentially repeatedly performed (Fig. 1P).

[0041] A first portion which is a region including at least a part of the outer surface of the three-dimensional structure 10 is formed as the first solidified portion 2A (solidified portion 2 formed by discharging the liquid 2' by an ink jet method and by curing the discharged liquid 2'), and a second portion which is a region of at least a part of portions other than the first portion of the three-dimensional structure 10 is formed as

the second solidified portion 2B (solidified portion 2 formed by ejecting the melted thermoplastic composition 2'' from the nozzle M81 and by solidifying the ejected melted thermoplastic composition 2'') (refer to Fig. 1Q).

[0042] In this manner, in the embodiment, each portion of the three-dimensional structure 10 is not formed by the same method, and the solidified portion 2 is formed by a different method depending on the portion of the three-dimensional structure 10.

[0043] Thereby, the advantages corresponding to each step act synergistically, and it is possible to manufacture a three-dimensional structure 10 which has a wide range of choice in color and design, and physical properties depending on the appearance, with high productivity.

[0044] More specifically, by forming a portion (first portion) corresponding to the outer surface of the finally obtained three-dimensional structure 10 by discharging the liquid 2' by an ink jet method and by curing the discharged liquid 2', it is possible to make the productivity of the three-dimensional structure 10 excellent. In the ink jet method, it is possible to suitably use the liquid 2' including, for example, various colorants, as the liquid 2' to be discharged, and thus, it is possible to make the range of choice in color and design of the three-dimensional structure 10 widen. In addition, in the ink jet method, it is possible to reproducibly apply the liquid 2' even in the case of fine patterns, and thus, it is possible to make the dimensional accuracy of the finally obtained three-dimensional structure 10 high. In particular, it is possible to make the texture (color, flatness of the surface, surface roughness, uneven shape, or the like) of the outer surface which greatly affects the appearance of the three-dimensional structure 10 excellent, and for example, in a case where the three-dimensional structure is a model (including dolls, figures, or the like), it is possible to express the texture as the actual object (object copied as a model).

[0045] By forming a region (second portion) of at least a part of portions other than the first portion by ejecting the melted thermoplastic composition 2'' from the nozzle M81 and by solidifying the ejected melted thermoplastic composition 2'', it is possible to suitably adjust the various physical properties (for example, specific gravity, hardness, elastic modulus, and flexibility) of the overall three-dimensional structure 10 to desired conditions.

[0046] This is because the method for forming the solidified portion 2 by ejecting the melted thermoplastic composition 2'' from the nozzle M81 and by solidifying the ejected melted thermoplastic composition 2'' can stably form the solidified portion 2 compared to a method for forming the solidified portion 2 using an ink jet method, even in the case of including various additives in the materials for forming the solidified portion 2 (case of including additives in high content).

[0047] More specifically, in the ink jet method, in a case where various additives are added

in the liquid 2' to be discharged, effects on discharge of liquid droplets is great, it is necessary to set the discharge conditions depending on the constitution of the liquid 2', variations in the amount of the liquid droplets are increased or position accuracy of the liquid droplet discharge is reduced, and in some cases, there is a problem in which the droplet discharge becomes impossible, however, in the method for forming the solidified portion 2 by ejecting the melted thermoplastic composition 2'' from the nozzle M81 and by solidifying the ejected melted thermoplastic composition 2'', even in a case where the thermoplastic composition 2'' includes various additives (in particular, case of including additives in high content), it is possible to stably supply the material (thermoplastic composition 2'') to an intended portion. As described below, typically, the thermoplastic composition 2'' is stored in a state of a solid of a filament shape before ejection is performed, and thus, for example, even in the case of including a filler (for example, a metal material or the like) having high specific gravity compared to a thermoplastic resin, it is possible to make the dispersed state of the filler or the like favorable, in a state in which the thermoplastic composition 2'' is solid. In addition, such a thermoplastic composition 2'' is melted typically just before ejection and extruded from the nozzle M81, and is in a state in which the viscosity is relatively high even at the time of ejection, and after thermoplastic composition 2'' is applied to the intended portion, the thermoplastic composition 2'' is solidified in a relatively short period of time. For this reason, even in the solidified portion 2 (second solidified portion 2B) at the time of ejecting or after ejection, it is possible to maintain the dispersed state of the filler or the like favorable. Therefore, it is possible to effectively prevent unintended variations in the constitution in the second portion, and it is possible to make the physical properties of the three-dimensional structure 10 reliably satisfy desired conditions.

[0048] Hereinafter, each step will be described.

#### Second Solidified Portion Forming Step

In the second solidified portion forming step, the solidified portion 2 (second solidified portion 2B) is formed by ejecting the melted thermoplastic composition 2'' from the nozzle M81 (refer to Fig. 1A, Fig. 1G, and Fig. 1M).

[0049] In particular, in a first second solidified portion forming step, the solidified portion 2 (second solidified portion 2B) having a predetermined pattern is formed (refer to Fig. 1A) by ejecting the melted thermoplastic composition 2'' on the surface of a stage (support) M41 from the nozzle M81, and in a second and subsequent second solidified portion forming steps, the solidified portion 2 (second solidified portion 2B) having a predetermined pattern is formed by ejecting the melted thermoplastic composition 2'' on the layer 1 provided with the solidified portion 2 (first solidified portion 2A, second solidified portion 2B) from the nozzle M81 (refer to Fig. 1G and Fig. 1M).

- [0050] The thermoplastic composition 2'' in a melted state is applied to a predetermined portion, solidified due to decrease of the temperature, and becomes the solidified portion 2 (second solidified portion 2B).
- [0051] In the step, as the second solidified portion 2B, a second portion which is a region of at least a part of portions other than the first portion of the three-dimensional structure 10 is formed.
- [0052] As described above, by having the solidified portion 2 (second solidified portion 2B) to be formed by ejecting the melted thermoplastic composition 2'' from the nozzle M81 and by solidifying the ejected melted thermoplastic composition 2'', it is possible to suitably adjust the physical properties (for example, specific gravity, hardness, elastic modulus, and flexibility) of the three-dimensional structure 10, and it is possible to obtain the three-dimensional structure 10 as a three-dimensional structure having physical properties depending on the appearance.
- [0053] In addition, in the embodiment, a second and subsequent second solidified portion forming steps (steps of forming the second solidified portion 2B on the layer 1) is performed in a state in which the solvent 12 is removed from the layer 1 (layer 1 with which the second solidified portion 2B should come into contact).
- [0054] Thereby, it is possible to more effectively prevent unintended deformation of the layer 1 in the step, and unintended deformation of the second solidified portion 2B is also more effectively prevented. As a result, the dimensional accuracy and the reliability of the finally obtained three-dimensional structure 10 become particularly excellent.
- [0055] In the step, the thermoplastic composition 2'' having a filament shape (thread shape) is heated, melted, and ejected from the nozzle M81.
- The thermoplastic composition 2'' will be described below in detail.
- [0056] In addition, in the step, thermoplastic composition 2'' in a melted state is also applied to a second region M412 which is a region different from a first region M411 which is a region at which the intended three-dimensional structure 10 of the stage M41 is manufactured, and by solidifying this, a solidified product 6 having the same height as that of the second solidified portion 2B formed in the same step is formed (refer to Fig. 1A, Fig. 1G, and Fig. 1M). As described below, the solidified product 6 is used in determining the thickness of the layer 1 to be formed in the layer forming step.
- [0057] In particular, in the embodiment, the solidified product 6 is formed so as to be stacked over a plurality of steps (refer to Fig. 1A, Fig. 1G, Fig. 1M, and Fig. 1P), to correspond to the plurality of layers 1.
- [0058] Thereby, it is possible to determine a suitable thickness for each of the plurality of layers 1, and it is possible to make the dimensional accuracy and the mechanical strength of the overall three-dimensional structure 10 particularly excellent.

[0059] In addition, in the embodiment, all of the plurality of solidified products 6 formed by being stacked over several steps have the same shape and the same area. In other words, when a solidified product formed in any step, of the plurality of solidified products 6 formed by being stacked over a plurality of steps, is defined as a first solidified product, and a solidified product formed in a later step than the first solidified product, of the plurality of solidified products 6 formed by being stacked over a plurality of steps, is defined as a second solidified product, the second solidified product does not have a region not overlapping with the first solidified product, when seen in a plan view.

[0060] Thereby, by such a configuration, it is possible to more effectively prevent unintended deformation (so-called sagging or the like) of the solidified product 6, it is possible to make the difference between the thickness of the solidified portion 2 and the thickness of the solidified product 6 smaller, and it is possible to make the dimensional accuracy and the mechanical strength of the overall three-dimensional structure 10 more excellent.

#### Layer Forming Step

[0061] In the layer forming step, the layer 1 having a predetermined thickness is formed using the particle containing composition (layer forming composition) 1' including the particles 11 and the solvent 12 (refer to Fig. 1B, Fig. 1C, Fig. 1D, Fig. 1H, Fig. 1I, Fig. 1J, Fig. 1N, and Fig. 1O).

[0062] In particular, in the first layer forming step, the layer 1 having a predetermined thickness is formed on the stage (support) M41 provided with the solidified portion 2 (second solidified portion 2B) using the layer forming composition 1' including the particles 11 and the solvent 12 (refer to Fig. 1B, Fig. 1C and Fig. 1D), and in the second and subsequent layer forming steps, a new layer 1 having a predetermined thickness is formed on the layer 1 (in the configuration in the figures, the layer 1 in which a bound portion 3 is formed) using the layer forming composition 1' including the particles 11 and the solvent 12 (refer to Fig. 1H, Fig. 1I, Fig. 1J, Fig. 1N, and Fig. 1O).

The layer forming composition (particle containing composition) 1' will be described below in detail.

[0063] In the step, the layer 1 of which the surface is flattened is formed using a squeegee as a flattening unit M42.

[0064] In the step, a flattening unit (for example, a roller or the like) other than a squeegee may be used.

[0065] In addition, in the embodiment, at least a part of the solidified portion 2 (second solidified portion 2B) formed previously is buried in the layer 1 formed in the step (refer to Fig. 1C, Fig. 1I, and Fig. 1O).

- [0066] Thereby, for example, stability of the shape of the solidified portion 2 to be formed in a subsequent step on the upper surface side of the solidified portion 2 (the solidified portion 2 buried in the layer 1 in the step) is improved. It is possible to suitably adjust the height of the layer 1 to be formed in the step. As a result, the dimensional accuracy of the three-dimensional structure 10 becomes particularly excellent. In addition, it is possible to make the productivity of the three-dimensional structure 10 particularly excellent.
- [0067] For example, in a case where the first solidified portion 2A is formed in a subsequent step on the portion in contact with the solidified portion 2 (second solidified portion 2B) of the layer 1 in which the solidified portion 2 (solidified portion 2 which is buried in the layer 1 in the step) is buried (refer to Fig. 1E, Fig. 1F, Fig. 1K, and Fig. 1L), it is possible to more effectively prevent an occurrence of an unintended difference of elevation between the solidified portion 2 buried in the layer 1 in the step and the second solidified portion 2B. As a result, the dimensional accuracy of the three-dimensional structure 10 becomes particularly excellent.
- [0068] In the step, it is preferably performed such that the layer forming composition 1' (in particular, particles 11) does not remain on the upper surface of the solidified portion 2 (second solidified portion 2B) buried in the step.
- [0069] Thereby, it is possible to prevent the reduction in the adhesion between the solidified portion 2 and the solidified portion 2 (first solidified portion 2A) formed in the subsequent first solidified portion forming step. In addition, it is possible to prevent an aesthetic appearance from being impaired.
- [0070] It is possible to use the solidified product 6 such that the layer forming composition 1' (in particular, particles 11) does not remain on the upper surface of the solidified portion 2 (second solidified portion 2B) buried in the step.
- [0071] That is, on the basis of the height of the upper surface of the solidified product 6 formed using the melted thermoplastic composition 2'', it is possible to determine the thickness of the layer 1 formed in the step.
- [0072] Thereby, it is possible to prevent the constituent (for example, the particles 11) of the layer forming composition 1' from unintentionally remaining on the upper surface of the solidified portion 2 (second solidified portion 2B) buried in the step at the time when the step ends. As a result, in a subsequent step, it is possible to reliably make the adhesion between the solidified portion 2 and the solidified portion 2 newly formed on the solidified portion 2 excellent. As a result, it is possible to make the mechanical strength of the finally obtained three-dimensional structure 10 particularly excellent. In addition, it is possible to more effectively prevent the reduction in the dimensional accuracy of the three-dimensional structure 10, caused by the unintentional presence of the particles 11 configuring the layer forming composition 1' between any solidified

portion 2 and the solidified portion 2 formed on the solidified portion 2.

[0073] In particular, in the embodiment, in the layer forming step, the flattening unit M42 is brought into contact with the upper surface of the solidified product 6, and, based on the height (contact surface) at which the flattening unit M42 is in contact with the solidified product 6, the layer 1 having a predetermined thickness is formed (refer to Fig. 1B, Fig. 1H, and Fig. 1N).

[0074] Thereby, with the simple configuration, it is possible to more effectively prevent an occurrence of the problem described above, and it is possible to manufacture the three-dimensional structure 10 having excellent mechanical strength and dimensional accuracy with excellent productivity.

[0075] In the configuration in the figures, the thickness of the layer 1 formed in the step is the same as the thickness of the buried solidified portion 2 (second solidified portion 2B), however, the thickness of the layer 1 formed in the step may be smaller than the thickness of the buried solidified portion 2 (second solidified portion 2B). For example, the height adjustment of the flattening unit M42 is performed so as to press the solidified product 6 with a predetermined pressure force, and as a result, the stress applied to the flattening unit M42 at a portion where the solidified portion 2 or solidified product 6 is not present becomes low compared to a portion where the solidified portion 2 or solidified product 6 is present, and it is possible to make the height of the layer 1 formed by the flattening unit M42 lower than that of the solidified portion 2 buried in the step. Thereby, it is possible to make the pressure force by the flattening unit M42, applied to the upper surface of the solidified portion 2 buried in the step, relatively large, and it is possible to more effectively prevent the layer forming composition 1' (in particular, particles 11) on the upper surface of the solidified portion 2 buried in the step from remaining.

[0076] Although the solidified product 6 may be formed in the region (first region M411) where a portion configuring an entity portion of an intended three-dimensional structure 10 is formed, on the stage M41, however, in the embodiment, the solidified product 6 is formed at the second region M412 different from the first region M411.

[0077] Thereby, when the flattening unit M42 is brought into contact with the upper surface of the solidified product 6 (when the thickness of the layer 1 to be newly formed is determined), it is possible to more reliably prevent an occurrence of unintended deformation in the layer 1 according to the solidified portion 2 or forming of the intended three-dimensional structure 10. As a result, it is possible to make the dimensional accuracy and the reliability of the finally obtained three-dimensional structure 10 excellent.

[0078] In the configuration in the figures, the second region M412 is provided on the outer peripheral side of the first region M411.



- [0079] Thereby, effects as described above are more significantly exhibited, it is possible to make the dimensional accuracy and the reliability of a finally obtained three-dimensional structure 10 more excellent, and it is possible to make the productivity of the three-dimensional structure 10 particularly excellent.
- [0080] In particular, in the configuration in the figures, regarding the relative moving direction with respect to the stage M41 of the flattening unit M42, the second region M412 is provided on the upstream side of the first region M411.
- [0081] Thereby, the relative height of the flattening unit M42 can be adjusted, and due to this, it is possible to efficiently perform formation of the layer 1 by the flattening unit M42, and it is possible to make the productivity of the three-dimensional structure 10 particularly excellent.
- [0082] In the embodiment, after the layer forming composition 1' is applied to the first region M411 in a predetermined thickness, the solvent 12 included in the layer forming composition 1' is removed (refer to Fig. 1D and Fig. 1J).
- [0083] Thereby, spaces 4 in which the solvent 12 is not present are formed between the particles 11 configuring the layer 1. The space 4 functions as an absorbing portion absorbing the liquid 2' in the subsequent first solidified portion forming step.
- [0084] Although removal of the solvent 12 may be performed under any condition, for example, the removal of the solvent 12 can be performed by a heat treatment, a pressure reduction treatment, blowing, or the like.
- [0085] In the case of performing the removal of the solvent 12 by heating, although the heating temperature varies depending on the constituent material or the like (type or the like of the particles 11, the solvent 12, or the like) of the layer 1, for example, the heating temperature is preferably 30 degrees centigrade to 100 degrees centigrade, and more preferably 60 degrees centigrade to 95 degrees centigrade. As the upper limit of the temperature range, the boiling point of the solvent 12 or lower is preferable for preventing shape change due to rapid vaporization thereof.
- [0086] Thereby, it is possible to efficiently remove the solvent 12, and it is possible to make the productivity of the three-dimensional structure 10 particularly excellent, while preventing unintended denaturation of the constituent material of the layer 1 or unintended deformation of the layer 1 or the like.
- [0087] Though the thickness of the layer 1 formed in the step is not particularly limited, for example, the thickness of the layer 1 is preferably 20 micrometers to 500 micrometers, and more preferably 30 micrometers to 150 micrometers.
- [0088] Thereby, it is possible to more effectively prevent an occurrence of unintended unevenness in the three-dimensional structure 10 to be manufactured, and it is possible to make the dimensional accuracy of the three-dimensional structure 10 particularly excellent, while making productivity of the three-dimensional structure 10 sufficiently

excellent.

[0089] The viscosity of the layer forming composition 1' in the layer forming step is preferably 500 mPa\*s to 1000000 mPa\*s.

[0090] Thereby, it is possible to more efficiently perform the step, and it is possible to make the productivity of the three-dimensional structure 10 particularly excellent. Moreover, in the specification, the viscosity refers to a value measured at 25 degrees centigrade using an E type viscometer (VISCONIC ELD manufactured by Tokyo Keiki Inc.).

#### First Solidified Portion Forming Step

[0091] In the first solidified portion forming step, the liquid 2' is applied by an ink jet method (refer to Fig. 1E and Fig. 1K), and then, by curing the liquid 2' (refer to Fig. 1F and Fig. 1L), the first solidified portion 2A is formed.

[0092] By applying the liquid 2' by an ink jet method, it is possible to reproducibly apply the liquid 2' even in a case where the applying pattern of the liquid 2' has a fine shape. As a result, it is possible to make the dimensional accuracy of the finally obtained three-dimensional structure 10 high. In general, various colorants or the like can be suitably included in the liquid 2' discharged using an ink jet method. For this reason, it is possible to easily and reliably control the color of the solidified portion 2 (first solidified portion 2A) formed using the liquid 2'. For example, using plural types of different liquid 2' in formation of the solidified portion 2 (first solidified portion 2A), for example, by making color in each part different or by adjusting the mixing ratio of the plural types of liquid 2' at the landing position of the liquid 2', it is possible to widen a color reproduction region that can be expressed using limited kinds of liquid 2' (for example, a full color representation). In addition, the first portion including the outer surface of the three-dimensional structure 10 is a portion which is particularly likely to affect the appearance of the three-dimensional structure 10, and by forming such a first portion by an ink jet method, it is possible to easily and reliably make the aesthetics of the three-dimensional structure 10 excellent.

[0093] In particular, in the embodiment, the solvent 12 is removed, the liquid 2' used in formation of the solidified portion 2 (first solidified portion 2A) in the layer 1 in a state of having the spaces 4 between the plurality of particles 11 is applied by an ink jet method, the liquid 2' is penetrated into the layer 1 (refer to Fig. 1E and Fig. 1K), and then, the liquid 2' penetrated into the layer 1 is cured (refer to Fig. 1F and Fig. 1L).

[0094] Thereby, it is possible to form the solidified portion 2 (first solidified portion 2A) in the inside (portion which is the spaces 4 between the particles 11) of the layer 1, and as a result, it is possible to form the bound portion 3 in which the particles 11 are bound by the solidified portion 2 (first solidified portion 2A). Since the bound portion 3 formed in this manner includes the particles 11 and the solidified portion 2 (first solidified portion 2A), the bound portion 3 has particularly excellent hardness and me-

chanical strength. Therefore, the finally obtained three-dimensional structure 10 has particularly excellent mechanical strength, unintended deformation thereof is more reliably prevented, and thus, the reliability thereof becomes higher.

[0095] The thickness of the first portion (the first solidified portion 2A provided as a region including the outer surface of the three-dimensional structure 10) is preferably 0.01 mm to 1.0 mm, and more preferably 0.02 mm to 0.5 mm.

[0096] Thereby, it is possible to more effectively exhibit the function of the second portion while more suitably controlling the surface characteristics of the three-dimensional structure 10. As a result, it is possible to make the range of choice in color and design of the three-dimensional structure 10 wider while more reliably making the three-dimensional structure 10 have physical properties depending on the appearance. It is possible to make the adhesion between the first portion and the second portion particularly excellent, and it is possible to make the durability of the three-dimensional structure 10 particularly excellent.

[0097] In the embodiment, the bottom surface of the three-dimensional structure 10 is not visually recognized in a normal using form (for example, in a case where the three-dimensional structure 10 is used in a state of being fixed on a support table or the weight of the three-dimensional structure 10 is large), and the entire outer surface capable of being visually recognized in a normal using form of the outer surface of the three-dimensional structure 10 is the first portion configured of the first solidified portion 2A (refer to Fig. 1Q).

[0098] By such a configuration, effects as described above are more significantly exhibited, and it is possible to make the aesthetics of the overall three-dimensional structure 10 particularly excellent.

#### Unbound Particle Removing Step

[0099] After the series of steps as described above is repeatedly performed (refer to Fig. 1P), as a post-treatment step, the unbound particle removing step (refer to Fig. 1Q) of removing particles (unbound particles) which are not bound by the solidified portion 2, of the particles 11 configuring each layer 1 is performed. Thereby, the three-dimensional structure 10 is obtained.

[0100] Examples of the specific method of the step include a method of removing unbound particles with a brush or the like, a method of removing unbound particles by suction, a method of blowing a gas such as air, a method of applying a liquid such as water (for example, a method of immersing the layered product obtained in the same manner as described above in a liquid, and a method of spraying a liquid), and a method of applying vibration such as ultrasonic vibration. In addition, two or more methods selected from these can be performed in combination. More specifically, a method of immersing into a liquid such as water after blowing a gas such as air, and a method of

applying ultrasonic vibration in a state of being immersed into a liquid such as water are exemplified. Among these, a method of applying a liquid including water (in particular, a method of immersing into a liquid including water) is preferably employed with respect to the layered product obtained in the same manner as described above.

[0101] By the manufacturing method according to the invention described above, it is possible to manufacture a three-dimensional structure which has a wide range of choice in color and design, and physical properties depending on the appearance, with high productivity.

[0102] In particular, by the method for manufacturing a three-dimensional structure of the embodiment, it is possible to efficiently manufacture a three-dimensional structure which has excellent dimensional accuracy or the like.

#### Second Embodiment

[0103] Next, a second embodiment of the method for manufacturing a three-dimensional structure according to the invention will be described.

[0104] Fig. 2A to Fig. 2Q are cross-sectional views schematically showing each step in the second embodiment of the method for manufacturing a three-dimensional structure according to the invention. In the following description, the second embodiment will be described while focusing on the difference from the embodiment described above, and the description of the same contents will not be repeated.

[0105] As shown in Fig. 2A to Fig. 2Q, although the method for manufacturing the three-dimensional structure 10 of the embodiment has the same steps as those in the embodiment described above, the thickness determining method of the layer 1 to be formed in the layer forming step is different from that in the embodiment described above.

[0106] That is, in the embodiment, the height (thickness) of the solidified product 6 formed using the melted thermoplastic composition 2" is measured by a height measuring unit M9, and, based on the measurement result, the thickness of the layer 1 to be newly formed after formation of the solidified product 6 is determined.

[0107] By such a configuration, for example, the flattening unit M42 does not need to be brought into contact with the solidified product 6, and thus, it is possible to prevent the unintended wear and deformation of the flattening unit M42, and an effect in which extension of the life of the flattening unit M42 is achieved, or the maintenance of the apparatus for manufacturing the three-dimensional structure 10 becomes easy is obtained. In addition, even in a case where the area of the solidified product 6 is relatively small, it is possible to accurately measure the height (thickness) of the solidified product 6, and it is possible to properly determine the thickness of the layer 1 to be newly formed. For this reason, it is possible to reduce the amount used of the

thermoplastic composition 2'' used in formation of the solidified product 6, and from the viewpoint of reduction of the production cost of the three-dimensional structure 10 and resource saving, such a configuration is preferable.

Thermoplastic Composition (Second Solidified Portion Forming Material)

[0108] Next, the thermoplastic composition (second solidified portion forming material) used in manufacturing the three-dimensional structure according to the invention will be described in detail.

[0109] The thermoplastic composition 2'' used in formation of the second solidified portion 2B is melted by heating, and ejected from the nozzle 81.

Thermoplastic Resin

[0110] The thermoplastic composition 2'' includes at least a thermoplastic resin.

[0111] Examples of the thermoplastic resin configuring the thermoplastic composition 2'' include acrylonitrile-butadiene-styrene (ABS), polyacrylate, polyolefin, a cyclic olefin polymer, polycarbonate, polyamide, polyimide, polyethylene, polybutylene terephthalate, a liquid crystal polymer resin (LCP), polyether ether ketone (PEEK), a thermoplastic elastomer (TPE), polystyrene, polyvinyl chloride, polysulfone, polyurethane, polyester, an epoxy resin, a silicone resin, a diallyl phthalate resin, cellulose plastic, a rosin-modified maleic acid resin, polycaprolactone, poly(lactide-co-glycolide), polylactide, poly(lactide-co-caprolactone), nylon 12, PPSF (polyphenyl sulfone), a PLA (polylactic acid) resin, and copolymers thereof, and one type or two or more types selected from these can be used singly or in combination.

[0112] Among these, as the thermoplastic resin, polycarbonate is preferable. By using polycarbonate, it is possible to make the impact resistance, the heat resistance, and the flame retardancy of the second solidified portion 2B particularly excellent. Polycarbonate has excellent dispersion stability of a filler (in particular, a filler configured of a material having high specific gravity such as a metal material) even in a melted state. In addition, polycarbonate has excellent characteristics as described above, and polycarbonate is relatively inexpensive and excellent in cost performance as a raw material of the three-dimensional structure 10.

[0113] Since polycarbonate has excellent affinity with a polymer of an acryl-based polymer compound, in a case where the first solidified portion 2A is configured of a polymer of an acryl-based polymer compound (in a case where the liquid 2' includes an acryl-based polymer compound), it is possible to make the adhesion between the first solidified portion 2A and the second solidified portion 2B particularly excellent, and it is possible to make the durability and the reliability of the three-dimensional structure 10 particularly excellent.

Other Components

[0114] The thermoplastic composition 2'' may include components (other components) other

than the thermoplastic resin. For example, the thermoplastic composition 2'' may include various colorants such as a pigment and a dye; a wetting agent (humectant); a fixing agent; a fungicide; a preservative; an antioxidant; an ultraviolet absorbent; a chelating agent; a pH adjusting agent; a thickener; or a filler.

[0115] In particular, if the thermoplastic composition 2'' includes a filler, it is possible to make the mechanical strength of the second solidified portion 2B formed using the thermoplastic composition 2'' particularly excellent, and it is possible to make the mechanical strength and the reliability of the overall finally obtained three-dimensional structure 10 particularly excellent. Since it is possible to increase the hardness of the second solidified portion 2B formed using the thermoplastic composition 2'', and it is also possible to suitably adjust the hardness of the finally obtained three-dimensional structure 10. In addition, if the thermoplastic composition 2'' includes a filler, it is possible to easily adjust the specific gravity of the second solidified portion 2B formed using the thermoplastic composition 2''. For example, in the solidified portion 2 (first solidified portion 2A) formed using the liquid 2' discharged by an ink jet method, it is possible to easily form a solidified portion (second solidified portion 2B) having high specific gravity difficult to be realized. In this manner, it is possible to more suitably adjust the physical properties of the three-dimensional structure 10.

[0116] As the filler, various metal materials (including alloys), metal compounds (for example, metal oxide, metal nitride, and metal carbide), and carbon materials (graphite, carbon nanotubes, and the like) can be used. In the case of forming a solidified portion having high specific gravity as described above, a metal material is preferable. Since a metal material generally has high specific gravity and excellent strength, effects thereof are more significantly exhibited.

[0117] On the other hand, in a case where lightening is desired, it is preferable to use a hollow material such as a silica balloon, a glass balloon, or a shirasu balloon.

[0118] It is possible to apply conductivity using carbon black, carbon fiber, metal powder, metal foil, or the like, or it is also possible to apply magnetic properties using ferrite particles, magnetic iron oxide, or the like.

[0119] Thereby, it is possible to easily apply desired characteristics to the second solidified portion 2B formed using the thermoplastic composition 2'', and effects as described above can be more significantly exhibited.

[0120] The shape of the filler is not particularly limited, and the shape may be any shape of a spherical shape, a spindle shape, a needle shape, a cylindrical shape, and a scale shape, and may be an indefinite shape.

[0121] The content of the filler in the thermoplastic composition 2'' is preferably 30% by volume to 90% by volume, and more preferably 52% by volume to 74% by volume.

[0122] Thereby, effects as described above can be more significantly exhibited while more

effectively preventing an occurrence of unintended variations in the constitution in the second solidified portion 2B formed using the thermoplastic composition 2''.

[0123] In the second solidified portion forming step, the viscosity of the thermoplastic composition 2'' when applying the thermoplastic composition 2'' to a desired portion is preferably 10 Pa\*s to 2000 Pa\*s, and more preferably 50 Pa\*s to 1000 Pa\*s.

[0124] Thereby, it is possible to more reliably apply the thermoplastic composition 2'' to a desired portion in a desired shape and pattern, and it is possible to more reliably make the dimensional accuracy of the three-dimensional structure 10 excellent. It is possible to make the productivity of the three-dimensional structure 10 particularly excellent.

[0125] In addition, although the heating temperature of the thermoplastic composition 2'' when the thermoplastic composition 2'' is ejected from the nozzle M81 in the second solidified portion forming step also varies depending on the constitution of the thermoplastic composition 2'', the heating temperature of the thermoplastic composition 2'' is preferably 100 degrees centigrade to 400 degrees centigrade, and more preferably 150 degrees centigrade to 300 degrees centigrade.

[0126] Thereby, it is possible to suitably adjust the viscosity of the thermoplastic composition 2'' when the thermoplastic composition 2'' is ejected from the nozzle M81, it is possible to more reliably apply the thermoplastic composition 2'' to a desired portion in a desired shape and pattern, it is possible to shorten the time until the melted thermoplastic composition 2'' is cooled and solidified after the melted thermoplastic composition 2'' is applied to a desired portion, and it is possible to more reliably prevent the thermoplastic composition 2'' in a melted state from exercising adverse effects on other portions (for example, the already formed solidified portion 2). As a result, it is possible to more reliably make the dimensional accuracy and the reliability of the three-dimensional structure 10 excellent, and it is possible to make the productivity of the three-dimensional structure 10 particularly excellent.

[0127] The thermoplastic composition 2'' is ejected from the nozzle M81 in a heated and melted state, however, before being heated and melted, the thermoplastic composition 2'' preferably has a filament shape (thread shape).

[0128] Thereby, control of the amount of the thermoplastic composition 2'' to be heated and melted when needed is easy. By heating the thermoplastic composition 2'' from the outer peripheral direction of the filament, it is possible to efficiently melt the thermoplastic composition 2''. For this reason, this is preferable from the viewpoint of saving energy. For example, by winding the thermoplastic composition 2'' having a filament shape (thread shape) on the outer periphery of a roll shape member, it is possible to easily perform operation of sending a desired amount of the thermoplastic composition 2'' when needed. In addition, storage of the thermoplastic composition 2'' becomes easy.

[0129] The thickness of the thermoplastic composition 2'' having a filament shape (in a case where the cross-sectional shape is circular, diameter) is preferably 0.1 mm to 5 mm, and more preferably 0.5 mm to 3 mm.

[0130] In manufacturing the three-dimensional structure 10, the plural types of thermoplastic composition 2'' may be used. For example, using the plural types of thermoplastic composition 2'' having different physical properties such as specific gravity, it is possible to more suitably adjust the physical properties of the overall three-dimensional structure 10. In addition, for example, in the case of manufacturing plural types of three-dimensional structure 10, using properly the plural types of thermoplastic composition 2'', it is possible to suitably cope with a multi-product production.

Liquid (First Solidified Portion Forming Liquid)

[0131] Next, the liquid (first solidified portion forming liquid) used in manufacturing the three-dimensional structure according to the invention will be described in detail.

[0132] The liquid (first solidified portion forming liquid) 2' includes at least a constituent (including a precursor) of the first solidified portion (cured portion) 2A.

Curable Resin Material (Polymerizable Compound)

[0133] The liquid 2' includes a resin material (polymerizable compound) in which a curing reaction can be proceeded.

[0134] Thereby, it is possible to make the strength and the stability of the shape of the formed first solidified portion 2A (cured portion) particularly excellent. In the bound portion 3, the reaction product (cured product) of the resin material (polymerizable compound) can function as a binder to bind the particles 11. It is possible to make the binding force between the solidified portions 2 in the adjacent layers 1 sufficiently great. For this reason, it is possible to make the mechanical strength of the three-dimensional structure 10 excellent, and it is possible to effectively prevent unintended deformation of the three-dimensional structure 10. In addition, since the heat resistance of the first solidified portion 2A (in particular, the first portion configuring the outer surface of the three-dimensional structure 10) becomes excellent, it is possible to more effectively prevent unintended deformation in the three-dimensional structure 10, or unintended denaturation or deterioration of the material, and it is possible to make the reliability of the three-dimensional structure 10 excellent.

[0135] Examples of the curable resin material (polymerizable compound) include a thermosetting resin; various photocurable resins such as a visible light curable resin which is cured by light in the visible light region (photocurable resin in the narrow sense), a ultraviolet ray curable resin, and an infrared ray curable resin; and an X-ray curable resin, and one type or two or more types selected from these can be used singly or in combination.



- [0136] In particular, in a case where the liquid 2' includes a photocurable resin as a curable resin material (polymerizable compound), it is possible to make the mechanical strength of the obtained three-dimensional structure 10 and the productivity of the three-dimensional structure 10 particularly excellent, and it is possible to more effectively prevent unintended deformation at the time of manufacturing the three-dimensional structure 10.
- [0137] Among these, from the viewpoint of the mechanical strength of the obtained three-dimensional structure 10, the productivity of the three-dimensional structure 10, and the storage stability of the liquid 2', in particular, an ultraviolet ray curable resin (polymerizable compound) is preferable.
- [0138] As the ultraviolet ray curable resin (polymerizable compound), a resin in which an addition polymerization or a ring-opening polymerization is initiated by radical species or cationic species generated from a photopolymerization initiator by irradiation of ultraviolet rays, and a polymer is generated is preferably used. As the polymerization mode of addition polymerization, a radical, a cationic, an anionic, a metathesis, and a coordination polymerization can be exemplified. In addition, as the polymerization mode of ring-opening polymerization, a cationic, an anionic, a radical, a metathesis, and a coordination polymerization can be exemplified.
- [0139] Examples of the addition polymerizable compound include compounds having at least one ethylenically unsaturated double bond. As the addition polymerizable compound, a compound having at least one terminal ethylenically unsaturated bond, and preferably two or more terminal ethylenically unsaturated bonds can be preferably used.
- [0140] The ethylenically unsaturated polymerizable compound has a monofunctional polymerizable compound, a polyfunctional polymerizable compound, or a chemical form of mixture of these.
- Examples of the monofunctional polymerizable compound include an unsaturated carboxylic acid (for example, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, and maleic acid), esters thereof, and amides. As the polyfunctional polymerizable compound, esters of an unsaturated carboxylic acid and an aliphatic polyol compound, or an amides of an unsaturated carboxylic acid and an aliphatic polyamine compound are used.
- [0141] In particular, the liquid 2' preferably includes an acryl-based polymerizable compound such as acrylic acid, methacrylic acid, or a derivative thereof (for example, an ester compound) as the polymerizable compound.
- [0142] Thereby, it is possible to make the strength (in particular, surface strength) of the finally obtained three-dimensional structure 10 particularly excellent. Since a polymer obtained by reacting an acryl-based polymerizable compound generally has high

transparency, for example, it is possible to make coloring properties in the case of manufacturing a three-dimensional structure using a material including a colorant particularly excellent, and it is possible to make the aesthetics of the three-dimensional structure 10 particularly excellent. In a case where the thermoplastic composition 2" includes polycarbonate, effects as described above are obtained.

[0143] In addition, a product of an addition reaction between unsaturated carboxylic acid esters or amides, which have a nucleophilic substituent such as a hydroxyl group, an amino group, or a mercapto group, and isocyanates or epoxies, a product of a dehydration condensation reaction between the above unsaturated carboxylic acid esters or amides and carboxylic acids, and the like also can be used. Moreover, a product of an addition reaction between unsaturated carboxylic acid esters or amides, which have an electrophilic substituent such as an isocyanate group or an epoxy group, and alcohols, amines, or thiols, and a product of a substitution reaction between unsaturated carboxylic acid esters or amides, which have a leaving substituent such as a halogen group or a tosyloxy group, and alcohols, amines, or thiols also can be used.

[0144] As specific examples of the radical polymerizable compound which is an ester of an unsaturated carboxylic acid and an aliphatic polyol compound, (meth)acrylic acid ester is representatively exemplified, and any of a monofunctional compound and polyfunctional compound can be used.

[0145] Specific examples of a monofunctional (meth)acrylate include tolyloxyethyl (meth)acrylate, phenyloxyethyl (meth)acrylate, cyclohexyl (meth)acrylate, ethyl (meth)acrylate, methyl (meth)acrylate, isobornyl (meth)acrylate, and tetrahydrofurfuryl (meth)acrylate.

[0146] Specific examples of a bifunctional (meth)acrylate include 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, and dipentaerythritol di(meth)acrylate.

[0147] Specific examples of a trifunctional (meth)acrylate include trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, alkylene oxide-modified tri(meth)acrylate of trimethylolpropane, pentaerythritol tri(meth)acrylate, dipentaerythritol tri(meth)acrylate, trimethylolpropane tri((meth)acryloyloxypropyl)ether, isocyanuric acid alkylene oxide-modified tri(meth)acrylate, propionic acid dipentaerythritol tri(meth)acrylate, tri((meth)acryloyloxyethyl) isocyanurate, hydroxypivalaldehyde-modified dimethylol propane tri(meth)acrylate, and sorbitol tri(meth)acrylate.

[0148] Specific examples of a tetrafunctional (meth)acrylate include pentaerythritol

tetra(meth)acrylate, sorbitol tetra(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, propionic acid dipentaerythritol tetra(meth)acrylate, and ethoxylated pentaerythritol tetra(meth)acrylate.

- [0149] Specific examples of a pentafunctional (meth)acrylate include sorbitol penta(meth)acrylate and dipentaerythritol penta(meth)acrylate.
- [0150] Specific examples of a hexafunctional (meth)acrylate include dipentaerythritol hexa(meth)acrylate, sorbitol hexa(meth)acrylate, alkylene oxide-modified hexa(meth)acrylate of phosphazene, and caprolactone-modified dipentaerythritol hexa(meth)acrylate.
- [0151] Examples of polymerizable compounds other than (meth)acrylates include itaconic acid ester, crotonic acid ester, isocrotonic acid ester, and maleic acid ester.
- [0152] Examples of the itaconic acid ester include ethylene glycol diitaconate, propylene glycol diitaconate, 1,3-butanediol diitaconate, 1,4-butanediol diitaconate, tetramethylene glycol diitaconate, pentaerythritol diitaconate, and sorbitol tetraitaconate.
- [0153] Examples of the crotonic acid ester include ethylene glycol dicrotonate, tetramethylene glycol dicrotonate, pentaerythritol dicrotonate, and sorbitol tetracrotonate.
- [0154] Examples of the isocrotonic acid ester include ethylene glycol diisocrotonate, pentaerythritol diisocrotonate, and sorbitol tetraisocrotonate.
- [0155] Examples of the maleic acid ester include ethylene glycol dimaleate, triethylene glycol dimaleate, pentaerythritol dimaleate, and sorbitol tetramaleate.
- [0156] In addition, specific examples of the amide monomer of an unsaturated carboxylic acid and an aliphatic polyamine compound include methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene-bis-acrylamide, 1,6-hexamethylene-bis-methacrylamide, diethylenetriamine trisacrylamide, xylylene bis-acrylamide, and xylylene bis-methacrylamide.
- [0157] In addition, a urethane-based addition polymerizable compound manufactured by an addition reaction between isocyanate and a hydroxyl group is also suitable, and as such a specific example thereof, a vinyl urethane compound containing two or more polymerizable vinyl groups in a molecule obtained by adding a vinyl monomer containing a hydroxyl group represented by the following formula (1) to a polyisocyanate compound having two or more isocyanate groups in a molecule can be exemplified.
- [0158]  $\text{CH}_2=\text{C}(\text{R}1)\text{COOCH}_2\text{CH}(\text{R}2)\text{OH}$  (1)  
(Here, in Formula (1), each of R1 and R2 independently represents H or CH<sub>3</sub>.)
- [0159] In the invention, a cationic ring-opening polymerizable compound having one or more cyclic ether groups such as an epoxy group or an oxetane group in a molecule can be suitably used as an ultraviolet ray curable resin (polymerizable compound).
- [0160] As the cationic polymerizable compound, curable compounds including a ring-opening polymerizable group can be exemplified, and among these, a heterocyclic

group-containing curable compound is particularly preferable. Examples of such curable compounds include cyclic imino ethers such as epoxy derivatives, oxetane derivatives, tetrahydrofuran derivatives, cyclic lactone derivatives, cyclic carbonate derivatives, and oxazoline derivatives, and vinyl ethers, and among these, epoxy derivatives, oxetane derivatives, and vinyl ethers are preferable.

[0161] Examples of the preferred epoxy derivatives include monofunctional glycidyl ethers, polyfunctional glycidyl ethers, monofunctional alicyclic epoxies, and polyfunctional alicyclic epoxies.

[0162] Examples of the specific compounds of glycidyl ethers include diglycidyl ethers (for example, ethylene glycol diglycidyl ether and bisphenol A diglycidyl ether), tri- or higher functional glycidyl ethers (for example, trimethylol ethane triglycidyl ether, trimethylol propane triglycidyl ether, glycerol triglycidyl ether, and triglycidyl trishydroxyethyl isocyanurate), tetra- or higher functional glycidyl ethers (for example, sorbitol tetraglycidyl ether, pentaerythritol tetraglycidyl ether, polyglycidyl ether of a cresol novolac resin, and polyglycidyl ether of a phenolic novolac resin), alicyclic epoxies (for example, polycyclohexyl epoxymethyl ether of a phenolic novolac resin), and oxetanes.

[0163] As the polymerizable compound, alicyclic epoxy derivatives can be preferably used. An "alicyclic epoxy group" refers to a substructure obtained by epoxidizing the double bond in the cycloalkene ring of a cyclopentene group, a cyclohexene group, or the like with a suitable oxidant such as hydrogen peroxide, peroxy acid, or the like.

[0164] As the alicyclic epoxy compound, polyfunctional alicyclic epoxy compounds having two or more cyclohexene oxide groups or cyclopentene oxide groups in a molecule is preferable.

Specific examples of the alicyclic epoxy compound include 4-vinylcyclohexene dioxide, (3,4-epoxycyclohexyl)methyl-3,4-epoxycyclohexyl carboxylate, di(3,4-epoxycyclohexyl)adipate, di(3,4-epoxycyclohexylmethyl)adipate, bis(2,3-epoxycyclopentyl)ether, di(2,3-epoxy-6-methylcyclohexylmethyl)adipate, and dicyclopentadiene dioxide.

[0165] A glycidyl compound having an ordinary epoxy group which does not have an alicyclic structure in the molecule may be used alone or in combination with the above alicyclic epoxy compounds.

[0166] As such an ordinary glycidyl compound, a glycidyl ether compound and a glycidyl ester compound can be exemplified, and the glycidyl ether compound is preferably used in combination.

[0167] Specific examples of the glycidyl ether compound include aromatic glycidyl ether compounds 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, and aliphatic glycidyl ether compounds such as 1,4-butanediol glycidyl ether, glycerol triglycidyl ether, propylene glycol diglycidyl ether, and trimethylolpropane triglycidyl ether. Examples of the glycidyl ester include glycidyl esters of a linolenic acid dimer.

[0168] As the polymerizable compound, a compound (hereinafter, simply referred to as an "oxetane compound") having an oxetanyl group which is a cyclic ether having a four-membered ring can be used. An oxetanyl group-containing compound is a compound having one or more oxetanyl groups in a molecule.

[0169] In addition, the liquid 2' may include a silicone-based polymerizable compound (silicone-based resin obtained by polymerization) as the polymerizable compound.

[0170] Thereby, for example, it is possible to suitably manufacture the three-dimensional structure 10 which is configured of a rubber-like material having elasticity. As a result, it is possible to suitably manufacture a three-dimensional structure having a movable portion and a deforming portion by elastic deformation.

[0171] The content of the curable resin material in the liquid 2' is preferably equal to or greater than 80% by mass, and more preferably equal to or greater than 85% by mass. Thereby, it is possible to make the mechanical strength or the like of the finally obtained three-dimensional structure 10 particularly excellent.

#### Other Components

[0172] In addition, the liquid 2' may include components other than the components described above. Examples of such components include various colorants such as a pigment and a dye; a dispersant; a surfactant; a polymerization initiator; a polymerization accelerator; a solvent; a penetration enhancer; a wetting agent (humectant); a fixing agent; a fungicide; a preservative; an antioxidant; an ultraviolet absorbent; a chelating agent; a pH adjusting agent; a thickener; a filler; an aggregation preventing agent; and a defoamer.

[0173] In particular, in a case where the liquid 2' includes a colorant, it is possible to obtain the three-dimensional structure 10 which is colored in the color corresponding to the color of the colorant, and it is possible to improve the design of the three-dimensional structure 10.

[0174] In particular, by including a pigment as a colorant, it is possible to make the light resistance of the liquid 2' and the three-dimensional structure 10 favorable. Both an inorganic pigment and an organic pigment can be used as the pigment.

[0175] Examples of the inorganic pigment include carbon blacks (C. I. Pigment Black 7) such as a furnace black, a lamp black, an acetylene black, and a channel black, iron oxide, and titanium oxide, and one type or two or more types selected from these can be used singly or in combination.

Among the inorganic pigments, titanium oxide is preferable in order to exhibit a

preferred white color.

- [0176] Examples of the organic pigments include azo pigments such as an insoluble azo pigment, a condensed azo pigment, an azo lake, and a chelate azo pigment, polycyclic pigments such as a phthalocyanine pigment, a perylene and a perinone 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, a basic dye type chelate, an acidic dye type chelate, and the like), a dyeing lake (a basic dye type lake and an acidic dye type lake), a nitro pigment, a nitroso pigment, an aniline black, and a daylight fluorescent pigment, and one type or two or more types selected from these can be used singly or in combination.
- [0177] In a case where the liquid 2' includes a pigment, the average particle diameter of the pigment is preferably equal to or less than 300 nm, and more preferably 50 nm to 250 nm. Thereby, it is possible to be made the discharge stability of the liquid 2' and the dispersion stability of the pigment in the liquid 2' particularly excellent, and it is possible to form an image having more excellent image quality.
- [0178] Moreover, in the specification, the average particle diameter refers to an average particle diameter based on volume, and for example, after a sample is added to methanol, the mixture is dispersed for 3 minutes with an ultrasonic wave disperser, and the average particle size of the obtained dispersion is measured using an aperture of 50 micrometers by a Coulter counter method particle size distribution measuring instrument (TA-II type manufactured by COULTER ELECTRONICS INS.).
- [0179] In addition, examples of the dyes include an acidic dye, a direct dye, a reactive dye, and a basic dye, and one type or two or more types selected from these can be used singly or in combination.
- [0180] In a case where the liquid 2' includes a colorant, the content of the colorant in the liquid 2' is preferably 1% by mass to 20% by mass. Thereby, particularly excellent concealing properties and color reproducibility are obtained.
- [0181] In particular, in a case where the liquid 2' includes titanium oxide as a colorant, the content of the titanium oxide in the liquid 2' is preferably 12% by mass to 18% by mass, and more preferably 14% by mass to 16% by mass. Thereby, particularly excellent concealing properties are obtained.
- [0182] In a case where the liquid 2' includes a pigment, if the liquid 2' further includes a dispersant, it is possible to make the dispersibility of the pigment more favorable. Examples of the dispersant, which are not particularly limited, include dispersants which are commonly used in the preparation of pigment dispersions such as a polymer dispersant. Specific examples of the polymer dispersant include dispersants containing one or more types among 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.

[0183] If the liquid 2' includes a surfactant, it is possible to make the abrasion resistance of the three-dimensional structure 10 more favorable. The surfactant is not particularly limited, and for example, silicone-based surfactants such as polyester-modified silicone or polyether-modified silicone can be used, and among these, polyether-modified polydimethyl siloxane or polyester-modified polydimethyl siloxane is preferably used.

[0184] In addition, the liquid 2' may include a solvent. Thereby, it is possible to suitably adjust the viscosity of the liquid 2', and even in a case where the liquid 2' includes a component having a high viscosity, it is possible to make the discharge stability of the liquid 2' by an ink jet method excellent.

[0185] Examples of the solvent include (poly)alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monomethyl ether, and propylene glycol monoethyl ether; acetic acid esters 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 acetyl acetone; and alcohols such as ethanol, propanol, and butanol, and one type or two or more types selected from these can be used singly or in combination.

[0186] In addition, the viscosity (viscosity when the liquid 2' is applied to a desired portion in the first solidified portion forming step) of the liquid 2' is preferably 2 mPa·s to 30 mPa·s, and more preferably 5 mPa·s to 20 mPa·s.

[0187] Thereby, it is possible to make the discharge stability of the liquid 2' by an ink jet method particularly excellent.

[0188] In addition, in manufacturing the three-dimensional structure 10, the plural types of liquid 2' may be used.

For example, the liquid 2' (color ink) including a colorant and the liquid 2' (clear ink) not including a colorant may be used. Thereby, for example, regarding an appearance of the three-dimensional structure 10, the liquid 2' including a colorant as the liquid 2' applied to a region that affects the color may be used, and regarding an appearance of the three-dimensional structure 10, the liquid 2' not including a colorant as the liquid 2' applied to a region that does not affect the color may be used. In addition, in the finally obtained three-dimensional structure 10, the plural types of liquid 2' may be used in combination such that a region (coating layer) formed using the liquid 2' not including a colorant is provided to the outer surface of a region formed using the liquid 2'

including a colorant.

[0189] In addition, for example, the plural types of liquid 2' including colorants having different constitutions may be used. Thereby, by combination of these liquids 2', it is possible to widen a color reproduction region that can be expressed.

In particular, since it is possible to suitably mix the plural types of liquid 2' in an arbitrary proportion in an ink jet method, it is possible to easily and reliably express a desired color.

[0190] In a case of using the plural types of liquid 2', it is preferable to use at least the liquid 2' having a cyan color, the liquid 2' having a magenta color, and the liquid 2' having a yellow color. Thereby, by combination of these liquids 2', it is possible to further widen a color reproduction region that can be expressed.

[0191] In addition, using the liquid 2' having a white color and other liquid 2' having a color in combination, for example, the following effect is obtained. That is, it is possible to make the finally obtained three-dimensional structure 10 have a first region where the liquid 2' having a white color is applied and a region (second region) where the liquid 2' having a color other than a white color is applied, and which is overlapped with the first region and provided on the outer surface than the first region. Thereby, the first region where the liquid 2' having a white color is applied can exhibit concealing properties, and it is possible to further increase color saturation of the three-dimensional structure 10.

Layer Forming Composition (Particle Containing Composition)

[0192] Next, the layer forming composition used in manufacturing the three-dimensional structure according to the invention will be described in detail.

[0193] The layer forming composition (particle containing composition) 1' includes the particles 11 as a filler, and the solvent 12 as a dispersion medium dispersing the particles 11.

[0194] By using the layer forming composition 1', it is possible to make the mechanical strength or the like of the finally obtained three-dimensional structure 10 particularly excellent, it is possible to make the fluidity of the layer forming composition 1' excellent and to also effectively prevent aggregation or the like of the particles 11, and it is possible to make ease of handling (handleability) of the layer forming composition 1' during manufacture particularly excellent.

Particles

[0195] The layer forming composition 1' includes the plurality of particles 11.

[0196] The particle 11 has preferably a high hardness.

Thereby, it is possible to make the mechanical strength or the like of the finally obtained three-dimensional structure 10 particularly excellent.

[0197] The hardness of the particles 11 can be determined, for example, by particle com-



pression strength evaluation using MCT-210 (manufactured by Shimadzu Corporation).

[0198] The particles 11 are preferably porous particles having pores which open to the outside and subjected to a hydrophobization treatment.

[0199] By such a configuration, it is possible to make the curable resin material (polymerizable compound) configuring the liquid 2' suitably penetrate into the pores when the three-dimensional structure 10 is manufactured (in the first solidified portion forming step), and an anchoring effect is exhibited. As a result, it is possible to make the bonding force of the particles 11 particularly excellent, and as a result, it is possible to make the mechanical strength of the overall three-dimensional structure 10 particularly excellent. In addition, when the curable resin material (polymerizable compound) configuring the liquid 2' enters into the pores of the particles 11, it is possible to effectively prevent unintended wet-spreading of the liquid 2'. As a result, it is possible to make the dimensional accuracy of the finally obtained three-dimensional structure 10 higher.

[0200] Examples of the constituent material of the particles 11 include an inorganic material, an organic material, and a complex of these.

[0201] Examples of the inorganic material configuring the particles 11 include various metals and metal compounds. Examples of the metal compound include 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; and various metal borates such as aluminum borate and magnesium borate, or composite compounds of these.

[0202] As the organic material configuring the particles 11, synthetic resins and natural polymers can be exemplified, and more specific examples thereof include a polyethylene resin; polypropylene; polyethylene oxide; polypropylene oxide, polyethylene imine; polystyrene; polyurethane; polyurea; polyester; a silicone resin; an acrylic silicone resin; polymers having (meth)acrylic acid ester as a constituent monomer such as polymethyl methacrylate; cross polymers having (meth)acrylic acid ester as a constituent monomer such as methyl methacrylate cross polymer (ethylene acrylic acid copolymer resin or the like); polyamide resins such as nylon 12, nylon 6, and copolymer nylon; polyimide; carboxymethyl cellulose; gelatin; starch; chitin; and

chitosan.

[0203] Among these, the particles 11 are preferably configured of a metal oxide, and more preferably configured of silica.

[0204] Thereby, it is possible to make characteristics such as mechanical strength and light resistance of the three-dimensional structure particularly excellent.

[0205] In addition, in particular, in a case where the particles 11 are configured of silica, the effect as described above is more significantly exhibited. In addition, since silica has also excellent fluidity, silica is useful for forming a layer having higher thickness uniformity, and silica is also advantageous from the viewpoint of making the productivity and dimensional accuracy of the three-dimensional structure particularly excellent.

[0206] The particles 11 may be subjected to a surface treatment such as a hydrophobization treatment.

As the hydrophobization treatment performed to the particles 11, any treatment may be used as long as it increases hydrophobicity of the particles (base particles), and it is preferable to introduce a hydrocarbon group.

[0207] Thereby, it is possible to further increase hydrophobicity of the particles 11. In addition, it is possible to easily and reliably further increase uniformity of the degree of the hydrophobization treatment at each portion (including the surface of the inside of a pore in the case of having a pore which opens to the outside) of each particle 11 or the surface of the particle 11.

[0208] As a compound used in the hydrophobization treatment, a silane compound including a silyl group is preferable. Specific examples of the compound which can be used in the hydrophobization treatment include hexamethyldisilazane, dimethyl dimethoxysilane, diethyl diethoxysilane, 1-propenylmethyl dichlorosilane, propyldimethyl chlorosilane, propylmethyl dichlorosilane, propyl trichlorosilane, propyl triethoxysilane, propyl trimethoxysilane, styrylethyl trimethoxysilane, tetradecyl trichlorosilane, 3-thiocyanatopropyl triethoxysilane, p-tolyldimethyl chlorosilane, p-tolylmethyl dichlorosilane, p-tolyl trichlorosilane, p-tolyl trimethoxysilane, p-tolyl triethoxysilane, di-n-propyl di-n-propoxysilane, diisopropyl diisopropoxysilane, di-n-butyl di-n-butyroxysilane, di-sec-butyl di-sec-butyroxysilane, di-t-butyl di-t-butyroxysilane, octadecyl trichlorosilane, octadecylmethyl diethoxysilane, octadecyl triethoxysilane, octadecyl trimethoxysilane, octadecyldimethyl chlorosilane, octadecylmethyl dichlorosilane, octadecyl methoxydichlorosilane, 7-octenyldimethyl chlorosilane, 7-octenyl trichlorosilane, 7-octenyl trimethoxysilane, octylmethyl dichlorosilane, octyldimethyl chlorosilane, octyl trichlorosilane, 10-undecenyldimethyl chlorosilane, undecyl trichlorosilane, vinyl dimethyl chlorosilane, methyloctadecyl dimethoxysilane, methyl dodecyl diethoxysilane, methyloctadecyl diethoxysilane, n-

octylmethyl dimethoxysilane, n-octylmethyl diethoxysilane, triacontyldimethyl chlorosilane, triacontyl trichlorosilane, methyl trimethoxysilane, methyl triethoxysilane, methyl tri-n-propoxysilane, methyl isopropoxysilane, methyl-n-butyroxysilane, methyl tri-sec-butyroxysilane, methyl tri-t-butyroxysilane, ethyl trimethoxysilane, ethyl triethoxysilane, ethyl tri-n-propoxysilane, ethyl isopropoxysilane, ethyl-n-butyroxysilane, ethyl tri-sec-butyroxysilane, ethyl tri-t-butyroxysilane, 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-octadecyl triethoxysilane, 2-[2-(trichlorosilyl)ethyl]pyridine, 4-[2-(trichlorosilyl)ethyl]pyridine, diphenyl dimethoxysilane, diphenyl diethoxysilane, 1,3-(trichlorosilylmethyl)heptacosane, dibenzyl dimethoxysilane, dibenzyl diethoxysilane, phenyl trimethoxysilane, phenylmethyl dimethoxysilane, phenyldimethyl methoxysilane, phenyl dimethoxysilane, phenyl diethoxysilane, phenylmethyl diethoxysilane, phenyldimethyl ethoxysilane, benzyl triethoxysilane, benzyl trimethoxysilane, benzylmethyl dimethoxysilane, benzyldimethyl methoxysilane, benzyl dimethoxysilane, benzyl diethoxysilane, benzylmethyl diethoxysilane, benzyldimethyl ethoxysilane, 3-acetoxypropyl trimethoxysilane, 3-acryloxypropyl trimethoxysilane, allyl trimethoxysilane, allyl triethoxysilane, 4-aminobutyl triethoxysilane, (aminoethylaminomethyl)phenethyl trimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyl dimethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, 6-(aminohexylaminopropyl) trimethoxysilane, p-aminophenyl trimethoxysilane, p-aminophenyl ethoxysilane, m-aminophenyl trimethoxysilane, m-aminophenyl ethoxysilane, 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, omega-aminoundecyl trimethoxysilane, amyl triethoxysilane, benzoxasilepine dimethylester, 5-(bicycloheptenyl) triethoxysilane, bis(2-hydroxyethyl)-3-aminopropyl triethoxysilane, 8-bromooctyl trimethoxysilane, bromophenyl trimethoxysilane, 3-bromopropyl trimethoxysilane, n-butyl trimethoxysilane, 2-chloromethyl triethoxysilane, chloromethylmethyl diethoxysilane, chloromethylmethyl diisopropoxysilane, p-(chloromethyl)phenyl trimethoxysilane, chloromethyl triethoxysilane, chlorophenyl triethoxysilane, 3-chloropropylmethyl dimethoxysilane, 3-chloropropyl triethoxysilane, 3-chloropropyl trimethoxysilane, 2-(4-chlorosulfonylphenyl)ethyl trimethoxysilane, 2-cyanoethyl triethoxysilane, 2-cyanoethyl trimethoxysilane, cyanomethylphenethyl 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)ethyldimethyl chlorosilane, 2-(3-cyclohexenyl)ethylmethyl dichlorosilane, cyclohexyldimethyl chlorosilane, cyclohexylethyl dimethoxysilane, cyclohexylmethyl dichlorosilane, cyclohexylmethyl dimethoxysilane, (cyclohexylmethyl)trichlorosilane, cyclohexyl trichlorosilane, cyclohexyl trimethoxysilane, cyclooctyl trichlorosilane, (4-cyclooctenyl)trichlorosilane, cyclopentyl trichlorosilane, cyclopentyl trimethoxysilane, 1,1-diethoxy-1-silacyclopenta-3-en, 3-(2,4-dinitrophenylamino)propyl triethoxysilane, (dimethylchlorosilyl)methyl-7,7-dimethylnorpinane, (cyclohexylaminomethyl)methyl diethoxysilane, (3-cyclopentadienylpropyl)triethoxysilane, N,N-diethyl-3-aminopropyl)trimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyl trimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyl triethoxysilane, (furfuryloxymethyl)triethoxysilane, 2-hydroxy-4-(3-triethoxypropoxy)diphenyl ketone, 3-(p-methoxyphenyl)propylmethyl dichlorosilane, 3-(p-methoxyphenyl)propyl trichlorosilane, p-(methylphenethyl)methyl dichlorosilane, p-(methylphenethyl)trichlorosilane, p-(methylphenethyl)dimethyl chlorosilane, 3-morpholinopropyl trimethoxysilane, (3-glycidoxypropyl)methyl diethoxysilane, 3-glycidoxypropyl 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-isocyanatopropyl triethoxysilane, (mercaptomethyl)methyl diethoxysilane, 3-mercaptopropylmethyl dimethoxysilane, 3-mercaptopropyl dimethoxysilane, 3-mercaptopropyl triethoxysilane, 3-methacryloxypropylmethyl diethoxysilane, 3-methacryloxypropyl trimethoxysilane, methyl {2-(3-trimethoxysilylpropylamino)ethylamino}-3-propionate, R-N-alpha-phenethyl-N'-triethoxysilylpropyl urea, S-N-alpha-phenethyl-N'-triethoxysilylpropyl urea, phenethyl trimethoxysilane, phenethylmethyl dimethoxysilane, phenethyl dimethyl methoxysilane, phenethyl dimethoxysilane, phenethyl diethoxysilane, phenethylmethyl diethoxysilane, phenethyl dimethyl ethoxysilane, phenethyl triethoxysilane, (3-phenylpropyl)dimethyl chlorosilane, (3-phenylpropyl)methyl dichlorosilane, N-phenylaminopropyl trimethoxysilane, N-(triethoxysilylpropyl)dansylamide, N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole, 2-(triethoxysilylethyl)-5-(chloroacetoxy)bicycloheptane, (S)-N-triethoxysilylpropyl-O-menthocarbamate, 3-(triethoxysilylpropyl)-p-nitrobenzamide, 3-(triethoxysilyl)propyl succinic anhydride, N-[5-(trimethoxysilyl)-2-aza-1-oxo-pentyl]caprolactam, 2-(trimethoxysilylethyl)pyridine, N-(trimethoxysilylethyl)benzyl-N,N,N-trimethyl ammonium chloride, phenylvinyl diethoxysilane, 3-thiocyanatopropyl triethoxysilane, (tridecafluoro-1,1,2,2,-tetrahydrooctyl)triethoxysilane, N-

{3-(triethoxysilyl)propyl}phthalamic acid, (3,3,3-trifluoropropyl)methyl dimethoxysilane, (3,3,3-trifluoropropyl)trimethoxysilane, 1-trimethoxysilyl-2-(chloromethyl)phenyl ethane, 2-(trimethoxysilyl)ethylphenylsulfonil azide, beta-trimethoxysilylethyl-2-pyridine, trimethoxysilylpropyldiethylene triamine, N-(3-trimethoxysilylpropyl)pyrrole, N-trimethoxysilylpropyl-N,N,N-tributyl ammonium bromide, N-trimethoxysilylpropyl-N,N,N-tributyl ammonium chloride, N-trimethoxysilylpropyl-N,N,N-trimethyl ammonium chloride, vinyl-methyldiethoxysilane, vinyl triethoxysilane, vinyl trimethoxysilane, vinylmethyl dimethoxysilane, vinyl dimethyl methoxysilane, vinyl dimethyl ethoxysilane, vinylmethyl dichlorosilane, vinylphenyl dichlorosilane, vinylphenyl diethoxysilane, vinylphenyl dimethyl silane, vinylphenylmethyl chlorosilane, vinyl triphenoxysilane, vinyl tris-t-butoxysilane, adamantylethyl trichlorosilane, allylphenyl trichlorosilane, 3-aminophenyldimethylvinyl silane, phenyl trichlorosilane, phenyldimethyl chlorosilane, phenylmethyl dichlorosilane, benzyl trichlorosilane, benzyldimethyl chlorosilane, benzylmethyl dichlorosilane, phenethyldiisopropyl chlorosilane, phenethyl trichlorosilane, phenethyldimethyl chlorosilane, phenethylmethyl dichlorosilane, 5-(bicycloheptyl)trichlorosilane, 2-(bicycloheptyl)dimethyl chlorosilane, 2-(bicycloheptyl)trichlorosilane, 1,4- bis(trimethoxysilylethyl)benzene, bromophenyl trichlorosilane, 3-phenoxypropyldimethyl chlorosilane, 3-phenoxypropyl trichlorosilane, t-butylphenyl chlorosilane, t-butylphenyl methoxysilane, t-butylphenyl dichlorosilane, p-(t-butyl)phenethyldimethyl chlorosilane, p-(t-butyl)phenethyl trichlorosilane, 1,3-(chlorodimethylsilylmethyl)heptacosane, ((chloromethyl)phenylethyl)dimethyl chlorosilane, ((chloromethyl)phenylethyl)methyl dichlorosilane, ((chloromethyl)phenylethyl)trichlorosilane, ((chloromethyl)phenylethyl)trimethoxysilane, chlorophenyl trichlorosilane, 2-cyanoethyl trichlorosilane, 2-cyanoethylmethyl dichlorosilane, 3-cyanopropylmethyl diethoxysilane, 3-cyanopropylmethyl dichlorosilane, 3-cyanopropyldimethyl ethoxysilane, 3-cyanopropyl trichlorosilane, and fluorinated alkyl silanes, and one type or two or more types selected from these can be used singly or in combination.

[0209] Among these, hexamethyl disilazane is preferably used in the hydrophobization treatment. Thereby, it is possible to further increase hydrophobicity of the particles 11. In addition, it is possible to easily and reliably further increase uniformity of the degree of the hydrophobization treatment at each portion (including the surface of the inside of a pore in the case of having a pore which opens to the outside) of each particle 11 or the surface of the particle 11.

[0210] In a case where the hydrophobization treatment using a silane compound is performed in a liquid phase, by immersing the particles (base particles) to be subjected

to the hydrophobization treatment in the liquid including the silane compound, it is possible to make a suitable desired reaction proceed, and it is possible to form a chemical adsorption film of the silane compound.

[0211] In addition, in a case where the hydrophobization treatment using a silane compound is performed in a gas phase, by exposing the particles (base particles) to be subjected to the hydrophobization treatment to the vapor of the silane compound, it is possible to make a suitable desired reaction proceed, and it is possible to form a chemical adsorption film of the silane compound.

[0212] Though the average particle diameter of the particles 11 is not particularly limited, the average particle diameter of the particles 11 is preferably 1 micrometer to 25 micrometers, and more preferably 1 micrometer to 15 micrometers.

[0213] Thereby, it is possible to make the mechanical strength of the three-dimensional structure 10 particularly excellent, it is possible to more effectively prevent an occurrence of unintended unevenness in the three-dimensional structure 10 to be manufactured, and it is possible to make the dimensional accuracy of the three-dimensional structure 10 particularly excellent. In addition, it is possible to make the fluidity of the layer forming composition 1' particularly excellent, and it is possible to make the productivity of the three-dimensional structure 10 particularly excellent.

[0214]  $D_{\max}$  of the particles 11 is preferably 3 micrometers to 40 micrometers, and more preferably 5 micrometers to 30 micrometers.

[0215] Thereby, it is possible to make the mechanical strength of the three-dimensional structure 10 particularly excellent, it is possible to more effectively prevent an occurrence of unintended unevenness in the three-dimensional structure 10 to be manufactured, and it is possible to make the dimensional accuracy of the three-dimensional structure 10 particularly excellent. In addition, it is possible to make the fluidity of the layer forming composition 1' particularly excellent, and it is possible to make the productivity of the three-dimensional structure 10 particularly excellent.

[0216] The porosity of the particles 11 is preferably equal to or greater than 50%, and more preferably 55% to 90%.

[0217] Thereby, the particles can have sufficient space (pores) into which the resin material (binder) enters, and it is possible to make the mechanical strength of the particles 11 excellent, and as a result, it is possible to make the mechanical strength of the three-dimensional structure 10 having the bound portion 3 obtained by penetration of the resin material (binder) into pores particularly excellent.

[0218] Moreover, in the present, the porosity of the particles 11 refers to a proportion (volume ratio) of pores which are present in the inside of the particles 11, with respect to the apparent volume of the particles 11, and when the density of the particles 11 is defined as  $\rho$  [ $\text{g}/\text{cm}^3$ ] and the true density of the constituent material of the particles

11 is defined as  $\rho_0$  [g/cm<sup>3</sup>], the porosity of the particles 11 is a value represented by  $\{(\rho_0 - \rho)/\rho_0\} \times 100$ .

[0219] The average pore diameter (fine pore diameter) of the particles 11 is preferably equal to or greater than 10 nm, and more preferably 50 nm to 300 nm.

[0220] Thereby, it is possible to make the mechanical strength of the finally obtained three-dimensional structure 10 particularly excellent. In addition, in the case of using the liquid 2' (color ink) including a pigment in manufacturing the three-dimensional structure 10, it is possible to suitably hold the pigment in pores of the particles 11. Therefore, it is possible to prevent unwanted diffusion of the pigment, and it is possible to more reliably form a high-definition image.

[0221] Although the particles 11 may have any shape, the particles 11 preferably have a spherical shape. Thereby, it is possible to make the fluidity of the layer forming composition 1' particularly excellent and make the productivity of the three-dimensional structure 10 particularly excellent, and it is possible to more effectively prevent an occurrence of unintended unevenness in the three-dimensional structure 10 to be manufactured and make the dimensional accuracy of the three-dimensional structure 10 particularly excellent.

[0222] The layer forming composition 1' may include the plural types of particles 11.

The content of the particles 11 in the layer forming composition 1' is preferably 8% by mass to 91% by mass, and more preferably 10% by mass to 53% by mass.

[0223] Thereby, it is possible to make the mechanical strength of the finally obtained three-dimensional structure 10 excellent, while making the fluidity of the layer forming composition 1' particularly excellent.

#### Solvent

[0224] The layer forming composition 1' includes the solvent 12.

[0225] Thereby, it is possible to make handleability (ease of handling) of the layer forming composition 1' particularly excellent, it is possible to easily form the layer 1 having higher thickness uniformity, and it is possible to more effectively prevent unintended deformation of the layer 1.

[0226] Examples of the solvent configuring the layer forming composition 1' include water; alcoholic solvents such as methanol, ethanol, and isopropanol; ketone-based solvents such as methyl ethyl ketone and acetone; glycol ether-based solvents such as ethylene glycol monoethyl ether and ethylene glycol monobutyl ether, glycol ether acetate-based solvents such as propylene glycol 1-monomethyl ether 2-acetate and propylene glycol 1-monoethyl ether 2-acetate; polyethylene glycol, and polypropylene glycol, and one type or two or more types selected from these can be used singly or in combination.

[0227] Among these, the layer forming composition 1' preferably includes an aqueous

solvent, and more preferably includes water.

[0228] Thereby, it is possible to make the fluidity of the layer forming composition 1' and the uniformity of the constitution of the layer 1 formed using the layer forming composition 1' particularly excellent. Water is easily removed after the layer 1 is formed, and scarcely exercises adverse effects even in a case where water remains in the three-dimensional structure 10. Water is also advantageous from the viewpoint of safety with respect to human body and environmental issues. In addition, in a case where the layer forming composition 1' includes a water-soluble resin as a binder described below in detail, it is possible to make the water-soluble resin be in a more suitable dissolved state in the layer forming composition 1', and effects due to including a binder (water-soluble resin) as described below in detail are more effectively exhibited.

[0229] The aqueous solvent is not limited as long as it has a high solubility in water, and specifically, for example, an aqueous solvent having a solubility (mass dissolvable in 100g of water) of equal to or greater than 30 [g/100 g water] in water at 25 degrees centigrade is preferable, and an aqueous solvent having a solubility of equal to or greater than 50 [g/100 g water] in water at 25 degrees centigrade is more preferable.

[0230] The content of the solvent 12 in the layer forming composition 1' is preferably 9% by mass to 92% by mass, and more preferably 29% by mass to 89% by mass.

[0231] Thereby, since effects due to including the solvent 12 as described above can be more significantly exhibited, and it is possible to easily remove the solvent 12 in a short period of time in the manufacturing step of the three-dimensional structure 10, including a solvent is advantageous from the viewpoint of productivity improvement of the three-dimensional structure 10.

[0232] In particular, the content of the water in the layer forming composition 1' is preferably 18% by mass to 92% by mass, and more preferably 47% by mass to 90% by mass. Thereby, effects as described above are more significantly exhibited.

#### Binder

[0233] The layer forming composition 1' may include the plurality of particles 11, the solvent 12, and a binder.

[0234] Thereby, in the layer 1 (in particular, the layer 1 in a state in which the solvent 12 is removed) formed using the layer forming composition 1', it is possible to suitably bind (temporarily fix) the plurality of particles 11, and it is possible to effectively prevent unintended scattering of the particles 11. Thereby, it is possible to further improve safety of a worker and the dimensional accuracy of the three-dimensional structure 10 to be manufactured.

[0235] In a case where the layer forming composition 1' includes a binder, it is preferable that the binder is dissolved in the solvent 12, in the layer forming composition 1'.

[0236] Thereby, it is possible to make the fluidity of the layer forming composition 1' par-



ticularly favorable, and it is possible to more effectively prevent unintended variations in the thickness of the layer 1 formed using the layer forming composition 1'. In addition, when the layer 1 in a state in which the solvent 12 is removed is formed, it is possible to attach the binder to the particles 11 with higher uniformity over the entire layer 1, and it is possible to more effectively prevent an occurrence of unintended constitution unevenness. For this reason, it is possible to more effectively prevent an occurrence of unintended variations in the mechanical strength at each portion of the finally obtained three-dimensional structure 10, and it is possible to further increase the reliability of the three-dimensional structure 10.

[0237] Although the binder may have a function of temporarily fixing the plurality of particles 11 in the layer 1 (in particular, the layer 1 in a state in which the solvent 12 is removed) formed using the layer forming composition 1', it is possible to suitably use a water-soluble resin.

[0238] In a case where the layer forming composition 1' includes an aqueous solvent (in particular, water) as the solvent 12 by including a water-soluble resin, the binder (water-soluble resin) can be included in the layer forming composition 1' in a dissolved state, and it is possible to make the fluidity, and the handleability (ease of handling) of the layer forming composition 1' particularly excellent. As a result, it is possible to make the productivity of the three-dimensional structure 10 particularly excellent.

[0239] It is possible to easily and efficiently remove the portion where the liquid 2' is not applied in the layer 1 in the manufacturing step of the three-dimensional structure 10, by applying an aqueous solvent (in particular, water). As a result, it is possible to make the productivity of the three-dimensional structure 10 particularly excellent. In addition, since it is possible to easily and reliably prevent the portion where the layer should be removed from attaching to or remaining in the finally obtained three-dimensional structure 10, it is possible to make the dimensional accuracy of the three-dimensional structure 10 particularly excellent.

[0240] Hereinafter, the water-soluble resin as a binder will be described mainly.

The water-soluble resin is not limited as long as at least a part thereof is soluble in an aqueous solvent, and for example, a water-soluble resin having a solubility of equal to or greater than 5 [g/100 g water] in water at 25 degrees centigrade is preferable, and a water-soluble resin having a solubility of equal to or greater than 10 [g/100 g water] in water at 25 degrees centigrade is more preferable.

[0241] Examples of the water-soluble resin include synthetic polymers such as polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), polycaprolactonediol, sodium polyacrylate, polyacryl amide, modified polyamide, polyethylene imine, polyethylene oxide, and a random copolymer of ethylene oxide and propylene oxide, natural polymers such as cornstarch, mannan, pectin, agar, alginic acid, dextran, glues, and

gelatin, and semi-synthetic polymers such as carboxymethyl cellulose, hydroxyethyl cellulose, oxidized starch, and modified starch, and one type or two or more types selected from these can be used singly or in combination.

- [0242] Specific examples of the water-soluble resin product include methyl cellulose (manufactured by Shin-Etsu Chemicals Co., Ltd., Metolose SM-15), hydroxyethyl cellulose (manufactured by Fuji Chemical Industry Co., Ltd., AL-15), hydroxypropyl cellulose (manufactured by Nippon Soda Co., Ltd., HPC-M), carboxymethyl cellulose (Nichirin Chemical Co., Ltd., CMC-30), sodium (I) starch phosphate (manufactured by Matsutani Chemical Industry Co., Ltd., Hoster 5100), polyvinyl pyrrolidone (manufactured by Tokyo Chemical Industry Co., Ltd., PVP K-90), a methyl vinyl ether/maleic anhydride copolymer (manufactured by GAF Gantrez, AN-139), polyacryl amide (manufactured by Wako Pure Chemical Industries, Ltd.), modified polyamide (modified nylon) (manufactured by Toray Industries, Inc., AQ nylon), polyethylene oxide (PEO-1 manufactured by Steel Chemical Co., Ltd., Alkox manufactured by Meisei Chemical Works, Ltd.), an ethylene oxide/propylene oxide random copolymer (manufactured by Meisei Chemical Works, Ltd., Alkox EP), sodium polyacrylate (manufactured by Wako Pure Chemical Industries, Ltd.), and a carboxyvinyl polymer/cross-linked acryl-based water-soluble resin (manufactured by Sumitomo Seika Chemicals Co., Ltd., AQUPEC).
- [0243] Among these, in a case where the water-soluble resin as a binder is polyvinyl alcohol, it is possible to make the mechanical strength of the three-dimensional structure 10 particularly excellent. In addition, by adjusting the saponification degree and the polymerization degree, it is possible to more suitably control characteristics (for example, water solubility and water resistance) of the binder or characteristics (for example, viscosity, fixing force of the particles 11, and wettability) of the layer forming composition 1'. Therefore, it is possible to more suitably cope with according to manufacture of the various three-dimensional structures 10. In addition, among various water-soluble resins, polyvinyl alcohol is inexpensive and a supply thereof is stable. Therefore, it is possible to manufacture the stable three-dimensional structure 10 while reducing the production cost.
- [0244] In a case where the water-soluble resin as a binder includes polyvinyl alcohol, the saponification degree of the polyvinyl alcohol is preferably 85 to 90. Thereby, it is possible to suppress decrease in the solubility of the polyvinyl alcohol in an aqueous solvent (in particular, water). For this reason, in a case where the layer forming composition 1' includes an aqueous solvent (in particular, water), it is possible to more effectively suppress reduction in the adhesion between the layers 1 which are adjacent.
- [0245] In a case where the water-soluble resin as a binder includes polyvinyl alcohol, the polymerization degree of the polyvinyl alcohol is preferably 300 to 1000. Thereby, in a

case where the layer forming composition 1' includes an aqueous solvent (in particular, water), it is possible to make the mechanical strength of each layer 1 or the adhesion between the layers 1 which are adjacent particularly excellent.

[0246] In addition, in a case where the water-soluble resin as a binder is polyvinyl pyrrolidone (PVP), the following effects are obtained. That is, since polyvinyl pyrrolidone has excellent adhesion with respect to various materials such as glass, metal, and plastic, it is possible to make the strength and stability of the shape of the portion where the liquid 2' is not applied in the layer 1 particularly excellent, and it is possible to make the dimensional accuracy of the finally obtained three-dimensional structure 10 particularly excellent. Since polyvinyl pyrrolidone shows high solubility in various organic solvents, in a case where the layer forming composition 1' includes an organic solvent, it is possible to make the fluidity of the layer forming composition 1' particularly excellent, it is possible to suitably form the layer 1' in which unintentional variations in the thickness are more effectively prevented, and it is possible to make the dimensional accuracy of the finally obtained three-dimensional structure 10 particularly excellent. Since polyvinyl pyrrolidone shows high solubility also in an aqueous solvent (in particular, water), in the unbound particle removing step (after forming ends), it is possible to easily and reliably remove the particles which are not bound by a binder (reaction product of the resin material (polymerizable compound) configuring the liquid 2') of the particles 11 configuring each layer 1. In addition, since polyvinyl pyrrolidone has excellent affinity with various colorants, in the case of using the liquid 2' including a colorant in the first solidified portion forming step, it is possible to effectively prevent the colorant from being unintentionally spread.

[0247] In a case where the water-soluble resin as a binder includes polyvinyl pyrrolidone, the weight average molecular weight of the polyvinyl pyrrolidone is preferably 10000 to 1700000, and more preferably 30000 to 1500000.

Thereby, it is possible to more effectively exhibit the function described above.

[0248] In a case where the water-soluble resin as a binder includes polycaprolactonediol, the weight average molecular weight of the polycaprolactonediol is preferably 10000 to 1700000, and more preferably 30000 to 1500000.

Thereby, it is possible to more effectively exhibit the function described above.

[0249] In the layer forming composition 1', the binder is preferably in a liquid state (for example, a dissolved state or a molten state) in the film forming step. Thereby, it is possible to easily and reliably further increase uniformity in the thickness of the layer 1 formed using the layer forming composition 1'.

[0250] In a case where the layer forming composition 1' includes a binder, the content of the binder in the layer forming composition 1' is preferably 0.5% by mass to 25% by mass, and more preferably 1.0% by mass to 10% by mass.

[0251] Thereby, effects due to including a binder as described above are more significantly exhibited, it is possible to sufficiently increase the content of the particles 11 in the layer forming composition 1', and it is possible to make the mechanical strength of the manufactured three-dimensional structure 10 particularly excellent.

#### Other Components

[0252] The layer forming composition may include components other than the components described above. Examples of such components include a polymerization initiator; a polymerization accelerator; a penetration enhancer; a wetting agent (humectant); a fixing agent; a fungicide; a preservative; an antioxidant; a ultraviolet absorbent; a chelating agent; and a pH adjusting agent.

#### Three-Dimensional Structure Manufacturing Apparatus

[0253] Next, the three-dimensional structure manufacturing apparatus according to the invention will be described.

[0254] Fig. 9 is a cross-sectional view schematically showing a preferred embodiment of the three-dimensional structure manufacturing apparatus according to the invention.

[0255] A three-dimensional structure manufacturing apparatus M100 is an apparatus for manufacturing the three-dimensional structure 10 by repeatedly forming the layers 1 using the liquid 2', the thermoplastic composition 2'', and the layer forming composition (particle containing composition) 1', and stacking the layers 1. In particular, the three-dimensional structure manufacturing apparatus M100 is an apparatus for manufacturing the three-dimensional structure 10 by performing the method for manufacturing a three-dimensional structure according to the invention as described above.

[0256] As shown in Fig. 9, the three-dimensional structure manufacturing apparatus M100 has a control portion M2, a particle containing composition supply portion M3 which accommodates the layer forming composition 1', a layer forming portion M4 which forms the layer 1 using the layer forming composition 1' supplied from the particle containing composition supply portion M3, a liquid discharge portion (liquid applying unit) M5 which discharges the liquid (first solidified portion forming liquid) 2' to the layer 1, an energy ray irradiation unit (curing unit) M6 which applies energy rays to cure the liquid 2', a thermoplastic composition applying unit M8 which applies the thermoplastic composition 2'' for forming the second solidified portion 2B in a melted state, and the height measuring unit M9 which measures the height of the solidified product 6 formed using the thermoplastic composition 2''.

[0257] The control portion M2 has a computer M21 and a drive control portion M22.

The computer M21 is a general desk type computer which is configured to equip a CPU and a memory therein. The computer M21 converts the shape of the three-dimensional structure 10 to model data, and a cross-sectional data (slice data) obtained by slicing the model data into several parallel layers of a thin cross-sectional body is

output to the drive control portion M22. In addition, the height of the upper surface of the solidified product 6 is measured by the height measuring unit M9 described below, and in the case of adjusting the thickness of the layer 1 based on the height, rewriting (correction and revision) of the cross-sectional data (slice data) is performed based on the thickness of the layer 1.

- [0258] The drive control portion M22 functions as a controller which drives the layer forming portion M4, the liquid discharge portion M5, the energy ray irradiation unit M6, the thermoplastic composition applying unit M8, the height measuring unit M9, or the like, respectively. Specifically, for example, the drive control portion M22 controls a discharge pattern or a discharge amount of the liquid 2' by the liquid discharge portion M5, the heating temperature, an ejection pattern, or an ejection amount of the thermoplastic composition 2'' by the thermoplastic composition applying unit M8, the supply amount of the layer forming composition 1' from the particle containing composition supply portion M3, and the extent of descent of the stage (lifting stage) M41.
- [0259] The particle containing composition supply portion M3 is moved by the instructions from the drive control portion M22, and configured such that the layer forming composition 1' accommodated therein is supplied to the stage M41.
- [0260] The layer forming portion M4 has, the stage (lifting stage) M41 to which the layer forming composition 1' is supplied and supports the layer 1 formed of the layer forming composition 1', the flattening unit (squeegee) M42 which forms the layer 1 while flattening the layer forming composition 1' held on the stage M41, a guide rail M43 which regulates the operation of the flattening unit M42, and a frame body M45 which surrounds the lifting stage M41 and is provided so as to be in close contact with the lifting stage M41.
- [0261] The lifting stage M41 descends sequentially by only a predetermined extent by the instructions from the drive control portion M22 when forming a new layer 1 on the layer 1 formed previously. By the extent of descent of the lifting stage M41 and the height of the flattening unit M42 described below in detail, the thickness of the layer 1 newly formed is defined.
- [0262] The stage M41 has the flat surface (a portion to which the layer forming composition 1', the liquid 2', and the thermoplastic composition 2'' are applied, a portion including the first region M411 and the second region M412). Thereby, it is possible to easily and reliably form the layer 1 having high thickness uniformity. In addition, on the basis of the height of the upper surface of the solidified product 6, it is possible to suitably adjust the thickness of the layer 1 newly formed.
- [0263] The stage M41 is preferably configured of a material having high strength. Examples of the constituent material of the stage M41 include various metal materials such as stainless steel.

- [0264] In addition, a surface treatment may be performed on the surface (a portion to which the layer forming composition 1', the liquid 2', and the thermoplastic composition 2'' are applied. a portion including the first region M411 and the second region M412) of the stage M41. Thereby, for example, it is possible to more effectively prevent the constituent material of the layer forming composition 1' or the constituent material of the liquid 2' from being strongly attached to the stage M41, it is possible to make the durability of the stage M41 particularly excellent, or it is possible to stably produce the three-dimensional structure 10 over a longer period of time. Examples of the material used in the surface treatment of the surface of the stage M41 include fluorine-based resins such as polytetrafluoroethylene.
- [0265] The squeegee as the flattening unit M42 has a long shape extending in the Y direction, and is equipped with a blade having a blade-like shape in which the lower tip is sharp.
- [0266] Since the layer 1 formed by flattening of the layer forming composition 1' by the flattening unit M42 is suitably adjusted as necessary based on information such as the height of the upper surface of the solidified product 6 by the height measuring unit M9, it is possible to prevent the constituent (for example, the particles 11) of the layer forming composition 1' from unintentionally remaining on the upper surface of the solidified portion 2 at the time when the layer forming step ends.
- [0267] The blade may be equipped with a vibration mechanism (not shown in the drawing) which applies fine vibration to the blade such that diffusion of the layer forming composition 1' by the flattening unit (squeegee) M42 is smoothly performed.
- [0268] For example, the three-dimensional structure manufacturing apparatus M100 may be equipped with a stress detecting unit (not shown in the drawing) which detects stress applied to the flattening unit M42 when the flattening unit M42 is in contact with the upper surface of the solidified product 6 formed at the second region M412 of the stage M41.
- [0269] Thereby, for example, in a case where the flattening unit M42 is in contact with the upper surface of the solidified product 6, it is possible to determine the state where a predetermined stress with respect to the flattening unit M42 becomes a predetermined value as the height of the flattening unit M42 at the time of formation of the layer 1.
- [0270] Moreover, bringing the flattening unit M42 into contact with the solidified product 6 can be more suitably performed by relatively moving the stage M41 and the flattening unit M42 in the Z direction, and for example, it may be performed by moving the flattening unit M42 in the downward direction, or may be performed by moving the stage M41 in the upward direction.
- [0271] The liquid discharge portion (liquid applying unit) M5 discharges the liquid 2' to the layer 1 by an ink jet method.

By equipping such a liquid discharge portion (liquid applying unit) M5, it is possible to apply the liquid 2' in fine patterns, and it is possible to manufacture even the three-dimensional structure 10 having a fine configuration with particularly excellent productivity.

- [0272] As a liquid droplet discharge system (system of an ink jet method), a piezo system or a system for discharging the liquid 2' by bubbles generated by heating the liquid 2' can be used, and from the viewpoint of the difficulty in changing quality of the constituent of the liquid 2', the piezo system is preferable.
- [0273] In the liquid discharge portion (liquid applying unit) M5, a pattern to be formed in each layer 1 or the amount of the liquid 2' to be applied in each portion of the layer 1 is controlled by the instructions from the drive control portion M22. The discharge pattern, the discharge amount, or the like of the liquid 2' by the liquid discharge portion (liquid applying unit) M5 is determined based on the slice data. Thereby, it is possible to apply the necessary and sufficient amount of the liquid 2', it is possible to reliably form the first solidified portion 2A having a desired pattern, and it is possible to more reliably make the dimensional accuracy of the three-dimensional structure 10 excellent. In addition, in a case where the liquid 2' includes a colorant, it is possible to reliably obtain a desired color, and it is possible to reliably prevent an occurrence of an unintentional color change and unintentional collapse of the color balance, due to the change in the thickness of the layer 1.
- [0274] The energy ray irradiation unit (curing unit) M6 applies energy rays to cure the liquid 2' applied to the layer 1.
- [0275] The type of energy rays that the energy ray irradiation unit M6 applies varies depending on the constituent materials of the liquid 2', and examples thereof include ultraviolet rays, visible rays, infrared rays, X-rays, gamma-rays, an electron beam, and an ion beam. Among these, ultraviolet rays are preferably used from the viewpoint of cost and productivity of the three-dimensional structure 10.
- [0276] The thermoplastic composition applying unit M8 ejects the melted thermoplastic composition 2". By equipping with the thermoplastic composition applying unit M8, it is possible to form the solidified portion 2 (second solidified portion 2B) having a desired shape. In particular, in the case of forming the solidified portion 2 on the layer 1, it is possible to prevent unintended penetration of a forming material (thermoplastic composition 2") of the solidified portion 2 into the layer 1, and it is possible to form the solidified portion 2 (second solidified portion 2B) having a desired shape. In addition, it is possible to suitably form the second solidified portion 2B and the solidified product 6 under the same conditions (for example, the same thickness, and the same density).
- [0277] The thermoplastic composition applying unit M8 has a configuration in which the

thermoplastic composition 2” having a filament shape, which is wound on the outer periphery of a roll shape member not shown in the drawing, is sent from the roll shape member, and heated and melted by a heating unit not shown in the drawing, and the melted thermoplastic composition 2” is ejected from the nozzle M81.

[0278] The thermoplastic composition applying unit M8 controls a pattern to be formed or the amount of the thermoplastic composition 2” to be applied by the instructions from the drive control portion M22. The ejection pattern, the ejection amount, or the like of the thermoplastic composition 2” by the thermoplastic composition applying unit M8 is determined based on the slice data. Thereby, it is possible to apply the necessary and sufficient amount of the thermoplastic composition 2”, it is possible to reliably form the second solidified portion 2B having a desired pattern, and it is possible to more reliably make the dimensional accuracy and the mechanical strength of the three-dimensional structure 10 excellent.

[0279] The height measuring unit M9 measures the height of the upper surface of the solidified product 6.

Information on the height of the upper surface of the solidified product 6 is transmitted to the control portion M2 from the height measuring unit M9, and is used in adjusting the thickness of the layer 1 formed and the relative height of the flattening unit M42.

[0280] In addition, in the configuration shown in Fig. 3, the height measuring unit M9 determines the height of the solidified product 6 by determining the focal length from the upper direction of the solidified product 6. Since it is possible to measure the height of the solidified product 6 without moving the height measuring unit M9 by such a configuration, it is possible to shorten the time required for measuring the height of the solidified product 6, and it is possible to make the productivity of the three-dimensional structure 10 particularly excellent.

[0281] By the three-dimensional structure manufacturing apparatus according to the invention described above, it is possible to manufacture a three-dimensional structure which has a wide range of choice in color and design, and physical properties depending on the appearance, with high productivity.

[0282] In particular, by the three-dimensional structure manufacturing apparatus of the embodiment, it is possible to efficiently manufacture a three-dimensional structure which has excellent dimensional accuracy or the like.

#### Three-Dimensional Structure

[0283] The three-dimensional structure according to the invention is manufactured using the three-dimensional forming method (in particular, the manufacturing method according to the invention) as described above, the first portion which is a region including at least a part of the outer surface is configured of a material including a cured product of



a curable resin, and the second portion which is a region of at least a part of portions other than the first portion is configured of a material including a thermoplastic resin.

[0284] Thereby, it is possible to provide a three-dimensional structure which is excellent in design and has physical properties depending on the appearance.

[0285] Such a three-dimensional structure can be suitably manufactured using the three-dimensional structure manufacturing apparatus according to the invention as described above.

[0286] Use of the three-dimensional structure according to the invention is not particularly limited, and examples thereof include items for appreciation and articles on exhibition such as a doll and a figure; and medical devices such as an implant.

[0287] In addition, the three-dimensional structure according to the invention may be applied to any of a prototype, mass-produced products, and tailor made products.

[0288] Hereinabove, the preferred embodiments of the invention have been described, but the invention is not limited to these embodiments.

[0289] For example, in the three-dimensional structure manufacturing apparatus and three-dimensional structure according to the invention, the configuration of each portion can be substituted with an arbitrary configuration exhibiting the same function, and an arbitrary configuration can be added. For example, the three-dimensional structure manufacturing apparatus according to the invention may be equipped with heating unit or pressure reducing unit not shown in the drawing. Thereby, for example, it is possible to efficiently remove the solvent from the layer forming composition, and it is possible to make the productivity of the three-dimensional structure particularly excellent. The three-dimensional structure manufacturing apparatus according to the invention may be equipped with cooling unit not shown in the drawing.

Thereby, for example, it is possible to quickly make the thermoplastic composition in a melted state, applied from the thermoplastic composition applying unit into a cure portion having sufficient stability of the shape, and it is possible to make the productivity of the three-dimensional structure particularly excellent.

[0290] In the above-described embodiments, it has been described that for all of the layers, a solidified portion is formed, however, the embodiments may have a layer in which a solidified portion is not formed. For example, a layer formed just on the stage may function as a sacrificial layer without forming a solidified portion thereon.

[0291] In the above-described embodiments, description has been made focused on the case of repeatedly performing the layer forming step, the first solidified portion forming step, and the second solidified portion forming step as a series of steps, however, the series of steps repeatedly performed may be different in each cycle, and for example, the series of steps repeatedly performed may have a cycle in which the first solidified portion forming step of the above steps is omitted, or may have a cycle in which the

second solidified portion forming step of the above steps is omitted.

[0292] In addition, in the method for manufacturing a three-dimensional structure according to the invention, the order of steps or treatments is not limited to those described above, and the steps or treatments may be performed by replacing at least a part thereof. For example, in the above-described embodiments, a case where a second and subsequent second solidified portion forming steps (in a case where  $n$  is an integer of equal to or greater than 1, the second solidified portion forming steps of forming the second solidified portion 2B which buried in the  $n+1^{\text{th}}$  layer 1 from the bottom) is performed after the first solidified portion 2A is formed in the lower layer ( $n^{\text{th}}$  layer 1 from the bottom) thereof has been described, however, a second and subsequent second solidified portion forming steps (second solidified portion forming steps of forming the second solidified portion 2B which buried in the  $n+1^{\text{th}}$  layer 1 from the bottom) may be performed before the first solidified portion 2A is formed in the lower layer ( $n^{\text{th}}$  layer 1 from the bottom) thereof.

[0293] For example, the curing treatment performed for formation of each first solidified portion (cured portion) may not repeatedly performed each time a pattern corresponding to each first solidified portion (cured portion) is formed, and may be collectively performed after a layered product in which uncured patterns are provided on the plurality of layers is formed.

[0294] In the above-described embodiments, a case where the layer forming composition includes a solvent has been representatively described, however, the layer forming composition may not include a solvent.

[0295] In the above-described embodiments, a case where the three-dimensional structure is formed of the first portion and the second portion has been representatively described, however, for example, the three-dimensional structure may have portions other than the first portion and the second portion.

[0296] In addition, in the above-described embodiments, a case where the three-dimensional structure is formed of the first solidified portion and the second solidified portion has been representatively described, however, for example, the three-dimensional structure may have solidified portions other than the first solidified portion and the second solidified portion. For example, the solidified portion (third solidified portion) may be formed by applying the liquid (solidified portion forming liquid) on a layer (layer including plurality of particles) in a state of including a solvent. In this manner, by applying the liquid (solidified portion forming liquid) on the layer in a state of including a solvent, it is possible to prevent the liquid from penetrating in the layer, and it is possible to easily and reliably form the solidified portion (third solidified portion) having a desired shape on the layer.

[0297] In the above-described embodiments, a case where the first portion is formed by

applying the liquid into the layer configured of plurality of particles by an ink jet method has been representatively described, however, in the invention, the first portion may be formed by discharging the liquid by an ink jet method, and then, by curing the discharged liquid, and for example, the first portion may be formed by applying the liquid to a portion not including particles.

[0298] In the above-described embodiments, a case where a three-dimensional structure is manufactured using the layer forming composition including plurality of particles (particle containing composition) in addition to the melted thermoplastic composition and the liquid discharged by an ink jet method has been described, however, in the invention, the layer forming composition including plurality of particles (particle containing composition) may not be used. In such a case, the three-dimensional structure is obtained as a structure formed by stacking layers including a solidified portion formed using the melted thermoplastic composition and a solidified portion (cured portion) formed by the liquid discharged by an ink jet method.

[0299] In the above-described embodiments, a case where a part of the outer surface of three-dimensional structure (entire outer surface excluding a part of the bottom surface of the three-dimensional structure) is the first portion has been representatively described, however, in the invention, the first portion may be the entire outer surface of the three-dimensional structure. In the above-described embodiments, it has been described that the entire outer surface capable of being visually recognized in a normal using form of the outer surface of the three-dimensional structure is the first portion, however, a part of the outer surface capable of being visually recognized in a normal using form of the outer surface of the three-dimensional structure may be a portion (for example, the second portion) other than the first portion.

[0300] In addition, in the manufacturing method according to the invention, a pretreatment step, an intermediate treatment step, or a post-treatment step may be performed, as necessary.

[0301] Examples of the pretreatment step include a cleaning step of the stage or the like.

Examples of the post-treatment step include a cleaning step, a shape adjusting step of performing deburring or the like, a coloring step, a coating layer forming step, and a curing completion step of performing a light irradiation treatment or a heating treatment for reliably curing an uncured polymerizable compound (curable resin material).

[0302] In the above-described embodiments, a case where a solidified product used in determining the thickness of a layer is formed at the second region different from the first region where a portion configuring an entity portion of an intended three-dimensional structure is formed on the forming stage has been described, however, the solidified product used in determining the thickness of a layer may be a solidified product

formed at the first region, in particular, a part of an entity portion of the three-dimensional structure.

[0303] In the above-described embodiments, a case where the height of the upper surface of a solidified product used in determining the thickness of a layer is determined by an observation from the upper surface of the solidified product has been representatively described, however, the height of the upper surface of a solidified product may be determined by an observation from the side surface of the solidified product.

[0304] In the above-described embodiments, the case of using a fixed height measuring unit has been representatively described, however, the height measuring unit may be movable (for example, movable in the XY direction of the stage). Thereby, for example, it is possible to measure the height of the upper surface of the solidified product at a plurality of points.

[0305] In addition, in the above-described embodiments, a case where all of a plurality of solidified products formed by being stacked over several steps have the same shape and the same area has been representatively described, however, for example, each area of the plurality of solidified products to be stacked decreases sequentially towards the upper side, and the layered product formed by stacking a plurality of solidified products, for example, may have a shape such as a pyramid shape or the like. Even in such a case, the same effects as described above are obtained.

In addition, in the invention, a solidified product used in determining the thickness of a layer may not be formed.

[0306] The three-dimensional structure manufacturing apparatus according to the invention may be equipped with a recovery mechanism not shown in the drawing for recovering the layer forming composition unused in formation of a layer of the layer forming composition (particle containing composition) supplied from the particle containing composition supply portion. Thereby, since it is possible to supply a sufficient amount of the layer forming composition (particle containing composition) while preventing the excessive layer forming composition (particle containing composition) from being accumulated in a layer forming portion, it is possible to manufacture a more stable three-dimensional structure while more effectively preventing an occurrence of defects in layers. Since it is possible to use the recovered layer forming composition (particle containing composition) in manufacturing a three-dimensional structure again, it is possible to contribute to reduction in the manufacturing cost of the three-dimensional structure, and the three-dimensional structure manufacturing apparatus according to the invention is preferable from the viewpoint of resource saving.

[0307] In addition, the three-dimensional structure manufacturing apparatus according to the invention may be equipped with a recovery mechanism for recovering the layer forming composition (particle containing composition) removed in the unbound

particle removing step.

### Reference Signs List

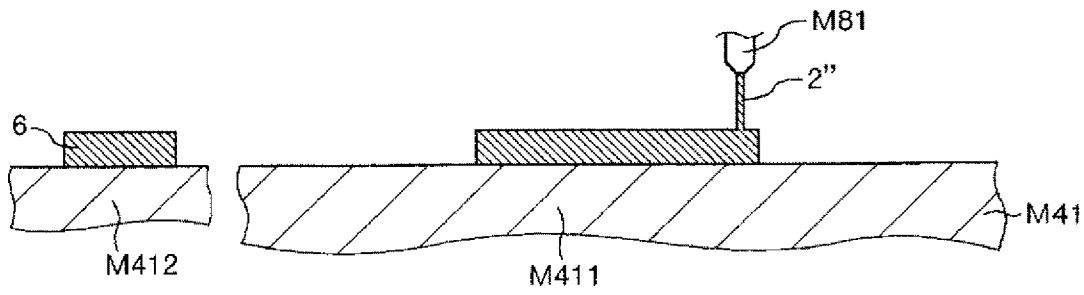
- [0308] 10: Three-dimensional structure  
1: Layer  
1': Particle containing composition (layer forming composition)  
11: Particles  
12: Solvent  
2: Solidified portion  
2A: First solidified portion (cured portion)  
2B: Second solidified portion  
2': Liquid (first solidified portion forming liquid)  
2'': Thermoplastic composition (second solidified portion forming material)  
3: Bound portion  
4: Space  
6: Solidified portion  
M100: Three-dimensional structure manufacturing apparatus  
M2: Control portion  
M21: Computer  
M22: Drive control portion  
M3: Particle containing composition supply portion  
M4: Layer forming portion  
M41: Stage (lifting stage, support)  
M411: First region  
M412: Second region  
M42: Flattening unit (squeegee)  
M43: Guide rail  
M45: Frame body  
M5: Liquid discharge portion (liquid applying unit)  
M6: Energy ray irradiation unit (curing unit)  
M8: Thermoplastic composition applying unit  
M81: Nozzle  
M9: Height measuring unit

## Claims

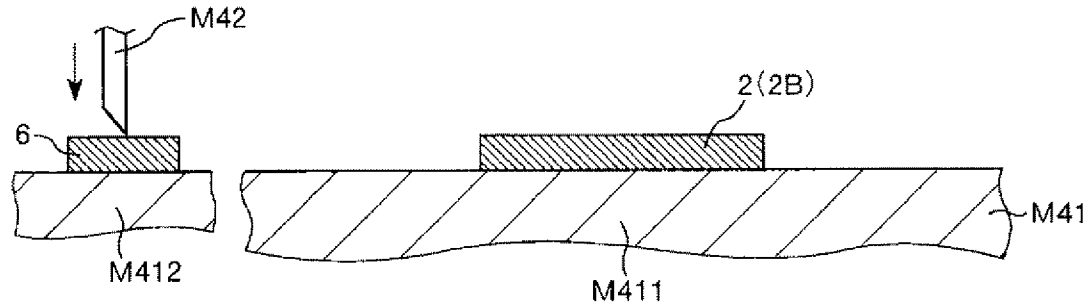
- [Claim 1] A method for manufacturing a three-dimensional structure by stacking layers, comprising:  
forming a first portion which is a region including at least a part of the outer surface of the three-dimensional structure by discharging a liquid by an ink jet method and then curing the discharged liquid, and  
forming a second portion which is a region of at least a part of portions other than the first portion of the three-dimensional structure by ejecting a thermoplastic composition including a melted thermoplastic resin from a nozzle and by solidifying the ejected thermoplastic composition.
- [Claim 2] The method for manufacturing a three-dimensional structure according to Claim 1,  
wherein the first portion is formed by applying the liquid to a layer formed using a particle containing composition including particles by the ink jet method, by penetrating the liquid into gaps between the particles, and by curing the liquid.
- [Claim 3] The method for manufacturing a three-dimensional structure according to Claim 2,  
wherein the particle containing composition includes a solvent, and the liquid is applied to the layer in a state of removing the solvent from the layer.
- [Claim 4] The method for manufacturing a three-dimensional structure according to Claim 3,  
wherein the particle containing composition includes an aqueous solvent as the solvent.
- [Claim 5] The method for manufacturing a three-dimensional structure according to Claim 3 or 4,  
wherein the particle containing composition further includes a binder.
- [Claim 6] The method for manufacturing a three-dimensional structure according to any one of Claims 3 to 5,  
wherein the layer is formed such that at least a part of the second portion is buried using the particle containing composition after forming the second portion using the thermoplastic composition.
- [Claim 7] The method for manufacturing a three-dimensional structure according to any one of Claims 1 to 6,  
wherein the liquid is a photocurable resin.

- [Claim 8] The method for manufacturing a three-dimensional structure according to any one of Claims 1 to 7, wherein the thermoplastic resin includes polycarbonate, and the liquid includes an acryl-based polymerizable compound.
- [Claim 9] The method for manufacturing a three-dimensional structure according to any one of Claims 1 to 8, wherein a thickness of the first portion is 0.01 mm to 1.0 mm.
- [Claim 10] The method for manufacturing a three-dimensional structure according to any one of Claims 1 to 9, wherein the thermoplastic composition includes a filler in addition to the thermoplastic resin.
- [Claim 11] A three-dimensional structure manufacturing apparatus for manufacturing a three-dimensional structure by stacking layers, comprising: a liquid discharge unit that discharges a liquid used in formation of a cured portion by an ink jet method; and a thermoplastic composition applying unit that applies a thermoplastic composition including a melted thermoplastic resin.
- [Claim 12] A three-dimensional structure manufactured using the method for manufacturing a three-dimensional structure according to any one of Claims 1 to 10.
- [Claim 13] A three-dimensional structure manufactured using the three-dimensional structure manufacturing apparatus according to Claim 11.
- [Claim 14] A three-dimensional structure manufactured using a three-dimensional forming method, wherein a first portion which is a region including at least a part of the outer surface is configured of a material including a cured product of a curable resin, and a second portion which is a region of at least a part of portions other than the first portion is configured of a material including a thermoplastic resin.

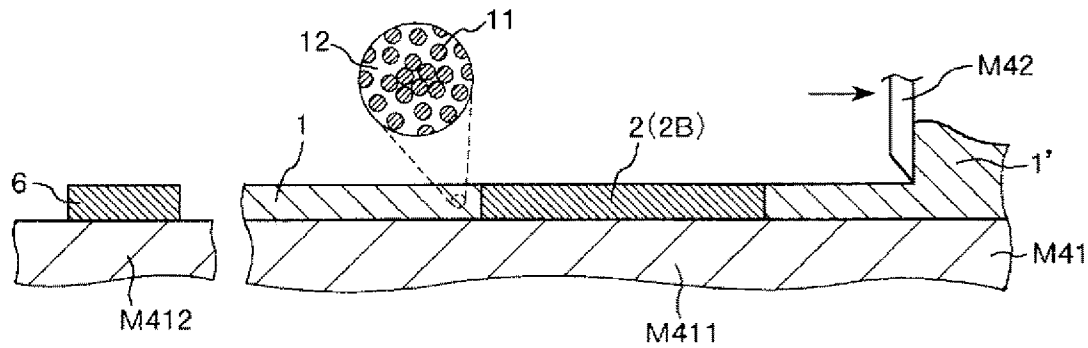
[Fig. 1A]



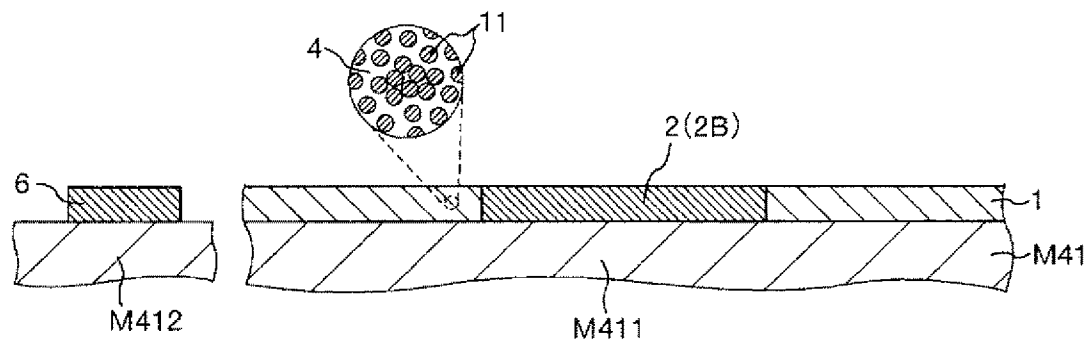
[Fig. 1B]



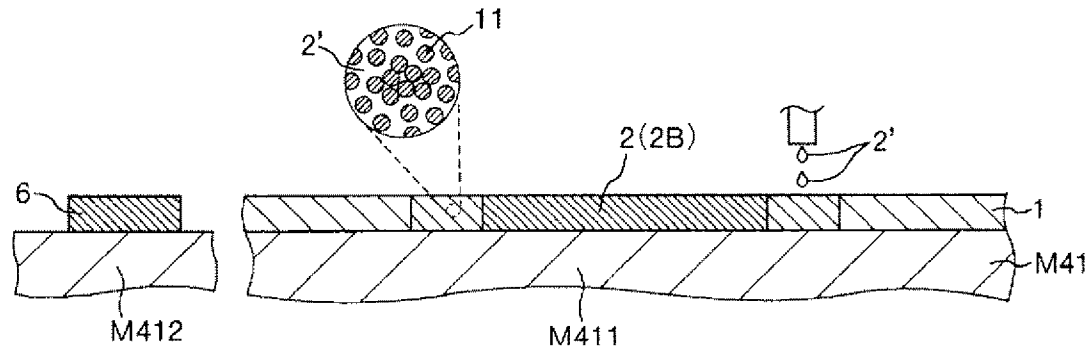
[Fig. 1C]



[Fig. 1D]

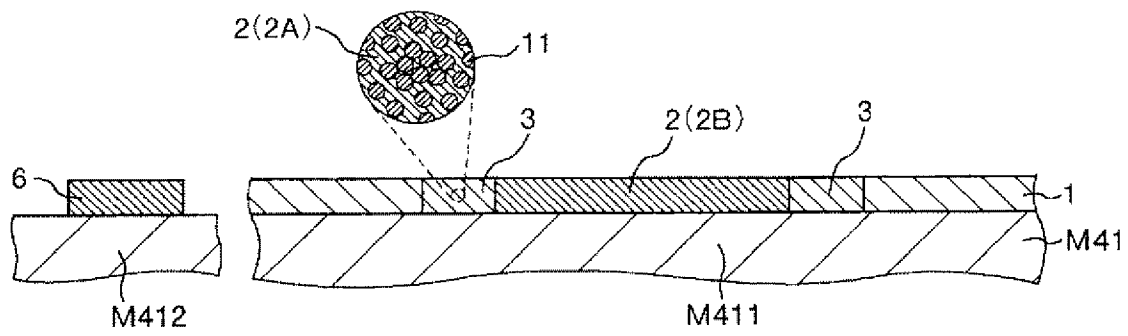


[Fig. 1E]

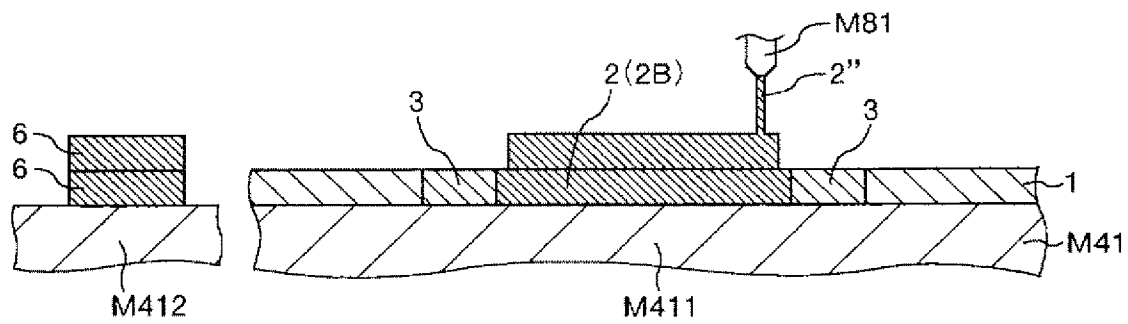




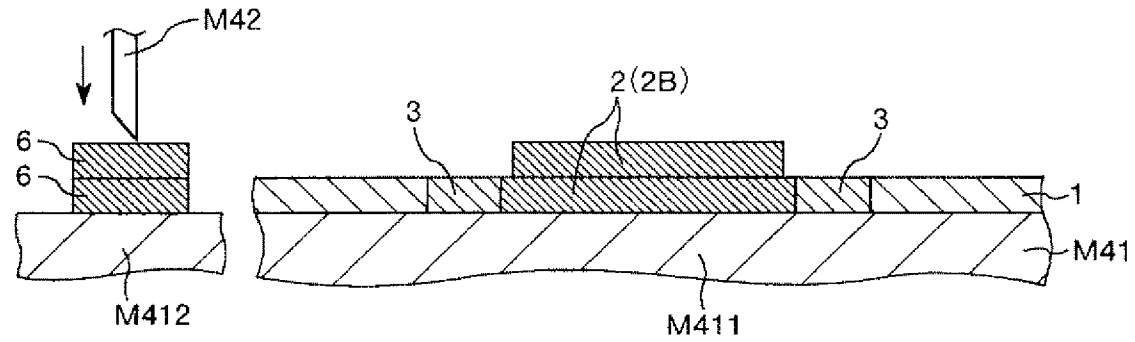
[Fig. 1F]



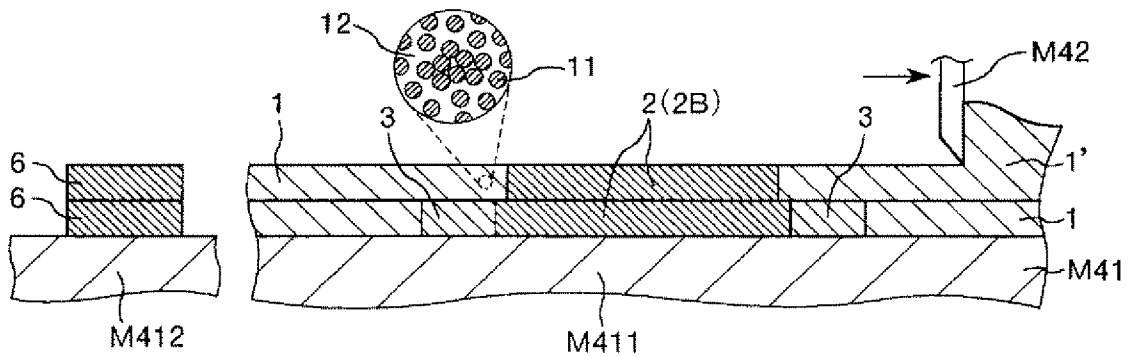
[Fig. 1G]



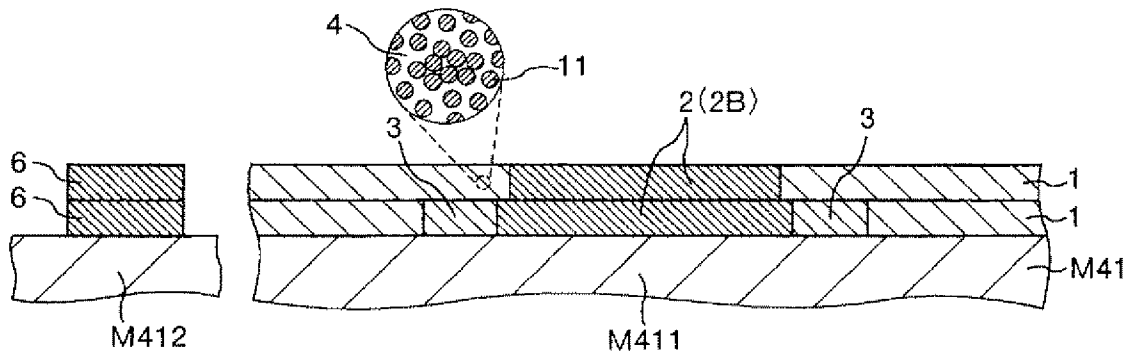
[Fig. 1H]



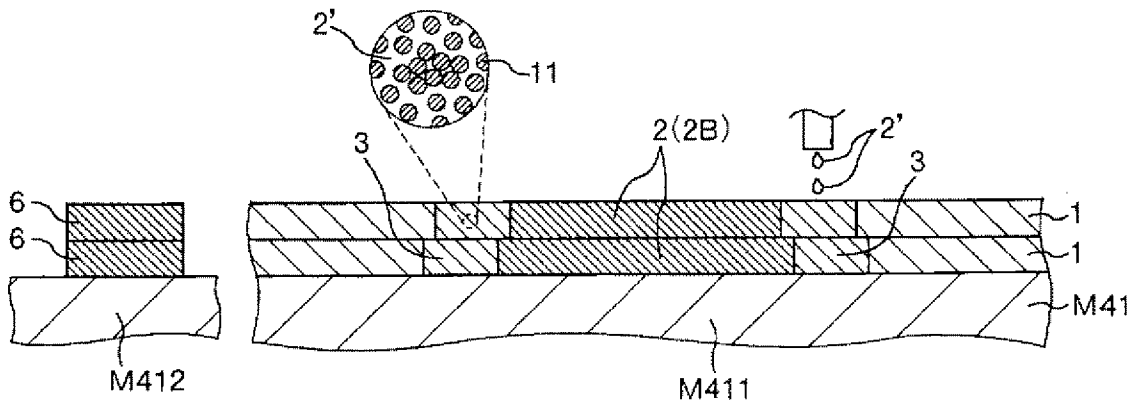
[Fig. 1I]



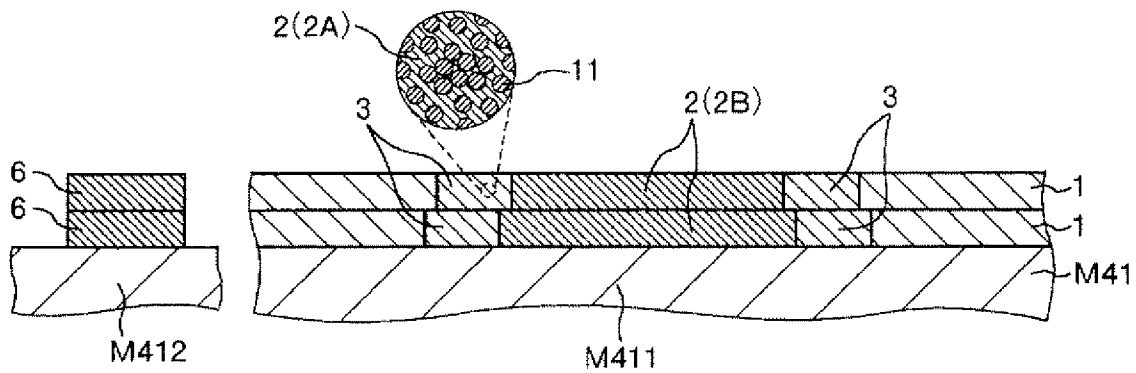
[Fig. 1J]



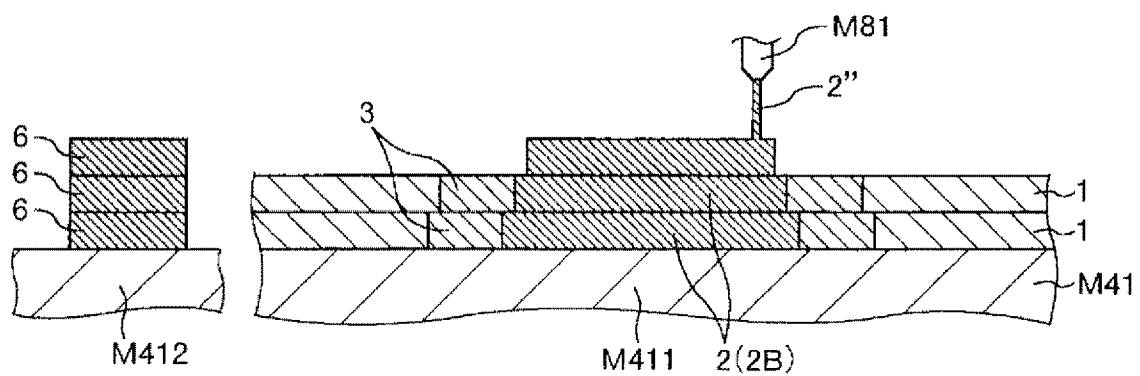
[Fig. 1K]



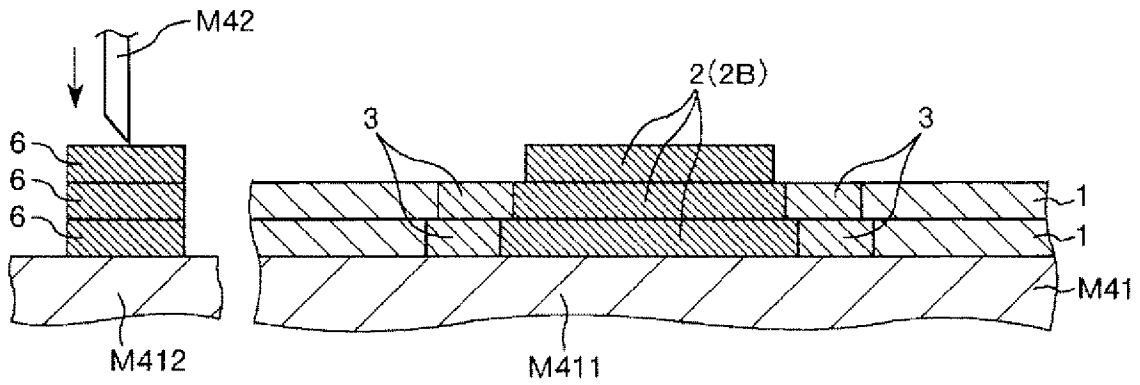
[Fig. 1L]



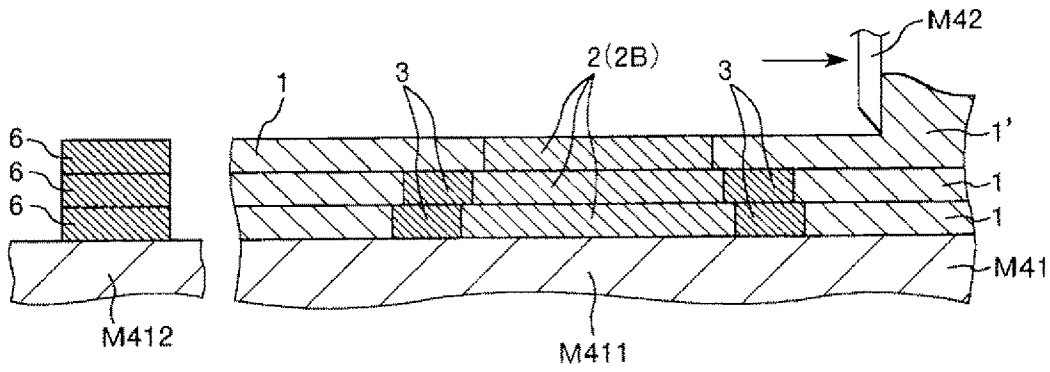
[Fig. 1M]



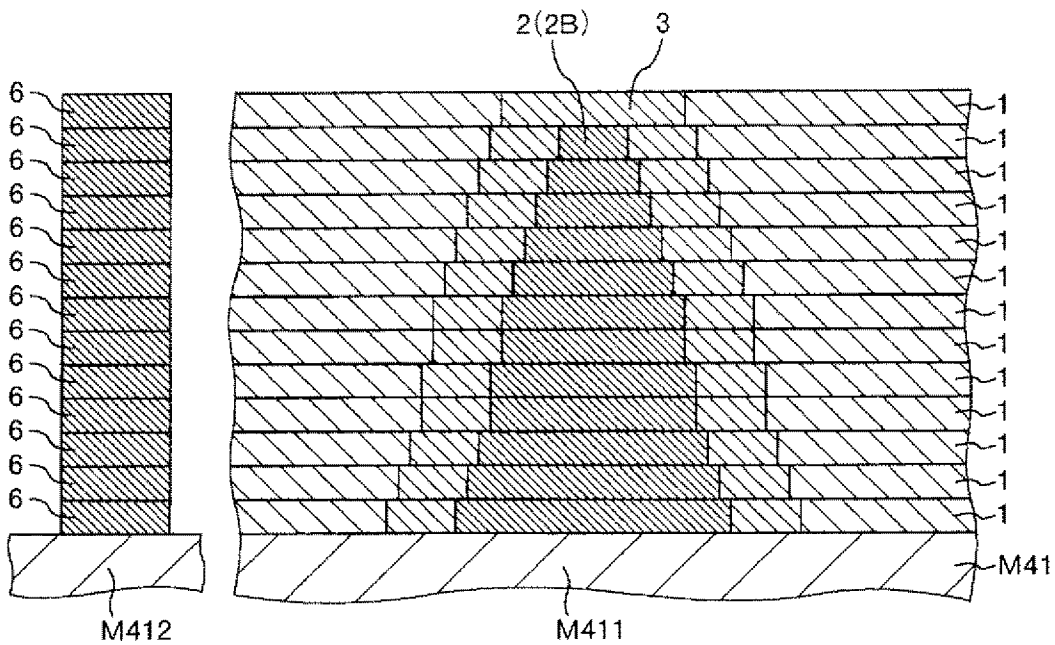
[Fig. 1N]



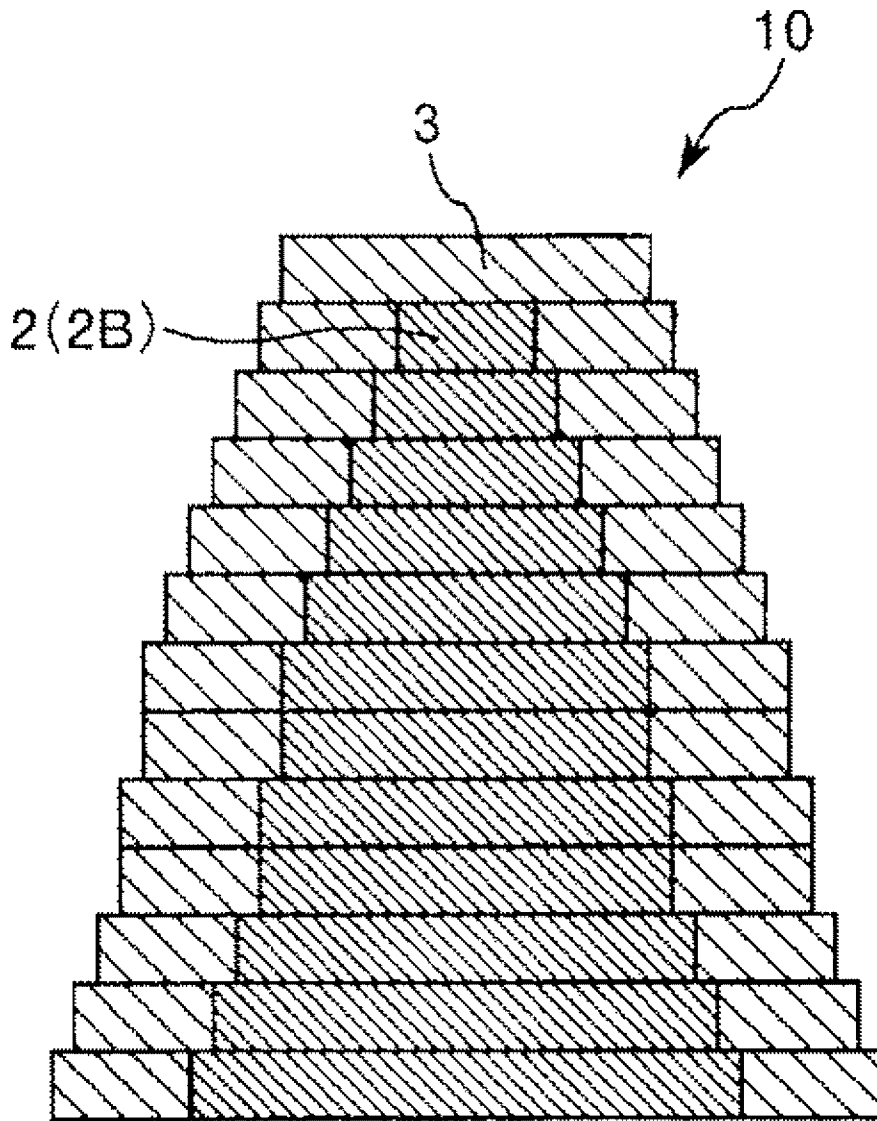
[Fig. 1O]



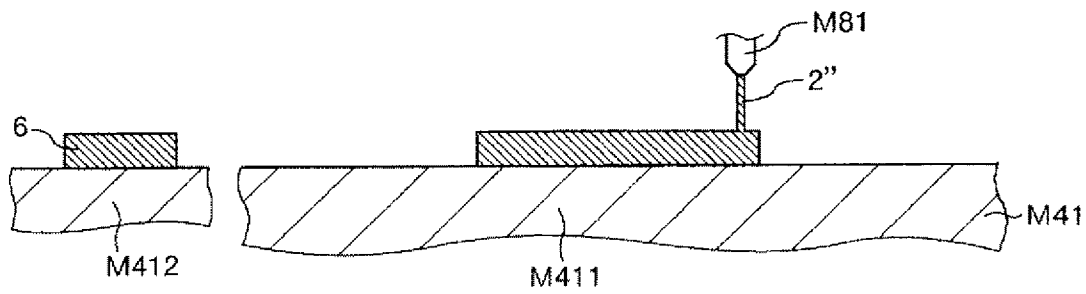
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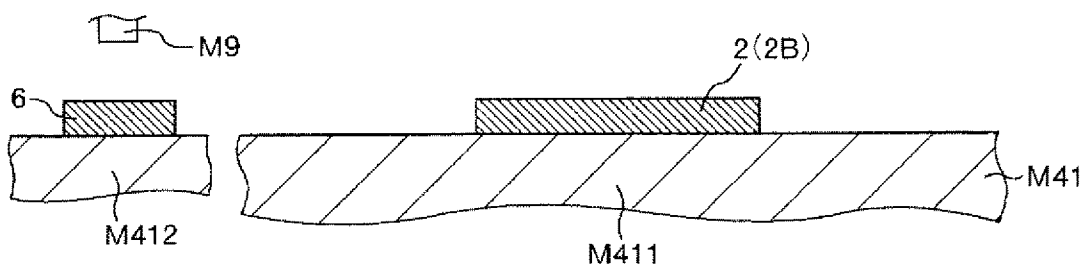
[Fig. 1Q]



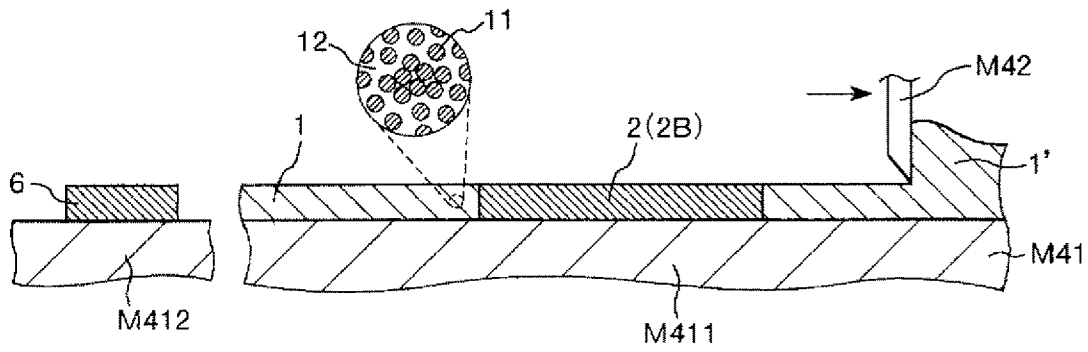
[Fig. 2A]



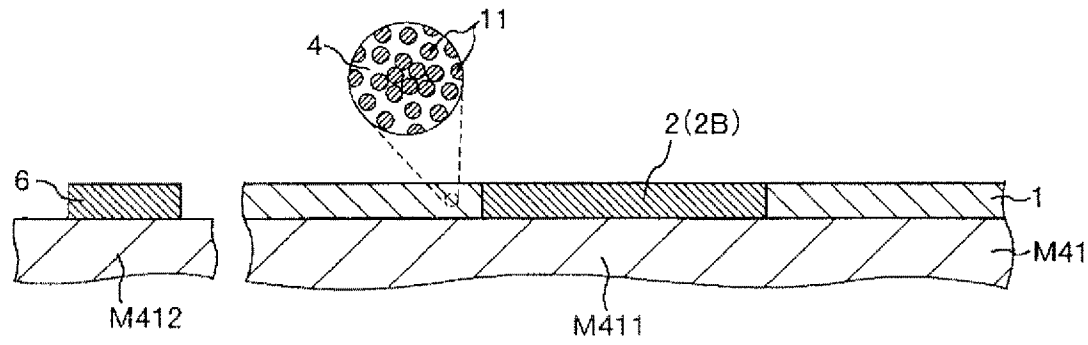
[Fig. 2B]



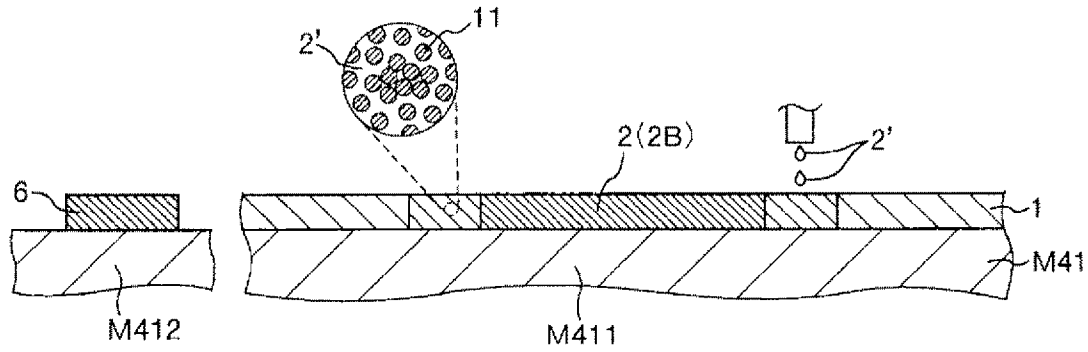
[Fig. 2C]



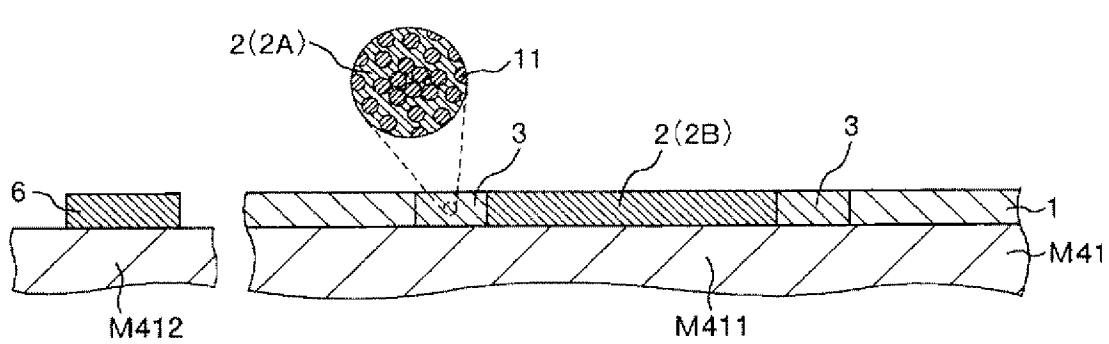
[Fig. 2D]



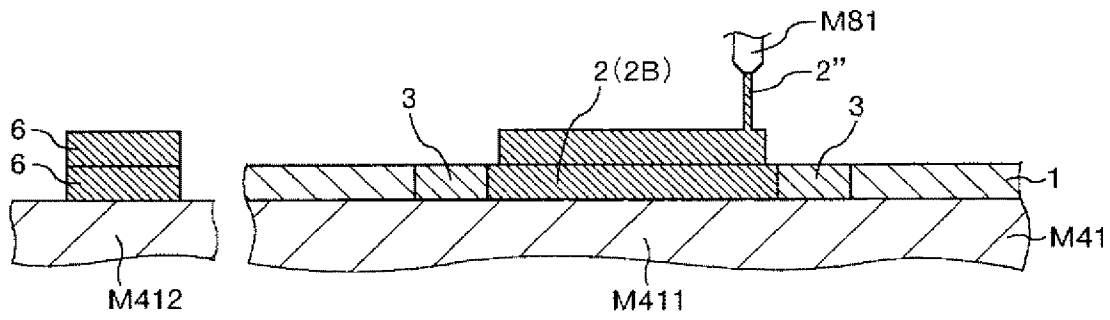
[Fig. 2E]



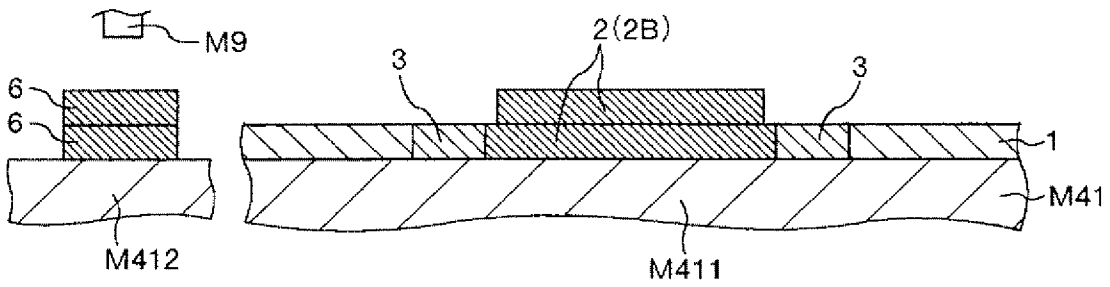
[Fig. 2F]



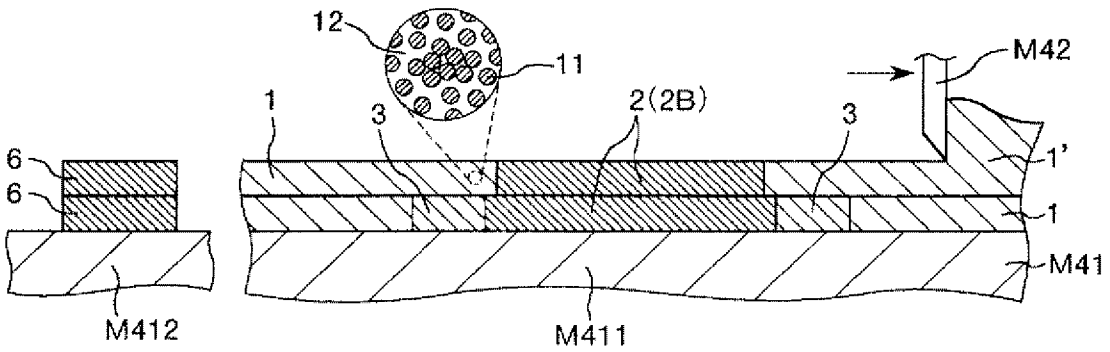
[Fig. 2G]



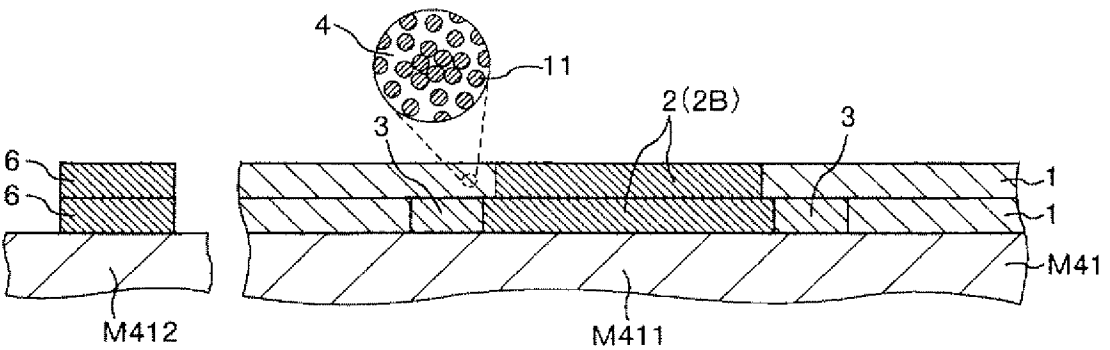
[Fig. 2H]



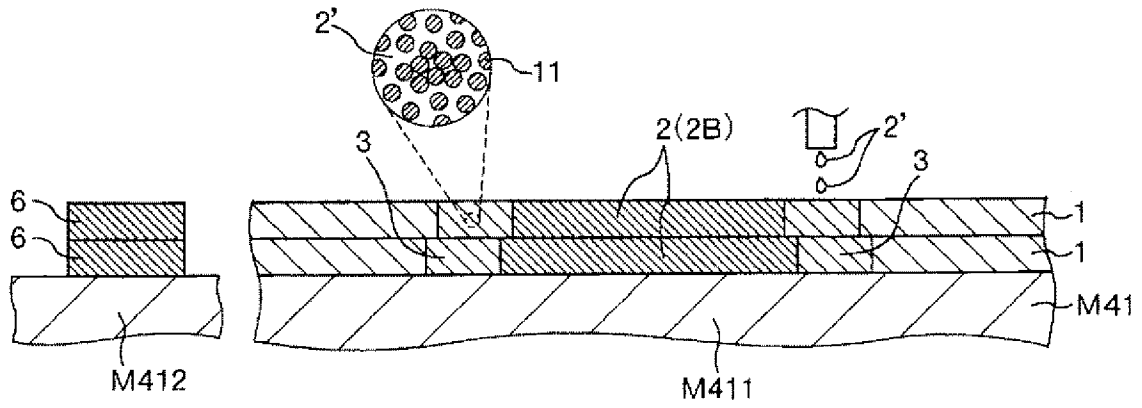
[Fig. 2I]



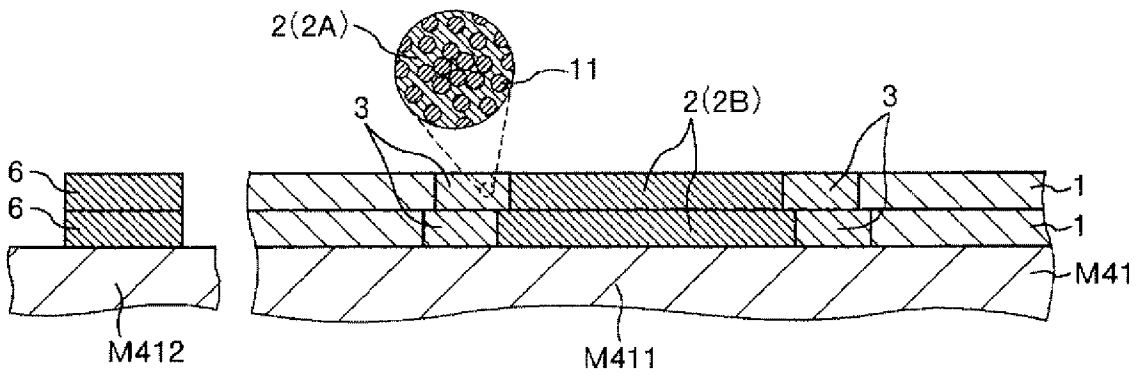
[Fig. 2J]



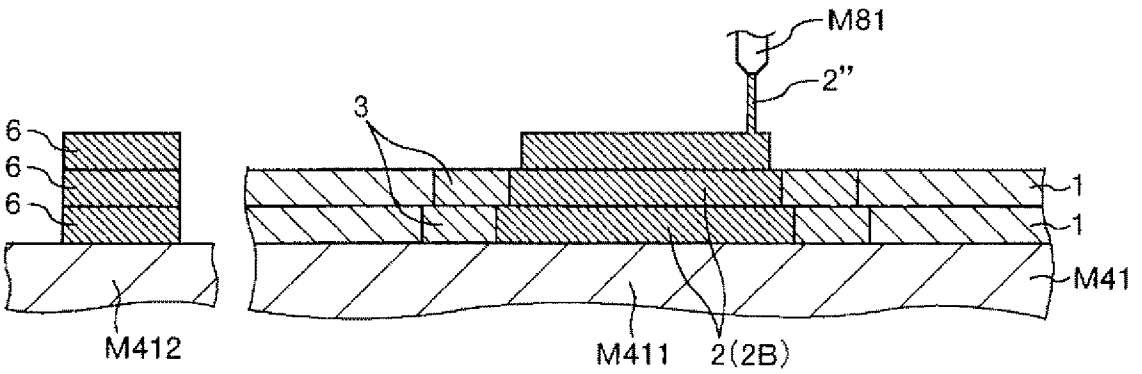
[Fig. 2K]



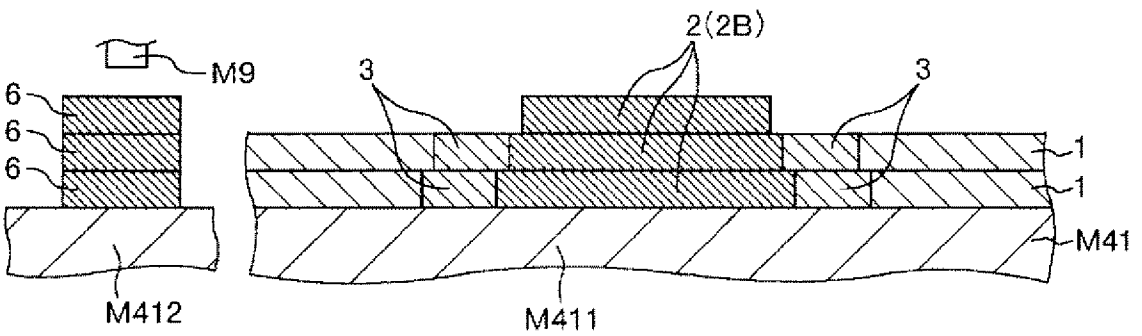
[Fig. 2L]



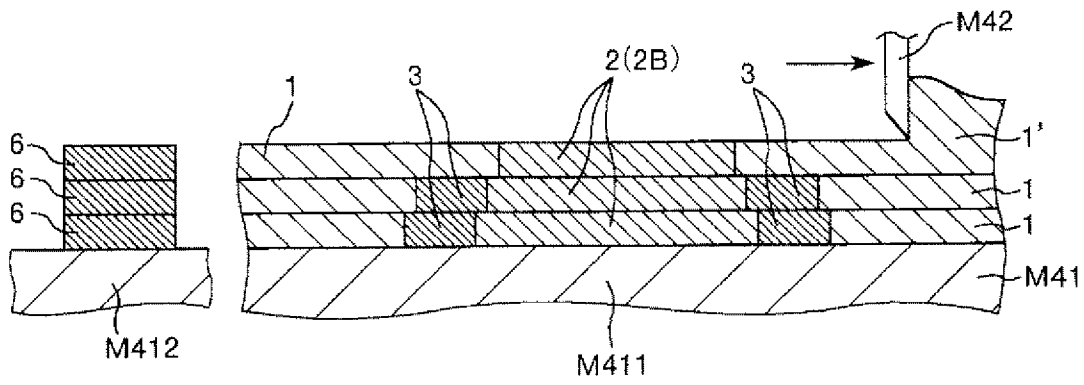
[Fig. 2M]



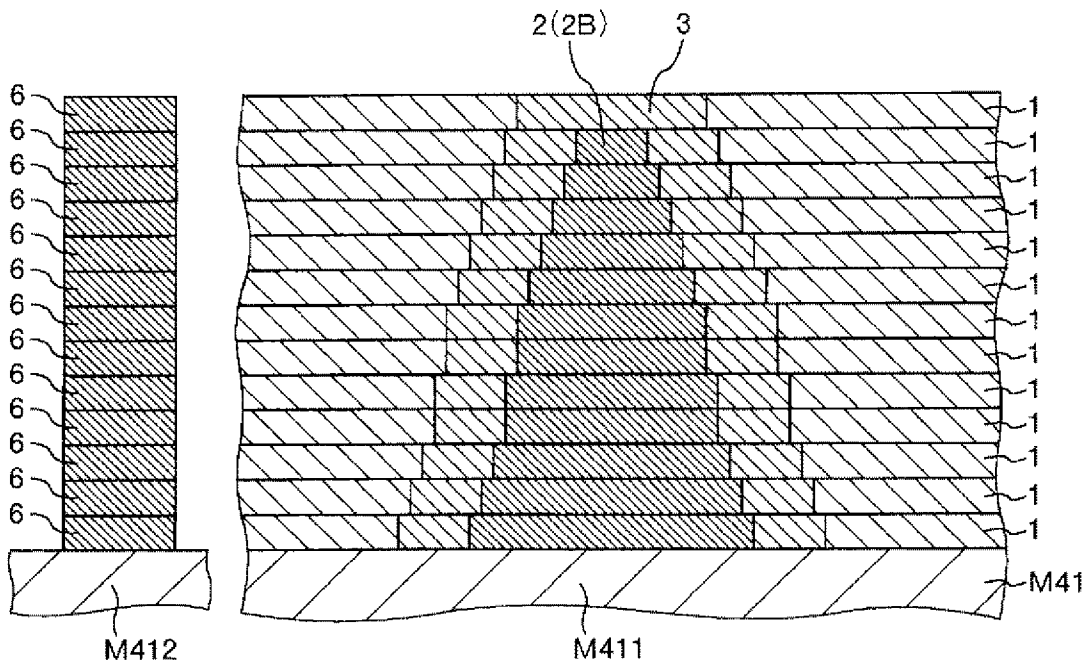
[Fig. 2N]



[Fig. 2O]

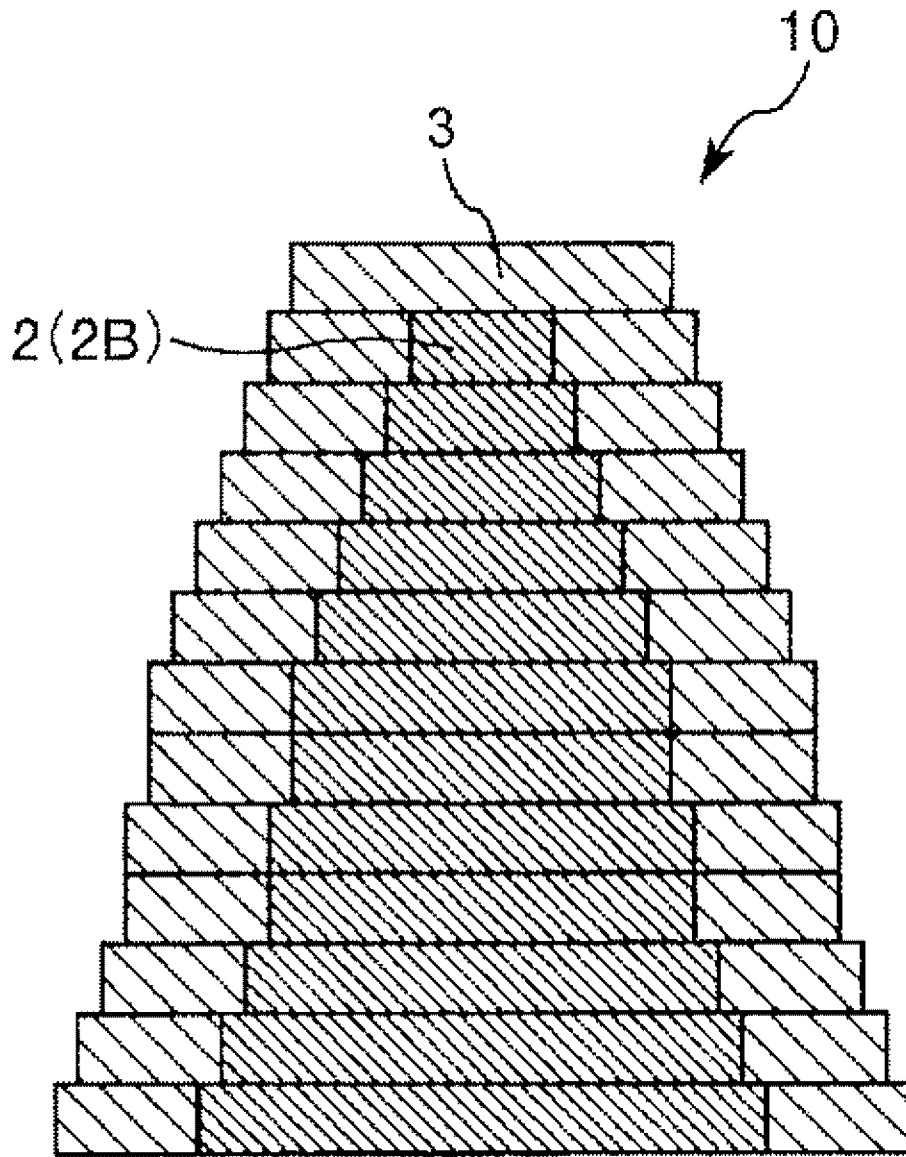


[Fig. 2P]

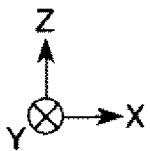
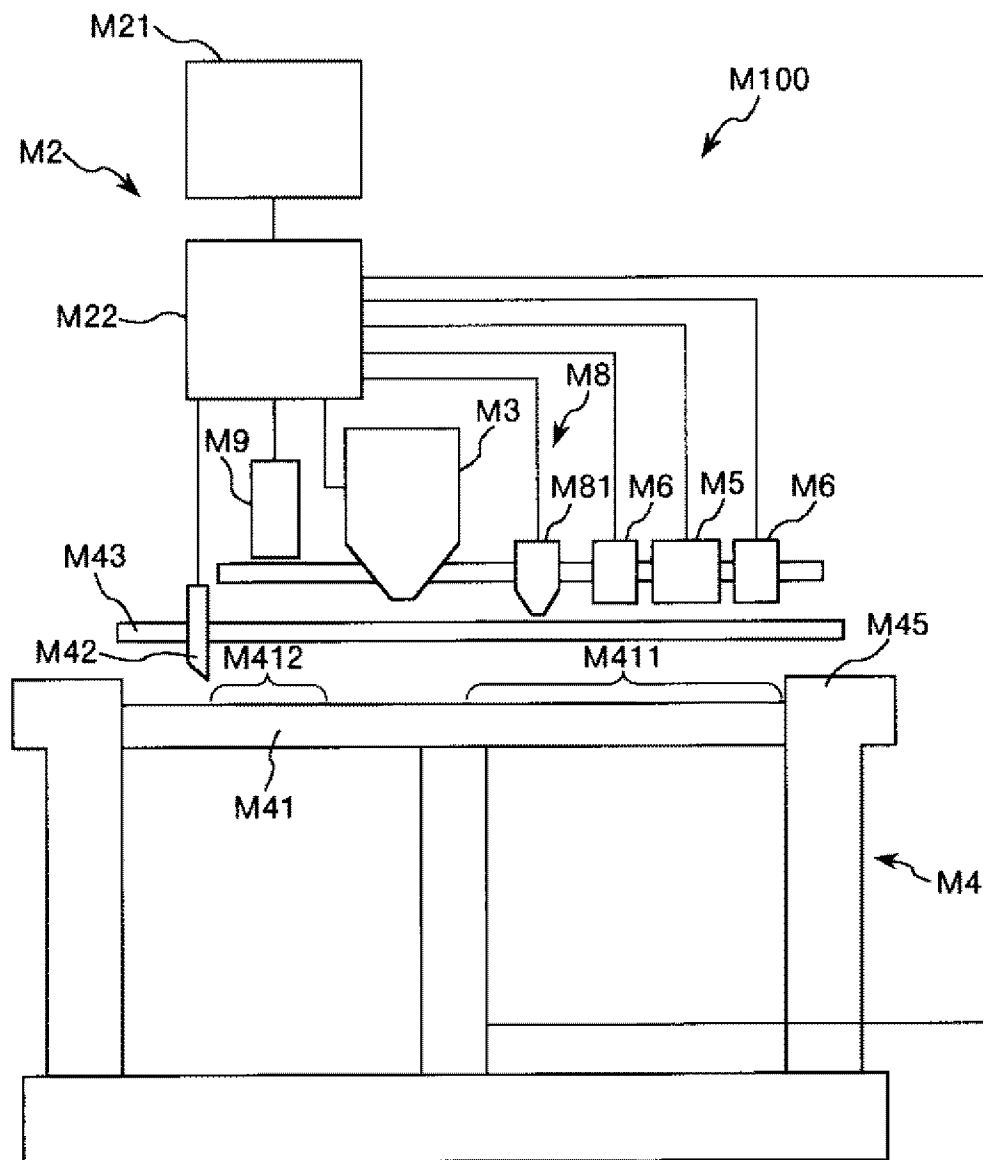




[Fig. 2Q]



[Fig. 3]



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JP2015/005461

A. CLASSIFICATION OF SUBJECT MATTER		
Int.Cl. B29C67/00(2006.01)i, B33Y10/00(2015.01)i, B33Y30/00(2015.01)i, B33Y80/00(2015.01)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, B33Y10/00, B33Y30/00, B33Y80/00		
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 1971-2016 Registered utility model specifications of Japan 1996-2016 Published registered utility model applications of Japan 1994-2016		
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.
X A	JP 2003-11237 A (KURARAY CO., LTD) 2003.01.15, [0037]-[0039],[0052]-[0054], Figs.9-11 (No Family)	11,13 1-10,12,14
X A	JP 2006-78604 A (TOIN GAKUEN) 2006.03.23, [0013]-[0020], Figs.1-2 (No Family)	14 1-13
A	JP 2005-88432 A (FUJIFILM CORPORATION) 2005.04.07, Claims 5-6 & US 2004/0222549 A1 Claims 5-6 & EP 1475220 A2	1-14
A	JP 2000-280354 A (MINOLTA CO., LTD) 2000.10.10, [0108],[0150], Figs.16-17 & US 2002/0167101 A1 [0158],[0229], Figs.16-17	1-14
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 13.01.2016		Date of mailing of the international search report 26.01.2016
Name and mailing address of the ISA/JP <b>Japan Patent Office</b> 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan		Authorized officer <b>YUMIKO INOUE</b> Telephone No. +81-3-3581-1101 Ext. 3471
		4R 4662

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JP2015/005461

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 6-143438 A (SANYO MACHINE WORKS, LTD) 1994.05.24, [0023]-[0032], Fig.2 (No Family)	1-14
A	JP 2000-272018 A (MATSUSHITA ELECTRIC WORKS CO., LTD) 2000.10.03, [0033],[0034], FIG.3 & TW 509602 B	1-14