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(54) Title: RADIATION-CURABLE LIQUID RESIN COMPOSITION FOR OPTICAL THREE-DIMENSIONAL SHAPING, AND OPTICALLY SHAPED ARTICLE OBTAINED BY PHOTO-CURING THE SAME

(57) Abstract: There is provided a radiation-curable liquid resin composition for optical three-dimensional shaping capable of obtaining an optically shaped article excellent in toughness and heat resistance. The radiation-curable liquid resin composition for optical three-dimensional shaping comprises: (A) a compound which has a carbonate group and two or more (meth)acryloyl groups and does not have a urethane bond; (B) a cationically polymerizable compound; (C) a photo-cationic polymerization initiator; (D) a radically polymerizable compound; and (E) a photo-radical polymerization initiator. A preferred example of the component (A) is a compound having two or more carbonate groups and three or more (meth)acryloyl groups. Examples of the preferred structural part included in the chemical structure of the (A) component include a branched structure and aromatic structure.



Title: Radiation-curable liquid resin composition for optical
 three-dimensional shaping, and optically shaped article obtained
 by photo-curing the same

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Technical field

[0001] The present invention relates to a radiation-curable liquid resin
composition for optical three-dimensional shaping, and an optically shaped
article obtained by photo-curing the same.

10

Background art

[0002] There is known an optical three-dimensional shaping method of
repeating the step of selectively irradiating a radiation-curable liquid
material (liquid resin composition) with light to form a cured resin layer,
15 thereby forming a three-dimensional article in which the cured resin layers
are integrally laminated (refer to Patent Literature 1). A representative
example of the optical three-dimensional shaping method will be described
as follows.

[0003] First, a cured resin layer having a predetermined pattern is
20 formed by selectively irradiating the liquid surface of a radiation-curable
liquid resin composition received by a container with light such as
ultraviolet laser. Next, a new cured resin layer is integrally laminated on
the previously formed cured resin layer by supplying the radiation-curable
liquid resin composition in an amount corresponding to one layer on the
25 cured resin and selectively irradiating the liquid surface of the radiation-
curable liquid resin composition with light, so that the new cured resin layer
may be continuous with the previously formed cured resin layer. Then, a
three-dimensional article in which a plurality of cured resin layers are
integrally laminated is formed by repeating the above steps a
30 predetermined number of times changing or without changing a pattern
which is irradiated with light.

[0004] This optical three-dimensional shaping method can provide a target three-dimensional article easily and in a short time even when the shape thereof is complicated. This technique is extremely useful in the trial production process in the new product development in motor vehicle or household appliance industry, and is becoming an indispensable means for the shortening of development period of time and the cost reduction.

[0005] Further, a radiation-curable liquid resin composition which comprises a cationically polymerizable compound having an oxetane structure and is used for an optical three-dimensional shaping method is also disclosed (refer to Patent Literatures 2 to 5). However, when producing an optically shaped article using a conventional liquid resin composition, the resulting optically shaped article has a disadvantage of being brittle and susceptible to breakage when mechanical stress is applied. There is also a problem that heat resistance is insufficient. Therefore, it is difficult to obtain an optically shaped article excellent in both the toughness and heat resistance.

[0006] Further, there is described the use of a dendrimer obtained by using ammonia, methyl acrylate, and ethylenediamine as starting materials and repeating Michael addition and condensation reaction in a three-dimensional image forming apparatus (Patent Literature 6). However, a specific radiation-curable liquid resin composition comprising a dendrimer is not disclosed.

Citation list

Patent Literature 1: Japanese Patent Application Laid-Open No. 60-247515

Patent Literature 2: Japanese Patent Application Laid-Open No. 10-168165

Patent Literature 3: Japanese Patent Application Laid-Open No. 2000-302964

Patent Literature 4: Japanese Patent Application Laid-Open No.
2002-60463

Patent Literature 5: Japanese Patent Application Laid-Open No.
2009-173781

5 Patent Literature 6: Japanese Patent Application Laid-Open No.
2005-14386

Summary of the invention

Technical problem

10 [0007] An object of the present invention is to provide a radiation-curable liquid resin composition for optical three-dimensional shaping capable of obtaining an optically shaped article excellent in toughness and heat resistance.

Solution to problem

15 [0008] As a result of intensive investigations to solve the above problems, the present inventor has found that it is possible to obtain an optically shaped article excellent in toughness and heat resistance by using a radiation-curable liquid resin composition for optical three-dimensional shaping comprising a compound which has a carbonate group and two or
20 more (meth)acryloyl groups and does not have a urethane bond, and has completed the present invention.

[0009] That is, the present invention provides the following (1) to (6).

(1) A radiation-curable liquid resin composition for optical three dimensional shaping comprising: (A) a compound which has a carbonate
25 group and two or more (meth)acryloyl groups and does not have a urethane bond; (B) a cationically polymerizable compound; (C) a photo cationic polymerization initiator; (D) a radically polymerizable compound; and (E) a photo-radical polymerization initiator.

(2) The radiation-curable liquid resin composition according to the above (1), wherein the (A) component has two or more carbonate groups and three or more (meth)acryloyl groups.

(3) The radiation-curable liquid resin composition according to the above
5 (1), wherein the (A) component has a branched structure.

(4) The radiation-curable liquid resin composition according to the above (1), wherein the (A) component has an aromatic structure.

(5) The radiation-curable liquid resin composition according to claim 1,
wherein the (A) component is a compound obtained by introducing a
10 (meth)acryloyl group into one or more compounds selected from the following [1] and [2]:

[1] a compound having three or more hydroxy groups obtained by reacting a compound represented by the following formula (1) with a compound represented by the following formula (3), and

15 [2] a compound having three or more hydroxy groups obtained by reacting a compound represented by the following formula (2) with a compound represented by the following formula (4),



wherein, R^1 and R^2 are each independently a monovalent organic group having an aliphatic, alicyclic or aromatic structure, R^3 and R^4 are each independently a monovalent organic group having an aliphatic, alicyclic or
25 aromatic structure, R^5 and R^6 are each independently an alkylene group, $n1$ and $n2$ are each independently an integer of 2 or more, $m1$ and $m3$ are each independently an integer of 3 or more, and $m2$ is an integer of 1 to 3, provided that at least one of R^1 and R^3 or R^2 and R^4 constituting one compound has an aromatic structure.

(6) An optically shaped article obtained by irradiating the radiation-curable liquid resin composition according to any one of the above (1) to (5) with light.

Effects of invention

- 5 [0010] According to the radiation-curable liquid resin composition for optical three-dimensional shaping of the present invention (hereinafter also referred to as the “composition of the present invention”), an optically shaped article excellent in toughness and heat resistance can be obtained.

10 Brief description of drawings

[0011] Figure 1 is a view showing an optically shaped article produced using a composition described in Examples and Comparative Examples.

Description of embodiments

- 15 Hereinafter, the present invention will be described in detail.

I. Radiation-curable Liquid Resin Composition for Optical Three-dimensional Shaping

- 20 [0012] The composition of the present invention comprises (A), (B), (C), (D), and (E) components to be described below as essential components. Further, the composition may also comprise (F), (G), and (H) components, and the like to be described below as optional components.

[0013] Hereinafter, each component will be described, individually.

- 25 [(A) Component]

[0014] The (A) component used as a component of the composition of the present invention is a compound which has a carbonate group and two or more (meth)acryloyl groups and does not have a urethane bond. The (A) component can provide an optically shaped article excellent in toughness

since it has a carbonate group and can provide an optically shaped article excellent in heat resistance since it has two or more (meth)acryloyl groups.

[0015] Since the (A) component does not have a urethane bond, a urethane (meth)acrylate does not correspond to the (A) component. The
5 composition for the optical three-dimensional shaping of the invention of the present application is a combined use system of a radical polymerization system and a cationic polymerization system; and the composition has a feature capable of reducing the distortion of the optically shaped article due to the crosslinking shrinkage compared with the case of the radical
10 polymerization system alone, and has an advantage of a higher cure rate compared with the case of the cationic polymerization system alone. When blending a urethane (meth)acrylate in the combined use system of the radical polymerization system and the cationic polymerization system, there is a tendency for the urethane (meth)acrylate to inhibit cationic
15 polymerization.

[0016] When blending a urethane (meth)acrylate as a component which is not the (A) component, the content is preferably 10 mass% or less, more preferably 3 mass% or less, and most preferably 0 mass% relative to the total amount of the composition.

20 [0017] The (A) component preferably has two or more carbonate groups and three or more (meth)acryloyl groups. Since the (A) component has two or more carbonate groups, it is possible to improve the kinetic properties of an optical shaping.

[0018] The (A) component preferably has a branched structure. An
25 optically shaped article excellent in toughness can be obtained by having a branched structure. The branched structure which the (A) component has is not particularly limited, but can be obtained, for example, by reacting a di- or higher-valent compound having a halogenated formyl group with a tri- or higher-hydric alcohol.

[0019] The (A) component preferably has an aromatic structure. An optically shaped article excellent in stiffness can be formed by having an aromatic structure.

[0020] The number average molecular weight of the component (A) is preferably 500 to 50 000 g/mol, more preferably 2000 to 30 000 g/mol. When the number average molecular weight of the component (A) is in the range of 500 to 50 000 g/mol, the viscosity of the composition is suitable for use in an optical shaping apparatus, and an optically shaped article excellent in heat resistance and toughness can be obtained. Here, the number average molecular weight is a number average molecular weight in terms of polystyrene measured by a gel permeation chromatography method.

[0021] The (A) component can be obtained, for example, by introducing a (meth)acryloyl group into one or more compounds selected from the following [1] and [2].

[1] A compound having three or more hydroxy groups obtained by reacting a compound represented by the following formula (1) with a compound represented by the following formula (3).

[2] A compound having three or more hydroxy groups obtained by reacting a compound represented by the following formula (2) with a compound represented by following formula (4).



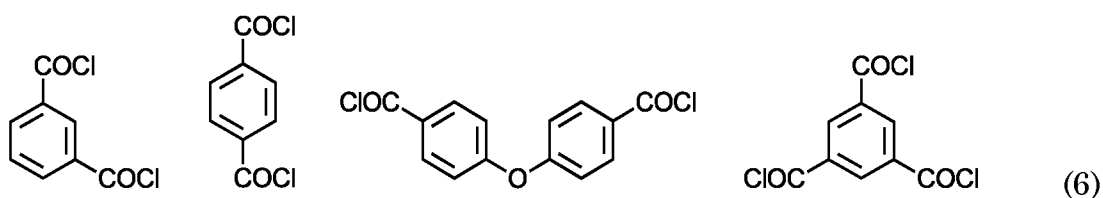
[0022] In formulas (1) to (4), R^1 and R^2 are each independently a monovalent organic group having an aliphatic, alicyclic or aromatic structure, R^3 and R^4 are each independently a monovalent organic group having an aliphatic, alicyclic or aromatic structure, and R^5 and R^6 are each independently an alkylene group. $n1$ and $n2$ are each independently an integer of 2 or more, $m1$ is an integer of 3 or more, $m3$ is an integer of 2 or

more, and m_2 is an integer of 1 to 3. Provided that, at least one of R^1 and R^3 or R^2 and R^4 constituting one compound has an aromatic structure.

[0023] Specific examples of the compound represented by the above formula (1) include the compound represented by the following formula (5).



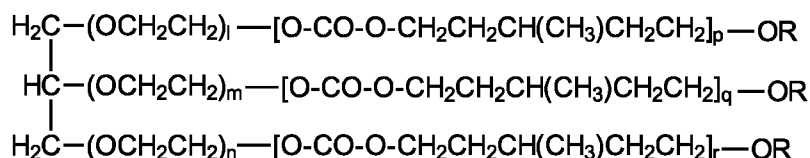
Specific examples of the compound represented by the above formula (2) include the compounds represented by the following formula (6).



[0024] Specific examples of the compound represented by the above formula (3) include the compound represented by the following formula (7).

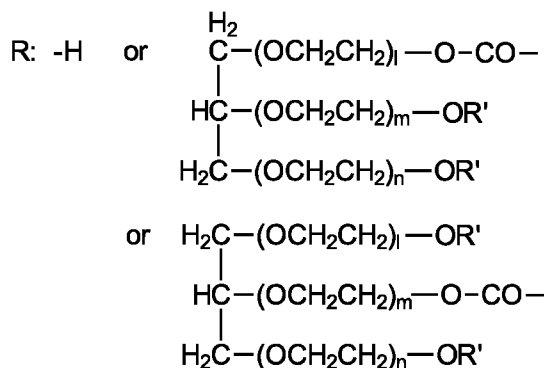


[0025] Specific examples of the compound represented by the above formula (4) include the compounds represented by the following formula (8) or (9).



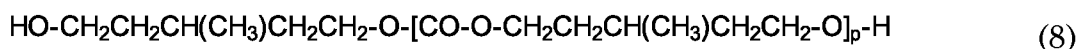
$l, m, n = 0, 1, 2, 3, 4 \quad l + m + n = 3.1$ (average value)

$p, q, r = 0, 1, 2, 3, 4, 5, 6 \quad p + q + r = 5.3$ (average value)



$\text{R}': -[\text{CO}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-\text{O}]_p-\text{H}$

and



wherein, m, n, p, q , and r are suitably selected so that the molecular weight of the compound represented by formula (8) may be 500 to 3000 g/mol.



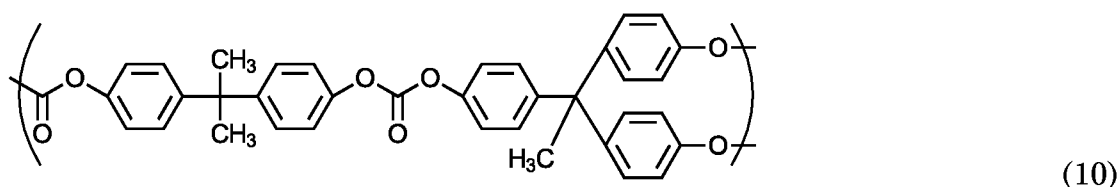
5 wherein, R^7 is an alkylene group or a divalent organic group having an alicyclic structure, and s is suitably selected so that the molecular weight of the compound represented by formula (9) may be 500 to 3000 g/mol.

[0020] Specific examples of the compound represented by the above formula (9) include a hydrogenated polybutadiene diol, 1,9-nonanediol

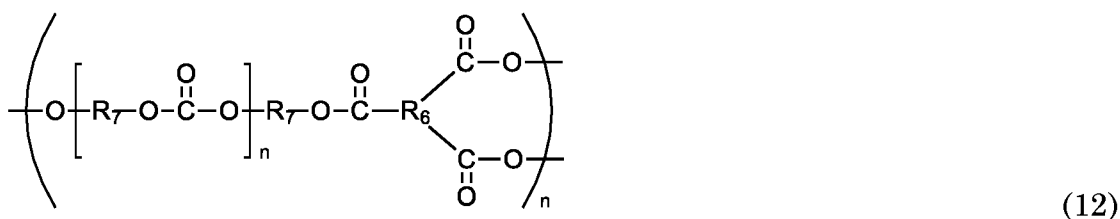
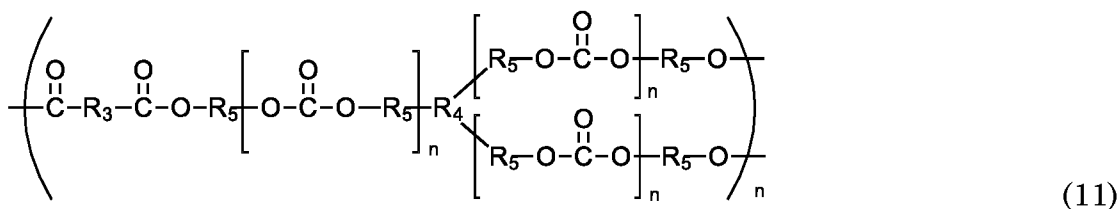
- 10 1,4-cyclohexanedimethanol carbonate diol,
- 1,4-cyclohexanedimethanol/1,6-hexanediol,
- 1,4-cyclohexanedimethanol/1,6-hexanediol,
- 1,4-cyclohexanedimethanol/1,6-hexanediol, 1,6-hexanediol carbonate diol,
- 1,6-hexanediol carbonate diol, 1,6-hexanediol carbonate diol,
- 15 1,6-hexanediol/1,5-pentanediol carbonate diol,

- 1,6-hexanediol/1,5-pentanediol carbonate diol,
 1,6-hexanediol/1,5-pentanediol carbonate diol, 1,6-hexanediol carbonate diol,
 1,5-pentanediol/1,6-hexanediol=5/5 carbonate diol,
 1,4-butanediol/1,6-hexanediol=7/3 carbonate diol,
 5 1,4-butanediol/1,6-hexanediol=9/1 carbonate diol, and
 2-methyl-1,3-propanediol/1,4-butanediol = 5/5 carbonate diol.

[0021] Specific examples of the reaction product of the compound represented by the above formula (1) with the compound represented by the above formula (3) for the (A) component include a compound having a repeated structure represented by the following formula (10) as described in
 10 Japanese Patent Application Laid-Open No. 2008-274239.



[0026] Specific examples of the reaction product of the compound represented by the above formula (2) with the compound represented by the above formula (4) for the (A) component include compounds having
 15 structures represented by the following formulas (11) and (12).



[0027] In the above formulas (11) and (12), preferably, R³ is a divalent organic group having an aromatic structure, R⁴ is a trivalent aliphatic group, R⁵s are each independently an alkylene group, R⁶ is a trivalent organic group having an aromatic structure, and R⁷s are each independently
 20

a divalent organic group having an alkylene group or an alicyclic structure. n is suitably selected so that the compound represented by formula (11) or formula (12) may have a suitable molecular weight as the component (A).

[0028] When the component (A) has a structure represented by formulas (10) to (12), the component (A) can have a polymer structure with a large number of branches (a polymer having such structure is also referred to as a dendrimer) by having branched structures in its repeated structures. An optically shaped article which is more excellent in heat resistance and toughness can be obtained by having a polymer structure with a large number of branches.

[0029] The synthesis of the component (A) which is the reaction product of the compound represented by the above formula (1) with the compound represented by the above formula (3) can be performed according to the method described in Japanese Patent Application Laid-Open No. 2008-274239 and the like. Specifically, the compound represented by the above formula (1), the compound represented by the above formula (3), and a basic catalyst such as pyridine are dissolved in an organic solvent and allowed to react, for example, at room temperature for 1 to 6 hours to obtain a compound having three or more hydroxy groups which is a precursor of the (A) component. Next, anhydrous (meth)acrylate or the like is allowed to react with a hydroxy group of the precursor compound to obtain a compound of the component (A).

[0030] The synthesis of the component (A) which is the reaction product of the compound represented by the above formula (2) with the compound represented by the above formula (4) can be performed, for example, by the following method 1 or method 2.

Method 1

[0031] A method comprising the steps of mixing the compound represented by the above formula (2), the compound represented by the

above formula (4), and a (meth)acryloyl ester having a hydroxy group and allowing them to react with each other in the presence of a basic catalyst.

Method 2

[0032] A method comprising the steps of synthesizing a reaction product
5 of the compound represented by the above formula (2) with the compound represented by the above formula (4) (a compound having three or more hydroxy groups which is a precursor of the (A) component), separately synthesizing a reaction product of the compound represented by the above formula (2) with a (meth)acryloyl ester having a hydroxy group (a compound
10 for introducing a (meth)acryloyl group), and then allowing the compound for introducing a (meth)acryloyl group to react with the compound having three or more hydroxy groups which is a precursor of the (A) component.

[0033] The content of the (A) component in the composition of the present invention is preferably 1 to 40 mass%, more preferably 2 to 30
15 mass%, and particularly preferably 5 to 20 mass% relative to the total amount of the composition. When the content of the (A) component is 1 to 40 mass%, the toughness of the optically shaped article can be further increased.

[(B) Component]

[0034] The (B) component used as a component of the composition of the present invention is a cationically polymerizable compound. The (B)
20 component is preferably a compound having one or more epoxy groups. Herein, an epoxy group means a group in which an oxygen atom is bonded to two carbon atoms in one molecule, and examples thereof include groups
25 such as three-membered rings such as a glycidyl group, four-membered rings such as an oxetanyl group, and five-membered rings. The epoxy group which the (B) component has is preferably a glycidyl group or an oxetanyl group.

[0035] Specific examples of the cationically polymerizable compound
30 having a glycidyl group (hereinafter also referred to as a (B1) component)

include bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol S diglycidyl ether, brominated bisphenol A diglycidyl ether, brominated bisphenol F diglycidyl ether, brominated bisphenol S diglycidyl ether, epoxy novolac resin, hydrogenated bisphenol A diglycidyl ether, hydrogenated

5 bisphenol F diglycidyl ether, hydrogenated bisphenol S diglycidyl ether, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexylcarboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-meta-dioxane, bis(3,4-epoxycyclohexylmethyl)adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate,

10 3,4-epoxy-6-methylcyclohexyl-3',4'-epoxy-6'-methylcyclohexanecarboxylate, ϵ -caprolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, trimethylcaprolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate,

15 β -methyl- δ -valerolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, methylenebis(3,4-epoxycyclohexane), di(3,4-epoxycyclohexylmethyl)ether of ethylene glycol, ethylenebis(3,4-epoxycyclohexanecarboxylate), dioctyl epoxycyclohexahydrophthalate, di-2-ethylhexyl

20 epoxycyclohexahydrophthalate, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, neopentyl glycol diglycidyl ether, trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether, glycerin triglycidyl ether, polypropylene glycol diglycidyl ether; polyglycidylethers of polyether polyol obtained by adding one or more

25 alkylene oxides to aliphatic polyhydric alcohol such as ethylene glycol, propylene glycol, and glycerin; diglycidyl esters of aliphatic long-chain dibasic acid; monoglycidyl ethers of aliphatic higher alcohol; monoglycidyl ethers of polyether alcohol obtained by adding phenol, cresol, butylphenol, or alkylene oxide; glycidyl esters of higher fatty acid; epoxidized soybean oil;

30 butyl epoxy stearate; octyl epoxy stearate; epoxidized linseed oil; and

epoxidized polybutadiene. These can be used alone or in combination of two or more.

[0036] Examples of the commercially available products of the (B1) component include UVR-6100, UVR-6105, UVR-6110, UVR-6128, UVR-6200, UVR-6216 (all manufactured by Union Carbide Corporation), CELLOXIDE 2021, CELLOXIDE 2021P, CELLOXIDE 2081, CELLOXIDE 2083, CELLOXIDE 2085, EPOLEAD GT-300, EPOLEAD GT-301, EPOLEAD GT-302, EPOLEAD GT-400, EPOLEAD 401, EPOLEAD 403 (all manufactured by Daicel Chemical Industries, Ltd.), KRM-2100, KRM-2110, KRM-2199, KRM-2400, KRM-2410, KRM-2408, KRM-2490, KRM-2200, KRM-2720, KRM-2750 (all manufactured by Asahi Denka Kogyo K.K.), Rapi-cure DVE-3, CHVE, PEPC (all manufactured by ISP Inc.), Epikote 828, Epikote 812, Epikote 1031, Epikote 872, Epikote CT508 (all manufactured by Japan Epoxy Resin Co., Ltd.), POX, EHOX (all manufactured by Toagosei Co., Ltd.), and VECOMER 2010, 2020, 4010, 4020 (all manufactured by Allied Signal, Inc.).

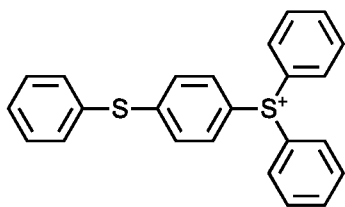
[0037] Specific examples of the cationically polymerizable compound having an oxetanyl group (hereinafter also referred to a (B2) component) include a compound having two or more oxetanyl groups such as 1,4-bis{[(3-ethyl-3-oxetanyl)methoxy]methyl}benzene (XDO) and di[2-(3-oxetanyl)butyl]ether (DOX), and a compound having one oxetanyl group such as 3-ethyl-3-(phenoxymethyl)oxetane (POX) and 3-ethyl-3-hydroxymethyloxetane (OXA).

[0038] The content of the (B) component in the composition of the present invention is 30 to 90 mass%, preferably 40 to 80 mass%, and more preferably 50 to 75 mass% relative to the total amount of the composition. When the content of the (B) component is 30 to 90 mass%, the mechanical and thermal properties of the optically shaped article is more improved.

[(C) Component]

[0039] The (C) component used as a component of the composition of the present invention is a photo-cationic polymerization initiator. The (C) component acts as a photo-cationic polymerization initiator in the polymerization of the cationically polymerizable compound ((B) component).

5 [0040] Examples of the (C) component include a salt of diphenyl(phenylthiophenyl)sulfonium including a structure represented by the following formula (3).



(3)

[0041] More specifically, specific examples of the (C) component include not only a salt containing an antimony atom such as diphenyl(phenylthiophenyl)sulfonium hexafluoroantimonate but also a salt which does not contain an antimony atom such as diphenyl(phenylthiophenyl)sulfonium hexafluorophosphate and diphenyl(phenylthiophenyl)sulfonium

15 tris(pentafluoroethyl)trifluorophosphate. Among them, a salt which does not contain an antimony atom is preferred from the point of view of safety.

[0042] Examples of the commercially available products of the (C) component include CPI-100A, CPI-101A, CPI-110A, and CPI-200K (manufactured by San-Apro Ltd.).

20 [0043] The content of the (C) component in the composition of the present invention is 0.1 to 15 mass%, preferably 0.5 to 10 mass%, and more preferably 1 to 7 mass% relative to the total amount of the composition. If the content of the (C) component is less than 0.1 mass%, the radiation-curability of a liquid resin composition may be reduced, and it may

25 be difficult to shape a three-dimensional article having sufficient mechanical strength. On the other hand, if the content of the (C) component exceeds 15 mass%, it may be impossible to obtain a suitable optical

transparency when a liquid resin composition is subjected to an optical three-dimensional shaping method, and as a result, it may be difficult to control the curing depth, and the shaping accuracy of the resulting three-dimensional article tends to be reduced.

5 [(D) Component]

[0044] The (D) component used as a component of the composition of the present invention is a radically polymerizable compound. Specifically, it is a compound having an ethylenically unsaturated bond (C=C), and examples thereof include monofunctional monomers each having one ethylenically
10 unsaturated bond in one molecule and polyfunctional monomers each having two or more ethylenically unsaturated bonds in one molecule.

[0045] Each of a monofunctional monomer and a polyfunctional monomer can be used alone or in combination of two or more. It is also possible to use at least one of the monofunctional monomers and at least one of the
15 polyfunctional monomers in combination.

[0046] It is preferred that, in the (D) component, a polyfunctional monomer having a functionality of three or more, that is, a polyfunctional monomer having three or more ethylenically unsaturated bonds in one molecule be contained at a proportion of 60 mass% or more relative to 100
20 mass% of the total amount of the (D) component. The content of the polyfunctional monomer having a functionality of three or more is more preferably 70 mass% or more, further preferably 80 mass% or more, and most preferably 100 mass%. When the content is 60 mass% or more, the radiation-curability of the resulting resin composition is further improved,
25 and the deformation with time of the three-dimensional article to be shaped tends to hardly occur.

[0047] Specific examples of the monofunctional monomer as the (D) component include acrylamide, (meth)acryloyl morpholine, 7-amino-3,7-dimethyloctyl (meth)acrylate, isobutoxymethyl
30 (meth)acrylamide, isobornylxyethyl (meth)acrylate, isobornyl

(meth)acrylate, 2-ethylhexyl (meth)acrylate, ethyldiethylene glycol (meth)acrylate, t-octyl (meth)acrylamide, diacetone (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, lauryl (meth)acrylate, dicyclopentadiene (meth)acrylate,

5 dicyclopentenylloxyethyl (meth)acrylate, dicyclopentenyl(meth)acrylate, *N,N*-dimethyl (meth)acrylamide tetrachlorophenyl (meth)acrylate, 2-tetrachlorophenoxyethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, tetrabromophenyl (meth)acrylate, 2-tetrabromophenoxyethyl (meth)acrylate, 2-trichlorophenoxyethyl

10 (meth)acrylate, tribromophenyl (meth)acrylate, 2-tribromophenoxyethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, vinylcaprolactam, *N*-vinylpyrrolidone, phenoxyethyl (meth)acrylate, butoxyethyl (meth)acrylate, pentachlorophenyl (meth)acrylate, pentabromophenyl (meth)acrylate, polyethylene glycol

15 mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, bornyl (meth)acrylate, and methyltriethylene diglycol (meth)acrylate.

[0048] Specific examples of the polyfunctional monomer as the (D) component include ethylene glycol di(meth)acrylate, dicyclopentenyl di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol

20 di(meth)acrylate, tricyclodecanedioldimethylene di(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, caprolactone-modified tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ethylene oxide (hereinafter also referred to as

25 "EO")-modified trimethylolpropane tri(meth)acrylate, propylene oxide (hereinafter also referred to as "PO")-modified trimethylolpropane tri(meth)acrylate, tripropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, both-terminal (meth)acrylic acid adduct of bisphenol A diglycidyl ether, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol

30 di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol

tetra(meth)acrylate, polyester di(meth)acrylate, polyethylene glycol di(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritolmonohydroxy penta(meth)acrylate, caprolactone-modified
5 dipentaerythritol hexa(meth)acrylate, caprolactone-modified dipentaerythritol penta(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, EO-modified bisphenol A di(meth)acrylate, PO-modified bisphenol A di(meth)acrylate, EO-modified hydrogenated bisphenol A di(meth)acrylate, PO-modified hydrogenated bisphenol A
10 di(meth)acrylate, EO-modified bisphenol F di(meth)acrylate, and (meth)acrylate of phenol novolac polyglycidyl ether.

[0049] Among these, it is preferred to contain a tri(meth)acrylate compound, a tetra(meth)acrylate compound, a penta(meth)acrylate compound, a hexa(meth)acrylate compound, or the like, which are
15 exemplified above, corresponding to a polyfunctional monomer having a functionality of three or more. More preferred examples among them include tris(acryloyloxyethyl) isocyanurate, trimethylolpropane tri(meth)acrylate, EO-modified trimethylolpropane tri(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol
20 penta(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, and dipentaerythritolmonohydroxy penta(meth)acrylate.

[0050] Examples of the commercially available products of the monofunctional monomer as the (D) component include Aronix M-101, M-102, M-111, M-113, M-117, M-152, TO-1210 (all manufactured by
25 Toagosei Co., Ltd.), KAYARAD TC-110S, R-564, R-128H (all manufactured by Nippon Kayaku Co., Ltd.), Biscoat 192, Biscoat 220, Biscoat 2311HP, Biscoat 2000, Biscoat 2100, Biscoat 2150, Biscoat 8F, Biscoat 17F (all manufactured by OSAKA ORGANIC CHEMICAL INDUSTRY, LTD.).

[0051] Examples of the commercially available products of the
30 polyfunctional monomer as the (D) component include SA1002

(manufactured by Mitsubishi Chemical Corporation), Biscoat 195, Biscoat 230, Biscoat 260, Biscoat 215, Biscoat 310, Biscoat 214HP, Biscoat 295, Biscoat 300, Biscoat 360, Biscoat GPT, Biscoat 400, Biscoat 700, Biscoat 540, Biscoat 3000, Biscoat 3700 (all manufactured by OSAKA ORGANIC
5 CHEMICAL INDUSTRY, LTD.), KAYARAD R-526, HDDA, NPGDA, TPGDA, MANDA, R-551, R-712, R-604, R-684, PET-30, GPO-303, TMPTA, THE-330, DPHA, DPHA-2H, DPHA-2C, DPHA-2I, D-310, D-330, DPCA-20, DPCA-30, DPCA-60, DPCA-120, DN-0075, DN-2475, T-1420, T-2020, T-2040, TPA-320, TPA-330, RP-1040, RP-2040, R-011, R-300, R-205 (all
10 manufactured by Nippon Kayaku Co., Ltd.), Aronix M-210, M-220, M-233, M-240, M-215, M-305, M-309, M-310, M-315, M-325, M-400, M-6200, M-6400 (all manufactured by Toagosei Co., Ltd.), Light Acrylate BP-4EA, BP-4PA, BP-2EA, BP-2PA, DCP-A (all manufactured by Kyoeisha Chemical Co., Ltd.), New Frontier BPE-4, BR-42M, GX-8345 (all manufactured by
15 Dai-Ichi Kogyo Seiyaku Co., Ltd.), ASF-400 (manufactured by Nippon Steel Chemical Co., Ltd.), Ripoxy SP-1506, SP-1507, SP-1509, VR-77, SP-4010, SP-4060 (all manufactured by Showa High Polymer Co., Ltd.), and NK Ester A-BPE-4 (manufactured by Shin-Nakamura Chemical Co., Ltd.).

[0052] The content of the (D) component in the composition of the
20 present invention is 1 to 50 mass%, preferably 5 to 40 mass%, and more preferably 10 to 30 mass% relative to the total amount of the composition. By adding the (D) component, the radiation-curability of the liquid resin composition is improved, and the deformation with time of the three-dimensional article to be shaped tends to hardly occur.

25 [(E) Component]

[0053] The (E) component used as a component of the composition of the present invention is a photo-radical polymerization initiator. The (E) component is a compound which decomposes by receiving radiation such as light and initiates the radical polymerization reaction of the (E) component
30 by the radicals generated.

[0054] Specific examples of the (E) component include acetophenone, acetophenone benzyl ketal, anthraquinone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, carbazole, xanthone, 4-chlorobenzophenone, 4,4'-diaminobenzophenone, 5 1,1-dimethoxydeoxybenzoin, 3,3'-dimethyl-4-methoxybenzophenone, a thioxanthone-based compound, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-2-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, triphenylamine, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, 10 bis(2,6-dimethoxybenzoyl)-2,4,4-tri-methylpentylphosphine oxide, benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, fluorenone, fluorene, benzaldehyde, benzoin ethyl ether, benzoin propyl ether, benzophenone, Michler's ketone, 3-methylacetophenone, 15 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone (BTTB), and a combination of BTTB and a dye sensitizer such as xanthene, thioxanthene, coumarin, and ketocoumarin.

[0055] Among these, benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, and 20 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one are preferred.

[0056] The above photo-radical polymerization initiator can be used alone or in combination of two or more.

[0057] The content of the (E) component in the composition of the 25 present invention is 0.01 to 10 mass%, preferably 0.1 to 5 mass%, and more preferably 1 to 4 mass% relative to the total amount of the composition. If the content of the (E) component is less than 0.01 mass%, there is a tendency that the radical polymerization reaction rate (cure rate) of a liquid resin composition is reduced, and that as a result, the time required for 30 shaping is increased or the resolution is reduced. On the other hand, if the

content of the (E) component exceeds 10 mass%, excessive amount of the polymerization initiator may reduce the curing characteristics of a liquid resin composition, or may have a bad influence on the moisture resistance and heat resistance of a three-dimensional article.

5 [(F) Component]

[0058] The composition of the present invention may comprise elastomer particles as a (F) component in a range that does not inhibit the effect of the present invention.

[0059] Specific examples of the (F) component include elastomer
10 particles using, as a base component, polybutadiene, polyisoprene, butadiene/acrylonitrile copolymer, a styrene/butadiene copolymer, a styrene/isoprene copolymer, an ethylene/propylene copolymer, an ethylene/ α -olefin copolymer, an ethylene/ α -olefin/polyene copolymer, acrylic rubber, a butadiene/(meth)acrylate copolymer, a styrene/butadiene block
15 copolymer, a styrene/isoprene block copolymer, and the like.

[0060] Further, other specific examples of the (F) component include core/shell-type particles in which these elastomer particles are covered with a methyl methacrylate polymer, a methyl methacrylate/glycidyl
methacrylate copolymer, or the like. Here, the ratio of the radius of the core
20 to the thickness of the shell (the radius of the core/the thickness of the shell) is generally 1/2 to 1000/1, preferably 1/1 to 200/1. For example, when the radius of the core is 350 nm and the thickness of the shell is 10 nm, the ratio of the radius of the core to the thickness of the shell is 35/1.

[0061] In the case of the core/shell-type particles, preferred among the
25 elastomer particles as described above are elastomer particles in which a core obtained by partially crosslinking polybutadiene, polyisoprene, a styrene/butadiene copolymer, a styrene/isoprene copolymer, a butadiene/(meth)acrylate copolymer, a styrene/butadiene block copolymer, a styrene/isoprene block copolymer, or the like is covered with a methyl

methacrylate polymer or covered with a methyl methacrylate/glycidyl methacrylate copolymer.

[0062] Further, the (F) component may have a crosslinking structure in the inner part of the particles, and can be crosslinked by generally used
5 means. Examples of the crosslinking agent used in this case include divinylbenzene, ethylene glycol di(meth)acrylate, diallyl maleate, triallyl cyanurate, triallyl isocyanurate, diallyl phthalate, trimethylolpropane triacrylate, and allyl methacrylate.

[0063] These elastomer particles can be produced by a generally used
10 method. Examples of the generally used method include an emulsion polymerization method. Examples of the emulsion polymerization method which can be adopted include a method wherein the whole amount of monomer components is charged in one lot, a method wherein a part of monomer components are polymerized, followed by continuously or
15 intermittently adding the remaining part, a method wherein monomer components are continuously added from the start of polymerization, and a method wherein seed particles are used.

[0064] The number average particle size of the elastomer particles obtained by these methods is preferably 10 to 1000 nm, more preferably 10
20 to 700 nm. If the number average particle size is less than 10 nm, the impact resistance and fracture toughness of the resulting three-dimensional article may be reduced and the viscosity of the resin liquid may be increased, thereby affecting the productivity and shaping accuracy of the three-dimensional article. On the other hand, if the number average particle
25 size exceeds 1000 nm, a three-dimensional article in which the surface is sufficiently smooth may not be obtained, or the shaping accuracy may be reduced.

[0065] Note that the number average particle size of the elastomer particles is measured as a number average particle size in terms of

polystyrene particles based on a light scattering method or a dynamic light scattering method.

[0066] Examples of the commercially available products of the above core/shell-type elastomer particles include Resinous Bond RKB

5 (manufactured by Resinous Kasei Co., Ltd.), and Techno MBS-61, MBS-69 (all manufactured by Techno Polymer Co., Ltd.).

[0067] These elastomer particles as the (F) component can be used alone or in combination of two or more.

[0068] The content of the (F) component in the composition of the present
10 invention is preferably 1 to 35 mass%, more preferably 3 to 30 mass%, and particularly preferably 5 to 20 mass% relative to the total amount of the composition. If the content is less than 1 mass%, the impact resistance and fracture toughness may be reduced. On the other hand, if the content exceeds 35 mass%, there is a tendency for the shaping accuracy of the
15 resulting three-dimensional article to be reduced.

[(G) Component]

[0069] The composition of the present invention may comprise, as a (G) component, a compound having a phenolic hydroxyl group and/or a phosphite group, in a range that does not inhibit the effect of the present
20 invention.

[0070] Examples of the (G) component include a known antioxidant. Among them, a hindered phenol-based compound or a phosphorus-based compound is preferred. Adding the (G) component can effectively reduce the discoloration (yellowing) of a three-dimensional shaped article with time to
25 maintain high transparency of the three-dimensional shaped article over a long period of time after shaping.

[0071] Specific examples of the (G) component include the following compounds. Note that those written in parentheses after the following compounds each are an example of a trade name.

[0072] Examples of the hindered phenol-based compound include pentaerythritol tetrakis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate] (Irganox 1010), thiodiethylene-bis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate] (Irganox 1035FF), benzenepropanoic acid-3,5-bis(1,1-dimethylethyl)-4-hydroxy, ethylenebis(oxyethylene)bis[3-(5-*tert*-butyl-4-hydroxy-*m*-tolyl)propionate] (Irganox 245), octadecyl-3-(3,5-*t*-butyl-4-hydroxyphenyl) propionate (Irganox 1076), 3,3',3'',5,5',5''-hexa-*t*-butyl-*a,a',a''*-(mesitylene-2,4,6-triyl)tri-*p*-cresol (Irganox 1330), 1,3,5-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (Irganox 3114), 4,6-bis(octylthiomethyl)-*o*-cresol (Irganox 1520L), 9-bis[2-{3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane (Sumilizer GA-80), and 2,6-di-*t*-butyl-4-methylphenol (Sumilizer BHT).

[0073] In the above list, Irganox is a registered trademark of Ciba Specialty Chemicals Corp., and Sumilizer is a registered trademark of Sumitomo Chemical Co., Ltd.

[0074] Examples of the phosphorus-based compound include tris(2,4-di-*t*-butylphenyl)phosphite (Irgafos 168), phosphorous acid bis[2,4-bis(1,1-dimethylethyl)-6-methylphenyl] ethyl ester (Irgafos 38), and 6-[3-(3-*t*-butyl-4-hydroxy-5-methylphenyl)-propoxy]-2,4,8,10-tetra-*t*-butylbenz[d,f][1,3,2]-dioxaphosphepine (Sumilizer GP).

[0075] In the above list, Irgafos is a registered trademark of Ciba Specialty Chemicals Corp., and Sumilizer is a registered trademark of Sumitomo Chemical Co., Ltd.

[0076] As described above, examples of the commercially available products of the hindered phenol-based (G) component include Irganox 1010, 1035FF, 245, 1076, 1330, 3114, 1520L, 3125 (all manufactured by Ciba Specialty Chemicals Corp.), Sumilizer BHT, GA-80 (manufactured by

Sumitomo Chemical Co., Ltd.), and Cyanox 1790 (manufactured by Cytech, Inc.).

[0077] As described above, examples of the commercially available products of the phosphorus-based (G) component include Irgafos 168, 12, 38 (all manufactured by Ciba Specialty Chemicals Corp.), ADK STAB 329K, PEP36, PEP-8 (all manufactured by Asahi Denka Kogyo K.K.), Sandstab P-EPQ (manufactured by Clariant, Corp.), Weston 618, 619G, Ultrinox 626 (all manufactured by General Electric Company), and Sumilizer GP (manufactured by Sumitomo Chemical Co., Ltd.).

10 [0078] Among the (G) components as listed above, pentaerythritol tetrakis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate], benzenepropanoic acid-3,5-bis(1,1-dimethylethyl)-4-hydroxy, ethylenebis(oxyethylene)bis[3-(5-*tert*-butyl-4-hydroxy-*m*-tolyl)propionate], 4,6-bis(octylthiomethyl)-*o*-cresol, phosphorous acid
15 bis[2,4-bis(1,1-dimethylethyl)-6-methylphenyl] ethyl ester, and 6-[3-(3-*t*-butyl-4-hydroxy-5-methylphenyl)-propoxy]-2,4,8,10-tetra-*t*-butylbenz[d,f][1,3,2]-dioxaphosphepine are preferred in that they can maintain the transparency of a three-dimensional article over a long period of time after shaping. Among these, pentaerythritol
20 tetrakis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate] is particularly preferred.

[0079] The content of the (G) component in the composition of the present invention is preferably 0.01 to 10 mass%, more preferably 0.1 to 5 mass%, and particularly preferably 1 to 4 mass% relative to the total
25 amount of the composition. If the content of the (G) component is less than 0.01 mass% or if it exceeds 10 mass%, a problem in which the transparency of an optically shaped article is reduced with time or the like may occur. Therefore, such a content is not preferred.

[(H) Component]

[0080] The composition of the present invention may comprise water as a (H) component in a range that does not inhibit the effect of the present invention.

[0081] By adding water, the radiation-curability of a liquid resin composition can be improved. Further, adding water can improve the mechanical properties, particularly elastic modulus, of a cured product obtained by irradiating a liquid resin composition with light to suppress the change with time of the shape and mechanical properties of a three-dimensional shaped article obtained by optical shaping.

5 [0082] The content of water in the composition of the present invention is preferably 0.1 to 2 mass%, more preferably 0.2 to 1 mass% relative to the total amount of the composition.

[0083] If the content of water is less than 0.1 mass%, there is a tendency that the sensitivity of a resin easily changes with time, resulting in that it is difficult to perform stable shaping. On the other hand, if the content of water exceeds 2 mass%, there is a tendency that the elastic modulus of the three-dimensional article obtained by optical shaping is reduced.

[0084] Further, in the radiation-curable liquid resin composition for optical shaping of the present invention, various additives may be contained as other optional components in a range that does not impair the purpose and effect of the present invention. Examples of these additives include polymers or oligomers such as epoxy resins, polyamides, polyamideimides, polyurethanes, polybutadienes, polychloroprenes, polyethers, polyesters, styrene-butadiene block copolymers, petroleum resins, xylene resins, ketone resins, cellulosic resins, fluorine-based oligomers, silicone-based oligomers, and polysulfide-based oligomers; polymerization inhibitors such as phenothiazine and 2,6-di-t-butyl-4-methyl phenol; polymerization initiation aids; leveling agents; wettability improving agents; surfactants; plasticizers; ultraviolet absorbers; silane coupling agents; inorganic fillers; pigments; and dyes.

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[0085] The composition of the present invention can be produced by charging a suitable amount of the above essential components (A), (B), (C), (D), and (E) and other optional components if needed to an agitation vessel and stirring these components at a temperature of generally 30 to 70 °C, preferably 50 to 60 °C for generally 1 to 6 hours, preferably 1 to 2 hours.

[0086] The viscosity at 25 °C of the composition of the present invention is preferably 50 to 2000 mPa·s, more preferably 70 to 1500 mPa·s.

[0087] The composition of the present invention obtainable as described above is suitably used as a radiation-curable liquid resin composition in an optical three-dimensional shaping method. That is, a three-dimensional article (optically shaped article) having a desired shape can be produced by an optical three-dimensional shaping method in which the radiation-curable liquid resin composition of the present invention is selectively irradiated with light such as visible light, ultraviolet light, and infrared light to supply energy necessary for curing.

[0088] When the composition of the present invention is used, an optically shaped article excellent in toughness, heat resistance, and transparency can be obtained.

20 *II. Optically Shaped Article*

[0089] The optically shaped article of the present invention can be obtained by irradiating the composition of the present invention with radiation such as light.

25 [0090] A means to selectively irradiate the composition of the present invention with light is not particularly limited, and various means can be adopted. Examples of the means that can be adopted include a means of irradiating a composition with light such as a laser beam or convergent light obtained using a lens, a mirror, or the like while scanning the light; a means
30 of using a mask having a light transmission part of a predetermined pattern

and irradiating a composition with non-convergent light through the mask;
and a means of using a light guide member prepared by bundling a large
number of optical fibers and irradiating a composition with light through
the optical fibers corresponding to a predetermined pattern in the light
5 guide member.

[0091] Further, in the means of using a mask, it is also possible to use a
mask in which a mask image consisting of a light-transmitting region and a
light non-transmitting region is electrooptically formed in a predetermined
pattern by the same principle as in a liquid crystal display.

10 [0092] When a target three-dimensional article has a fine part or is
required for high dimensional accuracy, it is preferred to adopt a means to
scan a laser beam having a small spot diameter as a means to selectively
irradiate a composition with light.

[0093] Note that a light irradiation surface (for example, scanning plane
15 of convergent light) of a resin composition received in a container may be
any of a liquid surface of the resin composition and a contact surface with a
container wall of a translucent container. When the liquid surface of the
resin composition or the contact surface with a container wall is used as the
light irradiation surface, it can be irradiated with light directly from the
20 outside of the container or through the container wall.

[0094] In the above optical three-dimensional shaping method, generally,
after curing a particular part of a resin composition, the light irradiation
position (irradiation surface) is moved continuously or stepwise from a cured
part to an uncured part to thereby laminate the curing part to form a
25 desired three-dimensional shape.

[0095] The transfer of the irradiation position can be performed by
various methods, and examples thereof include a method of moving any of a
light source, a receiving container of a resin composition, and a cured part of
a resin composition, and a method of additionally supplying a resin
30 composition to the container.

[0096] A representative example of the above optical three-dimensional shaping method is described as follows.

[0097] First, a supporting stage which is freely vertically movably provided in a receiving container is lowered (settled) by a fine amount from
5 the liquid surface of a resin composition to thereby supply the resin composition on the supporting stage to form a thin layer (1) thereof.

[0098] Next, the thin layer (1) is selectively irradiated with light to thereby form a solid cured resin layer (1).

[0099] Next, a radiation-curable liquid resin composition is supplied on
10 the cured resin layer (1) to form a thin layer (2) thereof, and the thin layer (2) is selectively irradiated with light to thereby form a new cured resin layer (2) on the above cured resin layer (1) so that the cured resin layer (2) may be continuously and integrally laminated with the cured resin layer (1).

[0100] Thus, a three-dimensional article in which a plurality of cured
15 resin layers (1, 2, ... n) are integrally laminated is shaped by repeating these steps a predetermined number of times while changing or without changing the pattern which is irradiated with light.

[0101] The three-dimensional article obtained in this way is taken out from the receiving container, and an unreacted resin composition remaining
20 on the surface thereof is removed, and then the article is washed if needed. Here, examples of the washing agent include an alcohol-based organic solvent typified by alcohols such as isopropyl alcohol and ethyl alcohol; a ketone-based organic solvent typified by acetone, ethyl acetate, methyl ethyl ketone, and the like; an aliphatic organic solvent typified by terpenes; and a
25 thermosetting resin and a radiation-curable resin each having a low viscosity.

[0102] Note that after washing with a washing agent, postcuring by heat irradiation or light irradiation may be performed if needed. The postcuring can cure an unreacted resin composition which may remain on the surface
30 and in the inner part of a three-dimensional article to suppress the

stickiness of the surface of a shaped article, and can improve the initial strength of a shaped article.

[0103] The optically shaped article of the present invention is excellent in toughness and heat resistance.

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Examples

[0104] Hereinafter, the present invention will be more specifically described with reference to Examples, but the present invention is not limited at all by these Examples.

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Synthesis Example 1: Synthesis of component (A)

[0105] In a three-necked recovery flask with a volume of 500 ml, were charged 2.48 g (0.008 mol) of 1,1,1-tris(4-hydroxyphenyl)ethane (THE) and 2.24 g (0.028 mol) of pyridine as a base, and they were dissolved in 160 ml of tetrahydrofuran (THF) to obtain a THE solution. Into the THE solution with stirring, was dropwise added over 1 hour a BABC solution in which 4.24 g (0.012 mol) of bisphenol A bis(chloroformate) (BABC) was dissolved in 24 ml of THF, and the mixture was allowed to react for 1 hour.

[0106] After completion of the reaction, the reaction liquid was separated into a gel part and a chloroform-soluble part by adding 160 ml of chloroform to the reaction liquid to dilute it and washing it with chloroform using a Kiriya funnel. The chloroform-soluble part was concentrated using an evaporator, and then subjected to reprecipitation purification by using chloroform as a good solvent and methanol as a poor solvent, followed by reduced pressure drying to obtain 4.63 g of a polymer having a hydroxy group of a white powder at a yield of 80%.

[0107] In a recovery flask with a volume of 100 ml, 2.50 g of the resulting polymer having a hydroxy group was dissolved in 30 ml of pyridine, and thereto was slowly dropwise added 3.70 g (0.024 mol) of anhydrous methacrylic acid with stirring under a condition of a nitrogen atmosphere

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and -5 °C, and the mixture was allowed to react at room temperature for 6 hours. After completion of the reaction, the reaction liquid was subjected to reprecipitation purification twice by using methanol as a poor solvent, followed by reduced pressure drying to obtain a polymer of a white powder (component (A) having a repeated structure represented by formula (10)) at a yield of 85%.

[0108] When the polymer was measured for the molecular weight and molecular weight distribution by gel permeation chromatography (GPC), the number average molecular weight M_n was 14 000 g/mol in terms of polystyrene, and the molecular weight distribution M_w/M_n was 5.3.

Synthesis Example 2: Synthesis of component (A)

[0109] In a three-necked recovery flask with a volume of 500 ml, 12.18 g (0.06 mol) of o-phthalic acid chloride (OPC manufactured by Iharanikkei Chemical Industry Co., Ltd.) was dissolved in 270 ml of ethyl acetate to obtain an OPC solution. To this OPC solution with stirring, was dropwise added over 1 hour a HEMA solution obtained by dissolving 7.81 g (0.06 mol) of 2-hydroxyethyl methacrylate (HEMA) and 5.62 g (0.07 mol) of pyridine as a base in 30 ml of ethyl acetate, and the mixture was allowed to react for 2 hours, at 5 to 10 °C.

[0110] Subsequently, to this reaction liquid, was dropwise added over 1 hour a PCTL solution obtained by dissolving 2.48 g (0.008 mol) of polycarbonate triol (PCTL: manufactured by Kuraray Co., Ltd. (CF-1000)) and 5.62 g (0.07 mol) of pyridine as a base in 30 ml of ethyl acetate, and the mixture was allowed to react for 1 hour.

[0111] The reaction mother liquor was filtered, separated, dehydrated, and then concentrated using an evaporator. Subsequently, the concentrated liquor was subjected to reprecipitation purification by using ethyl acetate as a good solvent and methanol as a poor solvent, followed by reduced pressure drying to obtain a polymer of viscous liquid at a yield of 60%.

[0112] When the polymer was measured for the molecular weight and molecular weight distribution by gel permeation chromatography (GPC), the number average molecular weight M_n was 2400 g/mol in terms of polystyrene, and the molecular weight distribution M_w/M_n was 2.2.

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Synthesis Example 3: Synthesis of a compound having three or more hydroxy groups to be obtained by reacting the compound represented by the above formula (2) with the compound represented by the above formula (4), which is a precursor of the component (A)

10 [0113] In a three-necked recovery flask with a volume of 500 ml, 1.71 g (0.0084 mol) of p-phthalic acid chloride (TPC manufactured by Iharanikkei Chemical Industry Co., Ltd.) was dissolved in 100 ml of ethyl acetate to obtain a TPC solution. To this TPC solution with stirring, was dropwise added over 1 hour a PCTL solution 1 obtained by dissolving 2.40 g (0.0024
15 mol) of polycarbonate triol (PCTL) and 0.67 g (0.0084 mol) of pyridine as a base in 100 ml of ethyl acetate, and the mixture was allowed to react for 1 hour, at 5 to 10 °C.

[0114] Subsequently, to this resulting PCTL solution 1, was dropwise added over 1 hour a PCTL solution 2 obtained by dissolving 9.60 g (0.0096
20 mol) of polycarbonate triol (PCTL) and 0.78 g (0.0098 mol) of pyridine as a base in 100 ml of ethyl acetate, and the mixture was allowed to react for 1 hour to obtain a precursor of the component (A) having three or more hydroxy groups.

25 *Synthesis Example 4: Synthesis of a compound for introducing a (meth)acryloyl group into the precursor of the (A) component obtained in Synthesis Example 3*

[0115] In a three-necked recovery flask with a volume of 200 ml, 4.87 g (0.0024 mol) of p-phthalic acid chloride (OPC) was dissolved in 50 ml of
30 ethyl acetate to obtain an OPC solution. To this OPC solution with stirring,

was dropwise added over 1 hour a HEMA solution obtained by dissolving 3.15 g (0.0242 mol) of 2-hydroxyethyl methacrylate (HEMA) and 1.94 g (0.0242 mol) of pyridine as a base in 50 ml of ethyl acetate, and the mixture was allowed to react for 1 hour, at 5 to 10 °C, to obtain a solution of the compound for introducing a (meth)acryloyl group.

Synthesis Example 5: Synthesis of component (A)

[0116] To the precursor solution of the component (A) obtained in Synthesis Example 3, were dropwise added the compound solution obtained in Synthesis Example 4 and 1.94 g (0.0242 mol) of pyridine over 30 minutes, and the mixture was allowed to react for 1 hour.

[0117] The reaction mother liquor was filtered, separated, dehydrated, and then concentrated using an evaporator. Subsequently, the concentrated liquor was subjected to reprecipitation purification by using ethyl acetate as a good solvent and methanol as a poor solvent, followed by reduced pressure drying to obtain a polymer (component (A)) of viscous liquid at a yield of 44%.

[0118] When the polymer was measured for the molecular weight and molecular weight distribution by gel permeation chromatography (GPC), the number average molecular weight M_n was 7000 g/mol in terms of polystyrene, and the molecular weight distribution M_w/M_n was 1.7.

Preparation of liquid resin composition

[0119] The liquid resin compositions of Examples 1 to 6 and Comparative Examples 1 to 4 were prepared by charging each components in a stirred vessel according to the formulation shown in Table 1 and stirring the components at 60 °C for 3 hours. The unit of the numerical values of the formulation in Table 1 is parts by mass.

Evaluation

[0120] The evaluation tests of the Young's modulus of cured films, film impact values, glass transition temperature (T_g), and color were performed using each of the liquid resin compositions of Examples 1 to 6 and Comparative Examples 1 to 4. The evaluation results are shown in Table 1.

5 [0121] The evaluation methods are as follows.

[0122] [Young's modulus of cured film]

(1) Preparation of test piece

A liquid resin composition was applied to a glass plate in a thickness of 200 μm and irradiated with 1 J/cm^2 using a metal-halide lamp to obtain a
10 cured film. Subsequently, it was allowed to stand in a constant temperature and humidity chamber at a temperature of 23 $^{\circ}\text{C}$ and a humidity of 50% for 24 hours.

(2) Measurement

A test piece having a dimension of 8 $\text{cm} \times 0.6 \text{ cm}$ was cut out from the
15 cured film prepared according to the above described procedure. The Young's modulus of the test piece was measured according to JIS K7127 using a tensile tester AGS-50G manufactured by Shimadzu Corp. At this time, the measurement was performed with a gauge length of 2.5 cm (grips at both ends of 2.75 cm) at a tension speed of 1 mm/min .

20 [0123] [Film impact value]

(1) Preparation of test piece

A cured film was prepared under the same conditions as in the preparation of the test piece of the Young's modulus of a cured film.

(2) Measurement

25 A test piece prepared according to the above described procedure was allowed to stand in a constant temperature and humidity chamber at a temperature of 23 $^{\circ}\text{C}$ and a humidity of 50% for 24 hours, and then a test piece having a dimension of 10 $\text{cm} \times 10 \text{ cm}$ was cut out. The film impact value was measured using a film impact tester manufactured by Yasuda

Seiki Seisakusho, Ltd. A plastic ball having a diameter of 12 mm was used as an impact ball.

[0124] [Glass transition temperature (T_g)]

A radiation-curable resin composition was applied to a glass plate
5 using a 15-mil (corresponding to a coating film thickness of about 200 μ m) applicator bar, and the coating film was irradiated with ultraviolet rays with energy of 1000 mJ/cm² in the air to cure the composition to obtain a film for measurement. A test piece having a size of 3 mm $\times$ 35 mm was cut out from this film for measurement and measured for the dynamic
10 viscoelasticity using RHEOVIBRON DDV-01FP manufactured by ORIENTEC Co., Ltd. The temperature showing the maximum value of a loss tangent ($\tan \delta$) at an oscillation frequency of 3.5 Hz was defined as glass transition temperature, and the glass transition temperature was obtained.

[0125] [Production of optically shaped article]

15 A pair of shaped articles having a fitting shape shown in Figure 1 (the size of the convex article is 62 $\times$ 34 $\times$ 11 mm, and the size of the concave article is 52 $\times$ 34 $\times$ 11 mm) was produced by repeating the step of selectively irradiating each liquid resin composition with a laser beam to form a cured resin layer (0.10 mm in thickness) under conditions of a laser power at the
20 irradiation surface (liquid surface) of 100 mW and a scanning rate at which curing depth is 0.2 mm in each composition, using a Solid Creator SCS-300P (manufactured by Sony Manufacturing Systems Co., Ltd.).

It was possible to produce target optically shaped articles in all of Examples and Comparative Examples

25 [0126]

[Table 1]

Component	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
(A)	Compound obtained in Synthesis Example 1	5	-	-	-	-	-	-	-	-
	Compound obtained in Synthesis Example 2	-	5	10	20	-	-	-	-	-
	Compound obtained in Synthesis Example 5	-	-	-	-	5	-	-	-	-
	Polycarbonatediol	-	-	-	-	-	-	10	-	-
Compound not corresponding to (A)	Hydroxy group-terminated polycarbonate-based dendrimer	-	-	-	-	-	-	-	10	-
	Hydroxy group-terminated polyester-based dendrimer	-	-	-	-	-	-	-	-	10
(B)	2021P	36.4	36.4	36.4	36.4	36.4	36.4	36.4	36.4	36.4
	EXA850CRP	20	20	20	20	20	20	20	20	20
	EXA830CRP	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4
	OXIPA	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8
(C)	OXA	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8
(D)	CPI-200K	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1
(E)	DPHA	10	10	10	10	10	10	10	10	10
Others	Irgacure184	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
	Elastomer particles	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3
	Irganox1010	1	1	1	1	1	1	1	1	1
	Water	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
Total	(parts by mass)	104.5	104.5	109.5	119.5	104.5	99.5	109.5	109.5	109.5
Physical properties of cured film	Young's modulus (MPa)	1,970	1,800	1,650	1,330	1,670	1,970	1,300	800	1,430
	Film impact value (cJ/m)	14	17	15	24	13	7	15	7	16
	T _g (°C)	134	124	120	108	128	122	116	110	104

[0127] Each component in Table 1 is as follows.

[(B) Component]

2021P: 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexyl carboxylate
5 (manufactured by Daicel Chemical Industries, Ltd.)

EXA850CRP; bisphenol A type diglycidyl ether (manufactured by
Dainippon Ink & Chemicals, Inc.)

EXA830CRP: bisphenol F type diglycidyl ether (manufactured by
Dainippon Ink & Chemicals, Inc.)

10 OXIPA: isophthalic acid bis[(3-ethyl-3-oxetanyl)methyl]ester
(manufactured by Ube Industries, Ltd.)

OXA: 3-ethyl-3-hydroxymethyloxetane (manufactured by Toagosei Co.,
Ltd.)

[(C) Component]

15 CPI-200K:
diphenyl(phenylthiophenyl)sulfonium(pentafluoroethyl)trifluorophosphate
(manufactured by San-Apro Ltd.)

[(D) Component]

DPHA: dipentaerythritol hexaacrylate (manufactured by Nippon
20 Kayaku Co., Ltd.)

[(E) Component]

Irgacure 184: 1-hydroxycyclohexyl phenyl ketone (manufactured by
Ciba Specialty Chemicals Corp.)

[(F) Component]

25 Elastomer particles: RKB5610CP-60 (manufactured by Resinous Kasei
Co., Ltd.)

[(G) Component]

Irganox 1010: hindered phenol-type antioxidant (manufactured by Ciba
Japan, K.K.)

30 [Others]

DOX: bis[1-ethyl(3-oxetanyl)]methyl ether (manufactured by Toagosei Co., Ltd.)

XDO: 1,4-bis{[(3-ethyl-oxetan-3-yl)methoxy]methyl}benzene (manufactured by Toagosei Co., Ltd.)

5 [Others; compounds not corresponding to (A) component]

Polycarbonatediol: Duranol G3452 (Asahi Kasei Chemicals Corporation, molecular weight: 2000)

Hydroxy group-terminated reactive polycarbonate-based dendrimer: a reaction product obtained by reacting bisphenol A bis(chloroformate) (BABC) with 1,1,1-tris(4-hydroxyphenyl ethane)ethane (THE)

Hydroxy group-terminated polyester-based dendrimer: Boltorn H2004 (Perstorp Inc.)

[0128] From the results of Table 1, it is found that an optically shaped article excellent in toughness and heat resistance can be obtained by using compositions of Examples 1 to 6 which satisfy the conditions of the composition specified in the present invention.

[0129] On the other hand, a film impact value and T_g are poor in Comparative Example 1 in which the component (A) was not blended. In Comparative Examples 2 to 4 using polycarbonatediol or a dendrimer not corresponding to the component (A) instead of the component (A), Young's modulus and T_g are poor in Comparative Example 2; Young's modulus and a film impact value are poor in Comparative Example 3; and Young's modulus and T_g are poor in Comparative Example 4.

Claims

1. A radiation-curable liquid resin composition for optical three-dimensional shaping comprising:
 - (A) a compound which has a carbonate group and two or more (meth)acryloyl groups and does not have a urethane bond;
 - 5 (B) a cationically polymerizable compound;
 - (C) a photo-cationic polymerization initiator;
 - (D) a radically polymerizable compound; and
 - (E) a photo-radical polymerization initiator.
- 10 2. The radiation-curable liquid resin composition according to claim 1, wherein the (A) component has two or more carbonate groups and three or more (meth)acryloyl groups.
3. The radiation-curable liquid resin composition according to claim
- 15 1, wherein the (A) component has a branched structure.
4. The radiation-curable liquid resin composition according to claim 1, wherein the (A) component has an aromatic structure.
- 20 5. The radiation-curable liquid resin composition according to claim 1, wherein the (A) component is a compound obtained by introducing a (meth)acryloyl group into one or more compounds selected from the following [1] and [2]:
 - [1] a compound having three or more hydroxy groups obtained by reacting a
 - 25 compound represented by the following formula (1) with a compound represented by the following formula (3), and

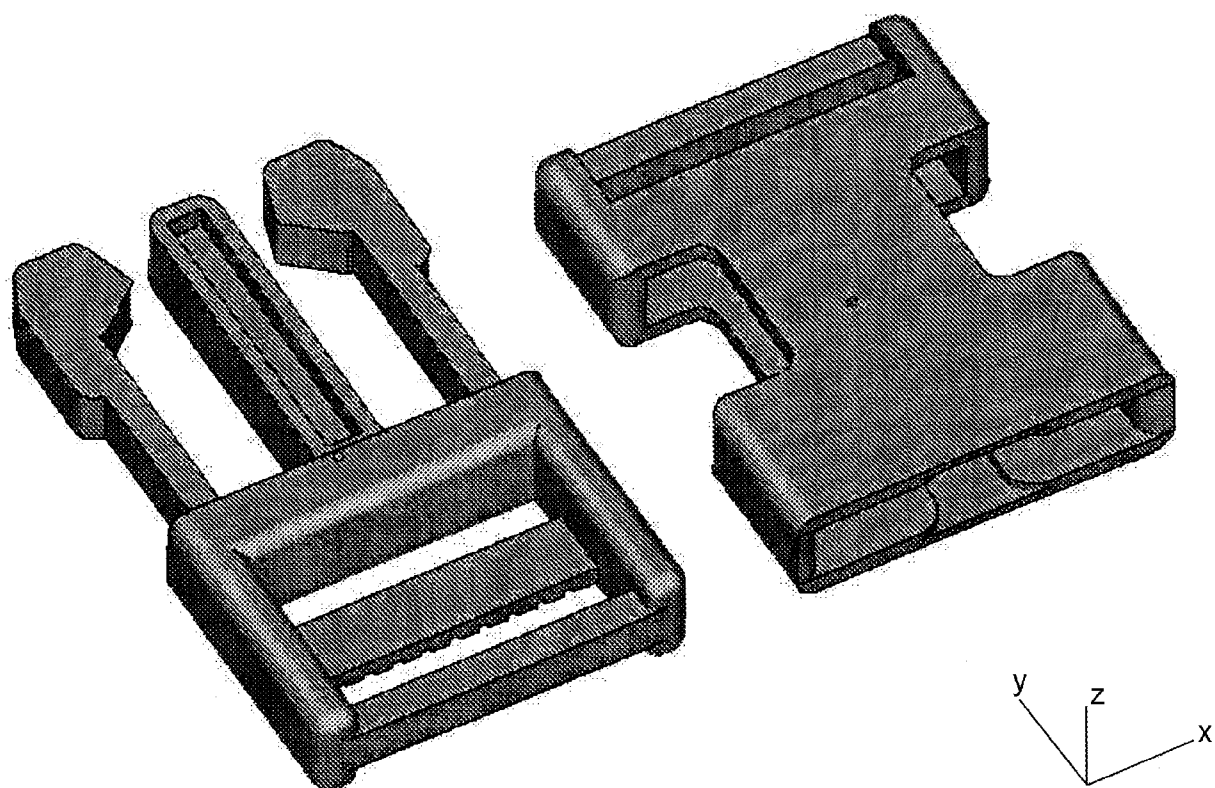
[2] a compound having three or more hydroxy groups obtained by reacting a compound represented by the following formula (2) with a compound represented by the following formula (4),



wherein, R^1 and R^2 are each independently a monovalent organic group having an aliphatic, alicyclic or aromatic structure, R^3 and R^4 are each independently a monovalent organic group having an aliphatic, alicyclic or aromatic structure, R^5 and R^6 are each independently an alkylene group, $n1$ and $n2$ are each independently an integer of 2 or more, $m1$ and $m3$ are each independently an integer of 3 or more, and $m2$ is an integer of 1 to 3, provided that at least one of R^1 and R^3 or R^2 and R^4 constituting one compound has an aromatic structure.

6. An optically shaped article obtained by irradiating the radiation-curable liquid resin composition according to any one of claims 1 to 5 with light.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2014/050126

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F220/26
ADD.

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)
C08F

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/053133 A1 (DSM IP ASSETS BV [NL]; JSR CORP [JP]; JAPAN FINE COATINGS CO LTD [JP];) 5 May 2011 (2011-05-05) the whole document -----	1-6
A	US 2010/227941 A1 (UEDA MASAHIRO [JP] ET AL) 9 September 2010 (2010-09-09) the whole document -----	1-6
A	WO 2008/115057 A1 (DSM IP ASSETS BV) 25 September 2008 (2008-09-25) the whole document -----	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2014/050126

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