

[Name of Document] Description
[Title of Invention] RELEASE SHEET AND METHOD FOR
PRODUCING RELEASE SHEET
[Technical Field]

5 [0001]

 The present invention relates to a release sheet and a
method for producing the release sheet and preferably to a
release sheet on which the pressure sensitive adhesive
layer of a pressure sensitive adhesive sheet is laminated,
10 a release sheet that can be used for production of ceramic
green sheets, and other similar release sheets and a method
for producing these release sheets.

[Background Art]

 [0002]

15 Release sheets have heretofore been used in the
production of pressure sensitive adhesive sheets. A
release sheet is provided with a release agent layer on the
surface of a base material. The release sheet is used, for
example, as follows. The surface of the release agent
20 layer opposite to the base material (this surface may be
referred to as a "release surface" in the present
description) of the release sheet is coated with a coating
liquid of a pressure sensitive adhesive composition for
forming a pressure sensitive adhesive layer of a pressure
25 sensitive adhesive sheet, and the coating liquid is dried
to form the pressure sensitive adhesive layer. Then, a
base material for the pressure sensitive adhesive sheet is
laminated on the surface of the pressure sensitive adhesive
layer opposite to the release sheet, and the pressure
30 sensitive adhesive sheet including the pressure sensitive
adhesive layer and the base material can thereby be
obtained. In this situation, the release sheet is in a
state of being laminated on the pressure sensitive adhesive

sheet, but if they are stored in this state, the release sheet can be used for protection of the surface of the pressure sensitive adhesive layer (this surface may be referred to as a "pressure sensitive adhesive surface" in the present description) of the pressure sensitive adhesive sheet to come into contact with an adherend.

[0003]

In another scene, to produce laminated ceramic products such as laminated ceramic capacitors and multilayer ceramic substrates, it has been performed to form ceramic green sheets, laminate the obtained ceramic green sheets, and fire them. Such a ceramic green sheet can be formed by coating the release surface of a release sheet as described above with a ceramic slurry that contains ceramic materials such as barium titanate and titanium oxide.

[0004]

Such a release sheet can be produced, for example, through coating one surface of a base material with a coating liquid of a release agent composition and curing the obtained coating film. For example, Patent Document 1 discloses a laminated film obtained by forming a conductive release layer as the release agent layer on one surface of a core layer as the base material (claim 1 of Patent Document 1, etc). In particular, Patent Document 1 discloses an example in which one surface of the core layer was coated with a coating liquid for forming the conductive release layer and the obtained coating film was then heated and thus cured to form the conductive release layer (paragraph 0095 of Patent Document 1, etc). Patent Documents 2 to 6 each disclose a release film obtained by forming a polymer layer as the release agent layer on one surface of a base material film (claim 1 of Patent Document

2, for example). In particular, Patent Documents 2 to 6 each disclose an example in which one surface of the base material film was coated with a coating liquid for forming the polymer layer and the obtained coating film was then
5 irradiated with ultraviolet rays and thus cured to form the polymer layer (paragraph 0117 of Patent Document 2, for example).

[Prior Art Documents]

[Patent Documents]

10 [0005]
[Patent Document 1] JP5157350B
[Patent Document 2] JP5381860B
[Patent Document 3] JP5423975B
[Patent Document 4] JP5423976B
15 [Patent Document 5] JP5482368B
[Patent Document 6] JP5531712B

[Summary of the Invention]

[Problems to be solved by the Invention]

[0006]

20 In order for the release sheet to exhibit excellent releasability, it is required that the release agent layer be well cured. In the conventional release sheets as disclosed in Patent Documents 1 to 6, however, the curing of the release agent layer tends to be insufficient. This
25 may result in a problem that the release sheets cannot exhibit excellent releasability.

[0007]

The present invention has been made in consideration of such actual circumstances and an object of the present
30 invention is to provide a release sheet that exhibit excellent releasability.

[Means for solving the Problems]

[0008]

To achieve the above object, first, the present invention provides a release sheet comprising a base material and a release agent layer provided on at least one surface side of the base material, the release agent layer
5 being formed from a release agent composition, the release agent composition containing a hydroxyl group-containing acrylic-based compound, polyorganosiloxane, and an isocyanate group-containing compound (Invention 1).

[0009]

10 In the release sheet according to the above invention (Invention 1), when the release agent layer is formed from the release agent composition, a urethane bond is generated between the hydroxyl group of the hydroxyl group-containing acrylic-based compound and the isocyanate group of the
15 isocyanate group-containing compound, and addition polymerization of acryloyl groups occurs between molecules of the hydroxyl group-containing acrylic-based compound; therefore, the obtained release agent layer is well cured. Thus, the release agent layer is well cured and the release
20 agent layer contains polyorganosiloxane, so that the above release sheet can exhibit excellent releasability.

[0010]

In the above invention (Invention 1), the polyorganosiloxane may preferably have a reactive group
25 capable of reacting with an isocyanate group (Invention 2).

[0011]

In the above invention (Invention 2), the reactive group may preferably be a hydroxyl group (Invention 3).

[0012]

30 In the above invention (Invention 1 to 3), the hydroxyl group-containing acrylic-based compound may preferably be at least one of pentaerythritol triacrylate and dipentaerythritol pentaacrylate (Invention 4).

[0013]

In the above invention (Invention 1 to 4), the isocyanate group-containing compound may preferably be an isocyanurate product of polyisocyanate (Invention 5).

5 [0014]

In the above invention (Invention 5), the polyisocyanate may preferably be hexamethylene diisocyanate (Invention 6).

[0015]

10 In the above invention (Invention 1 to 6), the release agent composition may preferably contain a photopolymerization initiator (Invention 7).

[0016]

15 In the above invention (Invention 1 to 7), the release agent composition may preferably contain a thermosetting catalyst (Invention 8).

[0017]

20 Second, the present invention provides a method for producing the above release sheet (Invention 1 to 8), comprising a step of forming a coating film composed of the release agent composition on one surface side of the base material and a step of curing the coating film through heating and irradiation with active energy rays to form the release agent layer (Invention 9).

25 [Advantageous Effect of the Invention]

[0018]

The release sheet according to the present invention can exhibit excellent releasability.

[Embodiments for Carrying out the Invention]

30 [0019]

Hereinafter, one or more embodiments of the present invention will be described.

The release sheet according to an embodiment of the

present invention is configured to include a base material and a release agent layer provided on one surface side of the base material.

[0020]

5 In the release sheet according to the present embodiment, the release agent layer is formed from a release agent composition. The release agent composition contains a hydroxyl group-containing acrylic-based compound, polyorganosiloxane, and an isocyanate group-containing
10 compound.

[0021]

 In the above release agent composition, the hydroxyl group of the hydroxyl group-containing acrylic-based compound and the isocyanate group of the isocyanate group-
15 containing compound can form a urethane bond. In the above release agent composition, molecules of the hydroxyl group-containing acrylic-based compound can undergo addition polymerization between acryloyl groups. In the release agent layer formed from the release agent composition,
20 therefore, the generation of the above urethane bond and the above addition polymerization result in the formation of a three-dimensional network structure composed of at least two systems of the hydroxyl group-containing acrylic-based compound and the isocyanate group-containing compound.
25 When the release agent layer is formed from the release agent composition, the coating film composed of the release agent composition can be heated and irradiated with active energy rays thereby to effectively form the above described three-dimensional network structure because the above
30 generation of the urethane bond is promoted by heating and the above addition polymerization is promoted by irradiation with active energy rays. As a result of the above, the release agent layer in the release sheet

according to the present embodiment is well cured.

[0022]

Moreover, the release agent composition contains the polyorganosiloxane which is excellent in releasability, and
5 the release agent layer formed from the release agent composition can thereby also have certain releasability.

[0023]

Thus, the release agent layer is well cured and the release agent layer contains polyorganosiloxane, so that
10 the release sheet according to the present embodiment can exhibit excellent releasability.

[0024]

1. Base Material

The base material of the release sheet according to
15 the present embodiment is not particularly limited, and any base material can be selected and used from those known in the art. Examples of such a base material include films of plastics, such as polyethylene terephthalate, polyethylene naphthalate and other polyesters, polypropylene,
20 polymethylpentene and other polyolefins, polycarbonate, and polyvinyl acetate. These plastic films may be in a single layer or may also be in a multilayer of two or more layers of the same type or different types. Among these, a polyester film may be preferred, and a polyethylene
25 terephthalate film may be particularly preferred. The polyethylene terephthalate film is less likely to generate dust and the like during the work, during the use, and during other operations and can therefore effectively prevent troubles, such as coating failure, for example, due
30 to dust and the like.

[0025]

For the purpose of improving the interfacial adhesion property of the base material with the release agent layer

provided on the surface of the base material, one surface or both surfaces of the base material can be subjected to surface treatment, such as using an oxidation method or a roughening method, or primer treatment, as necessary.

5 Examples of the above oxidation method include corona discharge treatment, plasma discharge treatment, chromium oxidation treatment (wet type), flame treatment, hot-air treatment, ozone exposure treatment, and ultraviolet ray irradiation treatment. Examples of the roughening method
10 include a sandblast method and a thermal spraying method. These surface treatment methods may be appropriately selected depending on the type of the base material, and the corona discharge treatment method may preferably be used in view of the effect and the operability in general.

15 [0026]

The thickness of the base material may be preferably 10 μm or more, particularly preferably 15 μm or more, and further preferably 20 μm or more. From another aspect, the thickness may be preferably 300 μm or less, particularly
20 preferably 200 μm or less, and further preferably 125 μm or less.

[0027]

2. Release Agent Layer

In the release sheet according to the present
25 embodiment, the release agent layer is formed from a release agent composition. The release agent composition contains a hydroxyl group-containing acrylic-based compound, polyorganosiloxane, and an isocyanate group-containing compound. The release agent composition may preferably
30 contain at least one of a photopolymerization initiator and a thermosetting catalyst.

[0028]

(1) Hydroxyl Group-containing Acrylic-based Compound

The hydroxyl group-containing acrylic-based compound is not particularly limited, provided that it has a hydroxyl group and a (meth)acryloyl group and the release agent layer can be formed using the release agent composition. As used in the present description, the (meth)acryloyl group refers to both the acryloyl group and the methacryloyl group. The same applies to other similar terms.

[0029]

The hydroxyl group-containing acrylic-based compound has at least one hydroxyl group in the molecule. The hydroxyl group-containing acrylic-based compound also has at least one (meth)acryloyl group in the molecule. When the hydroxyl group-containing acrylic-based compound has these groups in the molecule, the previously described three-dimensional network structure can be formed. From the viewpoint of effectively progressing the addition polymerization between molecules of the hydroxyl group-containing acrylic-based compound, the hydroxyl group-containing acrylic-based compound may preferably have two or more (meth)acryloyl groups. The upper limit of the number of (meth)acryloyl groups possessed by one molecule of the hydroxyl group-containing acrylic-based compound may be preferably 10 or less in general and particularly preferably 6 or less.

[0030]

Examples of the hydroxyl group-containing acrylic-based compound which can be used in the release sheet according to the present embodiment include those in which the hydrogen atom in at least one hydroxyl group possessed by polyhydric alcohol is substituted with a (meth)acryloyl group. Examples of such polyhydric alcohol include pentaerythritol, dipentaerythritol, trimethylolpropane,

glycerin, diglycerol, sugar alcohols, butanediol, polyethylene glycol, polypropylene glycol, polyhydric alcohol having a biphenyl skeleton, polyhydric alcohol having a dicyclohexadiene skeleton, and polyhydric alcohol
5 having a naphthalene skeleton. The hydroxyl group-containing acrylic-based compound in which the hydrogen atom in at least one hydroxyl group possessed by polyhydric alcohol is substituted with a (meth)acryloyl group can be obtained, for example, by an esterification reaction
10 between a polyhydric alcohol and a (meth)acrylic acid.

[0031]

Specific examples of the hydroxyl group-containing acrylic-based compound include pentaerythritol tri(meth)acrylate, dipentaerythritol tri(meth)acrylate,
15 dipentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, trimethylolpropane di(meth)acrylate, pentaerythritol mono(meth)acrylate, and pentaerythritol di(meth)acrylate. One type of these hydroxyl group-containing acrylic-based compounds may be used alone or two
20 or more types may also be used in combination. Among these, at least one of pentaerythritol triacrylate and dipentaerythritol pentaacrylate may be preferably used from the viewpoint that the previously described three-dimensional network structure can be well formed, and
25 pentaerythritol triacrylate may be further preferably used from an additional viewpoint that the coatability of a coating liquid of the release agent composition to the base material is excellent and the occurrence of troubles such as streaks and defects on the release surface of the formed
30 release agent layer can be effectively suppressed.

[0032]

In the release sheet according to the present embodiment, the molecular weight of the hydroxyl group-

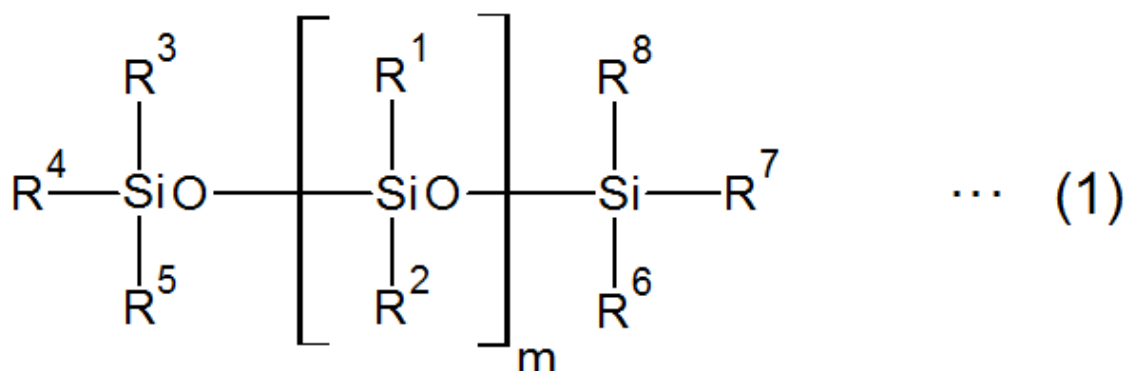
containing acrylic-based compound may be preferably 10,000 or less, particularly preferably 5,000 or less, and further preferably 1,000 or less. When the molecular weight of the hydroxyl group-containing acrylic-based compound is 10,000 or less, the coatability of a coating liquid of the release agent composition to the base material is excellent and it is possible to effectively suppress the occurrence of troubles such as streaks and defects on the release surface of the formed release agent layer. The lower limit of the molecular weight of the hydroxyl group-containing acrylic-based compound is not particularly limited, but it may be preferably 200 or more in general and particularly preferably 250 or more.

[0033]

15 (2) Polyorganosiloxane

The polyorganosiloxane is not particularly limited, provided that the release agent layer can be formed using the release agent composition. For example, a polymer of a silicon-containing compound represented by the following General Formula (1) can be used.

[Chemical Formula 1]



[0034]

In Formula (1), m is an integer of 1 or more. Preferably, R¹ to R⁸ are each independently a hydrogen atom, an alkyl group, or an organic group. R¹ to R⁸ may be or may not be the same. When a plurality of R¹ and a

plurality of R^2 exist, R^1 may be or may not be the same and R^2 may be or may not be the same.

[0035]

Examples of the above alkyl group include alkyl groups
5 having a carbon number of 1 to 12, and specific examples include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, and an octyl group. In particular, the methyl group may be preferred.

[0036]

10 The above organic group may preferably be at least one selected from a polyester group and a polyether group. Both the polyester group and the polyether group may exist in one molecule of the polyorganosiloxane.

[0037]

15 The polyorganosiloxane in the release sheet according to the present embodiment may preferably have a reactive group capable of reacting with an isocyanate group. That is, in the above Formula (1), at least one of R^1 to R^8 may preferably be a reactive group capable of reacting with an
20 isocyanate group, or an alkyl group or organic group having the reactive group. When the polyorganosiloxane has the above reactive group, a urethane bond may be generated between the reactive group and the isocyanate group of the isocyanate group-containing compound and, as a result, the
25 polyorganosiloxane can be fixed to the three-dimensional network structure composed of the hydroxyl group-containing acrylic-based compound and the isocyanate group-containing compound. This allows the release agent layer to be better cured and it is possible to suppress the migration of the
30 polyorganosiloxane from the release agent layer to an object to be laminated on the release surface of the release sheet according to the present embodiment.

[0038]

Examples of the above reactive group include a hydroxyl group, an amino group, a thiol group, and a carboxy group. From the viewpoint of excellent reactivity with the isocyanate group of the isocyanate group-
5 containing compound, the reactive group may preferably be a hydroxyl group.

[0039]

The position of the above reactive group in the polyorganosiloxane is not particularly limited, but from
10 the viewpoint that the generation of urethane bonds can effectively progress between the polyorganosiloxane and the isocyanate group-containing compound and the polyorganosiloxane can be effectively fixed to the previously described three-dimensional network structure,
15 the reactive group may preferably exist at an end of the polyorganosiloxane. That is, in the above Formula (1), at least one of R^3 to R^8 may preferably be the above reactive group or an alkyl group or organic group having the above reactive group.

20 [0040]

In the release sheet according to the present embodiment, in particular, the polyorganosiloxane may preferably be polyether-modified hydroxyl group-containing polydimethylsiloxane, and at least one of R^1 to R^8 in the
25 above Formula (1) may particularly preferably be a polyether group having a hydroxyl group. By using such polyorganosiloxane, the generation of urethane bonds between the polyorganosiloxane and the isocyanate group-containing compound can effectively progress. This allows
30 the release sheet to have more excellent releasability and it is possible to effectively suppress the migration of the polyorganosiloxane from the release agent layer to an object to be laminated on the release surface.

[0041]

The weight-average molecular weight of the polyorganosiloxane may be preferably 1,000 or more, particularly preferably 2,000 or more, and further
5 preferably 3,000 or more. From another aspect, the weight-average molecular weight may be preferably 50,000 or less, particularly preferably 40,000 or less, and further preferably 30,000 or less. When the weight-average molecular weight is 1,000 or more, the desired
10 releasability can be readily and effectively achieved. When the weight-average molecular weight is 50,000 or less, the coatability of a coating liquid of the release agent composition to the base material is excellent and it is possible to effectively suppress the occurrence of troubles
15 such as streaks and defects on the release surface of the formed release agent layer.

[0042]

In the release sheet according to the present embodiment, the compounding amount of the
20 polyorganosiloxane in the release agent composition may be preferably 0.1 mass parts or more, particularly preferably 0.2 mass parts or more, and further preferably 0.5 mass parts or more, with respect to 100 mass parts of the hydroxyl group-containing acrylic-based compound. From
25 another aspect, the compounding amount of the polyorganosiloxane in the release agent composition may be preferably 10 mass parts or less, particularly preferably 5 mass parts or less, and further preferably 2 mass parts or less, with respect to 100 mass parts of the hydroxyl group-
30 containing acrylic-based compound. When the compounding amount of the polyorganosiloxane falls within the above range, the release agent layer can be readily and well cured and the desired releasability can be readily achieved.

As a result, excellent releasability of the release sheet can be readily achieved.

[0043]

(3) Isocyanate Group-containing Compound

5 The isocyanate group-containing compound is not particularly limited, provided that it contains an isocyanate group and the release agent layer can be formed using the release agent composition. For example, the isocyanate group-containing compound may preferably be a
10 polyisocyanate compound having a plurality of isocyanate groups.

[0044]

Examples of the polyisocyanate compound include aliphatic polyisocyanates such as trimethylene diisocyanate,
15 tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, heptamethylene diisocyanate and octamethylene diisocyanate, alicyclic polyisocyanates such as isophorone diisocyanate and hydrogenated diphenylmethane diisocyanate, aromatic polyisocyanates such as tolylene
20 diisocyanate, diphenylmethane diisocyanate and xylylene diisocyanate, biuret products and isocyanurate products thereof, and adduct products that are reaction products with low-molecular active hydrogen-containing compounds such as ethylene glycol, propylene glycol, neopentyl glycol,
25 trimethylol propane and castor oil. Among the above, the isocyanate group-containing compound may be preferably an isocyanurate product of polyisocyanate, particularly preferably an isocyanurate product of diisocyanate, and further preferably an isocyanurate product of hexamethylene
30 diisocyanate from the viewpoint of excellent reactivity with the hydroxyl group of the hydroxyl group-containing acrylic-based compound.

[0045]

In the release sheet according to the present embodiment, the compounding amount of the isocyanate group-containing compound in the release agent composition may be preferably 5 mass parts or more, particularly preferably 10
5 mass parts or more, and further preferably 15 mass parts or more, with respect to 100 mass parts of the hydroxyl group-containing acrylic-based compound. From another aspect, the compounding amount of the isocyanate group-containing compound in the release agent composition may be preferably
10 100 mass parts or less, particularly preferably 50 mass parts or less, and further preferably 20 mass parts or less, with respect to 100 mass parts of the hydroxyl group-containing acrylic-based compound. When the compounding amount of the isocyanate group-containing compound falls
15 within the above range, the release agent layer can be readily and well cured and the desired releasability can be readily achieved. As a result, excellent releasability of the release sheet can be readily achieved.

[0046]

20 (4) Photopolymerization Initiator

In the release sheet according to the present embodiment, the release agent composition may preferably contain a photopolymerization initiator. When forming the release agent layer, the release agent composition
25 containing the photopolymerization initiator allows the addition polymerization to efficiently progress between molecules of the hydroxyl group-containing acrylic-based compound, and the well cured release agent layer can be readily formed. As a result, the release sheet according
30 to the present embodiment can exhibit more excellent releasability.

[0047]

Examples of the photopolymerization initiator are not

particularly limited, provided that the release agent layer can be formed using the release agent composition. Such examples include benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin-n-butyl ether, 5 benzoin isobutyl ether, acetophenone, dimethylaminoacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2-diethoxy-2-phenylacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-10 morpholino-propan-1-one, 4-(2-hydroxyethoxy)phenyl-2-(hydroxy-2-propyl)ketone, benzophenone, p-phenylbenzophenone, 4,4'-diethylaminobenzophenone, dichlorobenzophenone, 2-methylanthraquinone, 2-ethylanthraquinone, 2-tert-butylanthraquinone, 2-15 aminoanthraquinone, 2-methylthioxanthone, 2-ethylthioxanthone, 2-chlorothioxanthone, 2,4-dimethylthioxanthone, 2,4-diethylthioxanthone, benzyl dimethyl ketal, acetophenone dimethyl ketal, p-dimethylaminobenzoic ester, oligo[2-hydroxy-2-methyl-1[4-20 (1-methylvinyl)phenyl]propanone], 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide, and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide. These may each be used alone or two or more types may also be used in combination. Among these, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one 25 may preferably be used from the viewpoint that the addition polymerization can efficiently progress between molecules of the hydroxyl group-containing acrylic-based compound.

[0048]

In the release sheet according to the present 30 embodiment, the compounding amount of the photopolymerization initiator in the release agent composition may be preferably 1 mass part or more, particularly preferably 2.5 mass parts or more, and further

preferably 5 mass parts or more, with respect to 100 mass parts of the hydroxyl group-containing acrylic-based compound. From another aspect, the compounding amount of the photopolymerization initiator in the release agent composition may be preferably 30 mass parts or less, particularly preferably 20 mass parts or less, and further preferably 15 mass parts or less, with respect to 100 mass parts of the hydroxyl group-containing acrylic-based compound. When the compounding amount of the photopolymerization initiator falls within the above range, the previously described addition polymerization progresses more efficiently, and the release agent layer can be readily and well cured. As a result, excellent releasability of the release sheet can be readily achieved.

[0049]

(5) Thermosetting Catalyst

In the release sheet according to the present embodiment, the release agent composition may preferably contain a thermosetting catalyst. When forming the release agent layer, the release agent composition containing the thermosetting catalyst allows the generation of urethane bonds to efficiently progress between the hydroxyl group-containing acrylic-based compound and the isocyanate group-containing compound, and the well cured release agent layer can thereby be readily formed. As a result, the release sheet according to the present embodiment can exhibit more excellent releasability.

[0050]

Examples of the thermosetting catalyst are not particularly limited, provided that the release agent layer can be formed using the release agent composition. Such examples for use include a titanium-based catalyst, an aluminum-based catalyst, a zirconium-based catalyst, a

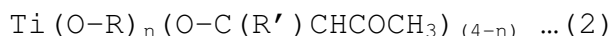
boron trifluoride-based catalyst, a tin-based catalyst, and an iron-based catalyst. These may each be used alone or two or more types may also be used in combination.

[0051]

5 Preferred examples of the above titanium-based catalyst include alkoxide of titanium, titanium chelate, and titanium (IV) chloride. Preferred examples of the above aluminum-based catalyst include alkoxide of aluminum, aluminum chelate, and aluminum (III) chloride. Preferred
10 examples of the above zirconium-based catalyst include alkoxide of zirconium, zirconium chelate, and zirconium (IV) chloride. Preferred examples of the above boron trifluoride-based catalyst include amine complex and alcohol complex of boron trifluoride.

15 [0052]

It may be particularly preferred to use titanium chelate as the above titanium-based catalyst. In particular, it may be preferred to use an organic titanium oxide compound having the structure of the following
20 Formula (2).



In the above Formula (2), R represents an alkyl group having a carbon number of 1 to 10, R' represents a methyl group or an ethoxy group, and n represents an integer of 1
25 to 4.

[0053]

Specific examples of the above organic titanium oxide compound include tetramethoxytitanium, tetraethoxytitanium, tetra-n-propoxytitanium, tetraisopropoxytitanium, tetra-n-
30 butoxytitanium, tetraisobutoxytitanium, tetra-t-butoxytitanium, tetrakis(2-ethylhexyloxy)titanium, titanium isopropoxy octylene glycolate, titanium tetrakis(acetylacetonate), titanium

tetrakis(ethylacetoacetate), diisopropoxytitanium
 bis(acetonate), diisopropoxytitanium bis(acetylacetonate),
 diisopropoxytitanium bis(ethylacetoacetate), di-n-
 butoxytitanium bis(acetonate), di-n-butoxytitanium
 5 bis(acetylacetonate), and di-n-butoxytitanium
 bis(ethylacetoacetate).

[0054]

Among the above, the organic titanium oxide compound
 as an organic titanium complex may be preferred. As such
 10 an organic titanium complex, from the viewpoint of
 resistance to moisture in the air (hydrolysis resistance),
 a titanium complex having the ligand of a β -dicarbonyl
 compound may be preferred. Examples of the β -dicarbonyl
 compound include β -diketones such as acetylacetone and
 15 benzoylacetone, and β -ketoesters such as ethylacetoacetate,
 among which acetylacetone and ethylacetoacetate may be
 preferred. Thus, as the organic titanium oxide compound,
 specifically, diisopropoxy bis(acetylacetonate)titanium and
 diisopropoxy bis(ethylacetoacetate)titanium may be
 20 particularly preferred. One type of the organic titanium
 oxide compound can be used alone or two or more types can
 also be used in combination.

[0055]

The molecular weight of the organic titanium oxide
 25 compound may be preferably 250 or more, particularly
 preferably 300 or more, and further preferably 400 or more.
 From another aspect, the molecular weight may be preferably
 750 or less, particularly preferably 600 or less, and
 further preferably 500 or less.

30 [0056]

In the release sheet according to the present
 embodiment, the compounding amount of the thermosetting
 catalyst in the release agent composition may be preferably

0.1 mass parts or more, particularly preferably 0.2 mass parts or more, and further preferably 0.5 mass parts or more, with respect to 100 mass parts of the hydroxyl group-containing acrylic-based compound. From another aspect, 5 the compounding amount of the thermosetting catalyst in the release agent composition may be preferably 15 mass parts or less, particularly preferably 10 mass parts or less, and further preferably 5 mass parts or less, with respect to 100 mass parts of the hydroxyl group-containing acrylic-based compound. 10 When the compounding amount of the thermosetting catalyst falls within the above range, the generation of the previously described urethane bonds progresses more efficiently, and the release agent layer can be readily and well cured. As a result, excellent 15 releasability of the release sheet can be readily achieved.

[0057]

(6) Other Components

The release agent composition may contain an antistatic agent, a reaction inhibitor, an adhesion 20 improver, etc. in addition to the previously described components.

[0058]

(7) Production of Release Agent Composition

The release agent composition can be produced by 25 mixing the previously described hydroxyl group-containing acrylic-based compound, polyorganosiloxane, and isocyanate group-containing compound and, optionally, other components. The obtained release agent composition may be diluted with a dilution solvent as necessary to obtain a coating liquid.

30 [0059]

Examples of the above dilution solvent for use include aliphatic hydrocarbons such as hexane, heptane and cyclohexane, aromatic hydrocarbons such as toluene and

xylene, halogenated hydrocarbons such as methylene chloride and ethylene chloride, alcohols such as methanol, ethanol, isopropyl alcohol, butanol and 1-methoxy-2-propanol, ketones such as acetone, methyl ethyl ketone, 2-pentanone, 5 isophorone and cyclohexanone, esters such as ethyl acetate and butyl acetate, cellosolve-based solvents such as ethyl cellosolve, and a mixture thereof.

[0060]

The concentration and viscosity of the coating liquid 10 thus prepared are not particularly limited, provided that they allow for coating, and can be appropriately selected depending on the situation. For example, the release agent composition may be diluted so as to have a concentration of 10 mass% or more and 60 mass% or less. When obtaining the 15 coating liquid, addition of a dilution solvent or the like is not a necessary condition, and if the release agent composition has viscosity and other properties that allow for coating, it is not necessary to add a dilution solvent.

[0061]

20 (8) Thickness of Release Agent Layer

In the release sheet according to the present embodiment, the thickness of the release agent layer may be preferably 10 nm or more and particularly preferably 50 nm or more. From another aspect, the thickness may be 25 preferably 10 μm or less and particularly preferably 5 μm or less. When the thickness of the release agent layer is 10 nm or more, the desired releasability can readily be achieved. When the thickness of the release agent layer is 10 μm or less, a well-cured release agent layer can readily 30 be formed.

[0062]

3. Physical Properties of Release Sheet, etc.

In the release sheet according to the present

embodiment, the release force, which is required when releasing a pressure sensitive adhesive sheet and the release sheet from each other after the pressure sensitive adhesive surface of the pressure sensitive adhesive sheet is attached to the release surface, can be appropriately set, but may be preferably 4,000 mN/20 mm or less, particularly preferably 3,000 mN/20 mm or less, and further preferably 2,500 mN/20 mm or less. The release sheet according to the present embodiment can well exhibit the releasability as described above because the release agent layer is formed using the previously described release agent composition. The lower limit of the release force is not particularly limited, but may be preferably 100 mN/20 mm or more in general, particularly preferably 150 mN/20 mm or more, and further preferably 200 mN/20 mm or more. The method of measuring the release force when releasing the release sheet from a pressure sensitive adhesive sheet is as specified in the testing example, which will be described later.

[0063]

In the release sheet according to the present embodiment, the release force, which is required when releasing the release sheet from a ceramic green sheet formed on the release surface, can be appropriately set, but may be preferably 100 mN/20 mm or less, particularly preferably 75 mN/20 mm or less, and further preferably 50 mN/20 mm or less. Such release force allows the release sheet according to the present embodiment to well exhibit the releasability as described above because the release agent layer is formed using the previously described release agent composition. The lower limit of the release force is not particularly limited, but may be preferably 5 mN/20 mm or more in general and particularly preferably 10

mN/20 mm or more. The method of measuring the release force when releasing the release sheet from a ceramic green sheet is as specified in the testing example, which will be described later.

5 [0064]

4. Production Method for Release Sheet

The method for producing the release sheet according to the present embodiment is not particularly limited. The release sheet according to the present embodiment may preferably be produced by a method comprising a step of forming a coating film composed of the release agent composition on one surface side of the base material (this step may be referred to as a "coating film formation step," hereinafter) and a step of curing the coating film through heating and irradiation with active energy rays to form the release agent layer (this step may be referred to as a "curing step," hereinafter).

[0065]

In the above coating film formation step, the method of forming the coating film composed of the release agent composition is not particularly limited. For example, the coating film can be formed by coating one surface of the base material with a coating liquid of the previously described release agent composition. In this case, examples of the method of coating for use include a gravure-coating method, a bar-coating method, a spray-coating method, a spin-coating method, a knife-coating method, a roll-coating method, and a die-coating method.

[0066]

30 In the above curing step, any of the heating and the irradiation with active energy rays may be performed first, and these may also be concurrently performed.

[0067]

The temperature of the above heating may be preferably 100°C or higher and particularly preferably 120°C or higher. From another aspect, the temperature may be preferably 180°C or lower and particularly preferably 150°C or lower.

5 The heating time may be preferably 10 seconds or more and particularly preferably 15 seconds or more. From another aspect, the heating time may be preferably 60 seconds or less and particularly preferably 30 seconds or less. The heating in the curing step can be combined with a heating
10 and drying process for volatilizing the solvent and the like in the coating liquid from the coating film.

[0068]

As the active energy rays used in the irradiation with active energy rays, for example, ultraviolet rays, electron
15 rays, or the like can be used, among which ultraviolet rays may be particularly preferred because of easy management.

[0069]

Irradiation with ultraviolet rays can be performed using a high-pressure mercury lamp, xenon lamp, or the like.
20 The irradiance level of ultraviolet rays may be preferably 50 mW/cm² or more and particularly preferably 200 mW/cm² or more as the illuminance. From another aspect, the illuminance may be preferably 5,000 mW/cm² or less and particularly preferably 3,000 mW/cm² or less. The light
25 amount of ultraviolet rays may be preferably 10 mJ/cm² or more and particularly preferably 30 mJ/cm² or more. From another aspect, the light amount may be preferably 250 mJ/cm² or less and particularly preferably 150 mJ/cm² or less. When the irradiation with ultraviolet rays is
30 carried out under the condition according to the above range, the release agent composition can be better cured, and a satisfactory release agent layer can be effectively formed.

[0070]

Irradiation with electron rays can be performed using an electron ray accelerator or the like. The irradiance level of electron rays may be preferably 0.1 kGy or more
5 and particularly preferably 1 kGy or more. From another aspect, the irradiance level may be preferably 50 kGy or less and particularly preferably 30 kGy or less.

[0071]

According to the above described production method,
10 the heating in the heating step allows the generation of urethane bonds to efficiently progress between the hydroxyl group-containing acrylic-based compound and the isocyanate group-containing compound while the irradiation with energy rays allows the addition polymerization to efficiently
15 progress between molecules of the hydroxyl group-containing acrylic-based compound, and the well cured release agent layer can thereby be formed. As a result, the obtained release sheet can exhibit more excellent releasability.

[0072]

20 5. Method of using Release Sheet

The release sheet according to the present embodiment can be used in the same application as that of a commonly-used release sheet.

[0073]

25 For example, the release sheet according to the present embodiment can be used in the production of a pressure sensitive adhesive sheet. In this case, the release surface of the release sheet according to the present embodiment may be coated with a coating liquid of a
30 pressure sensitive adhesive composition for forming a pressure sensitive adhesive layer of the pressure sensitive adhesive sheet, and the coating liquid may be dried to form the pressure sensitive adhesive layer. Then, a base

material for the pressure sensitive adhesive sheet may be laminated on the surface of the pressure sensitive adhesive layer opposite to the release sheet, and the pressure sensitive adhesive sheet to which the release sheet is
5 attached can thus be produced. In an alternative embodiment, the release surface of another release sheet, preferably of a release sheet according to the present embodiment, may be applied to the surface of the pressure sensitive adhesive layer, formed as described above,
10 opposite to the former release sheet, and a double-sided pressure sensitive adhesive sheet can also be produced, comprising two release sheets and the pressure sensitive adhesive layer interposed between the two release sheets. Moreover, the pressure sensitive adhesive sheet thus
15 produced may be stored in a state of being attached with the release sheet or sheets, and the pressure sensitive adhesive surface or surfaces of the pressure sensitive adhesive sheet can thereby be protected by the release sheet or sheets.

20 [0074]

Furthermore, the release sheet according to the present embodiment can also be used to produce a ceramic green sheet. For example, the release surface of the release sheet may be coated with a ceramic slurry that
25 contains a ceramic material such as barium titanate or titanium oxide, and the ceramic slurry can then be dried to produce a ceramic green sheet to which the release sheet is attached.

[0075]

30 In the release sheet according to the present embodiment, when the release agent layer is formed from the release agent composition, urethane bonds are generated between the hydroxyl group-containing acrylic-based

compound and the isocyanate group-containing compound while addition polymerization occurs between molecules of the hydroxyl group-containing acrylic-based compound and, as a result, the release agent layer is well cured. Thus, the release agent layer is well cured and the release agent layer contains polyorganosiloxane, so that the release sheet according to the present embodiment can exhibit excellent releasability from a pressure sensitive adhesive sheet or a ceramic green sheet laminated on the release surface.

[0076]

It should be appreciated that the embodiments heretofore explained are described to facilitate understanding of the present invention and are not described to limit the present invention. It is therefore intended that the elements disclosed in the above embodiments include all design changes and equivalents to fall within the technical scope of the present invention.

[0077]

For example, in the release sheet, one or more other layers such as an antistatic layer may be provided on the surface of the base material opposite to the release agent layer and/or between the base material and the release agent layer.

[Examples]

[0078]

Hereinafter, the present invention will be described further specifically with reference to examples, etc., but the scope of the present invention is not limited to these examples, etc.

[0079]

<Example 1>

A coating liquid was obtained by mixing 100 mass parts

(equivalent amount to the solid content, here and hereinafter) of pentaerythritol triacrylate (available from Shin Nakamura Chemical Co., Ltd., product name "A-TMM-3L") as the hydroxyl group-containing acrylic-based compound, 5 0.75 mass parts of polyether-modified hydroxyl group-containing polydimethylsiloxane (available from BYK-Chemie Japan, product name "BYK-377") as the polyorganosiloxane, 20 mass parts of an isocyanurate product of hexamethylene diisocyanate (available from Asahi Kasei Corporation, 10 product name "MFA-75B") as the isocyanate group-containing compound, 10.0 mass parts of 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one (available from Ciba, product name "Irgacure 907") as the photopolymerization initiator, and 1.0 mass parts of 15 diisopropoxy bis(ethylacetoacetate)titanium (available from Matsumoto Fine Chemical Co., Ltd., product name "TC-750") as the thermosetting catalyst in a mixed solvent of methyl ethyl ketone and isopropyl alcohol. The solid content of the coating liquid was 18 mass%.

20 [0080]

One surface of a biaxially-stretched polyethylene terephthalate film (available from Toray Industries, Inc., product name "Lumirror S10," thickness: 23 μm , maximum peak height R_p on both surfaces: 452 nm) as the base material 25 was coated with the obtained coating liquid of the release agent composition using a Meyer bar #5 to form a coating film. The coating film was heated at 120°C for 15 seconds and then irradiated with ultraviolet rays (illuminance: 1,000 mW/cm^2 , light amount: 50 mJ/cm^2) from the opposite 30 surface side of the coating film to the base material to form a release agent layer having a thickness of 1.0 μm . A release sheet was thus obtained in which the base material and the release agent layer were laminated on each other.

[0081]

The thicknesses of the base material and the obtained release agent layer were measured using a reflective film thickness meter (available from Filmetrics, Inc., product
5 name "F20").

[0082]

<Examples 2 to 11 and Comparative Examples 1 and 2>

Release sheets were produced in the same manner as in Example 1 except that the compounding amount of the
10 polyorganosiloxane, the type of the isocyanate group-containing compound, and the compounding amount of the isocyanate group-containing compound in the release agent composition were modified as listed in Table 1.

[0083]

15 <Comparative Example 3>

A release sheet was produced in the same manner as in Example 1 except using a release agent composition prepared using 100 weight parts of pentaerythritol tetraacrylate (available from Shin Nakamura Chemical Co., Ltd., product
20 name "A-TMMT") as substitute for the hydroxyl group-containing acrylic-based compound. The pentaerythritol tetraacrylate is an acrylic-based compound free from hydroxyl groups.

[0084]

25 <Testing Example 1> (Evaluation of Curability of Release Agent Layer)

The release surface of the release sheet obtained in each of Examples and Comparative Examples was rubbed ten times with a finger, and the presence or absence of tarnish
30 (smear) and drop-off (rub-off) of the release agent layer was visually confirmed. Furthermore, the release surface was wiped back and forth for 20 cycles with a load of about 2 kg/cm² using a nonwoven cloth wiper (available from Asahi

Kasei Corporation, Bemcot AP-2) containing an appropriate amount of methyl ethyl ketone, and the presence or absence of drop-off of the release agent layer from the base material was visually confirmed under a fluorescent light
5 (solvent resistance test). Then, the curability of the release agent layer was evaluated in accordance with the following determination criteria. Results are listed in Table 1.

o; None of smear, rub-off, and drop-off of the release
10 agent layer in the solvent resistance test was confirmed.

x; At least one of smear, rub-off, and drop-off of the release agent layer in the solvent resistance test was confirmed.

[0085]

15 <Testing Example 2> (Evaluation of Releasability from Pressure Sensitive Adhesive Sheet)

An acrylic pressure sensitive adhesive tape having a width of 20 mm (available from Nitto Denko Corporation, product name "31B Tape") was attached, using a hand roller
20 of 2 kg, to the release surface of the release sheet according to each of Examples 1 to 11 and Comparative Example 2 for which the curability of the release agent layer was evaluated as "o" in Testing Example 1.

[0086]

25 After each sample was stored under a condition of 23°C and 50% RH for 30 minutes, the release sheet side was fixed to a stainless steel plate and the acrylic pressure sensitive adhesive tape side was peeled off at a release angle of 180° and a release speed of 300 mm/min using a
30 tensile tester (available from SHIMADZU CORPORATION, product name "AG-IS500N") to measure the force necessary for the peeling (release force; mN/20 mm).

[0087]

The releasability from a pressure sensitive adhesive sheet was evaluated on the basis of the obtained release force (mN/20 mm) in accordance with the following determination criteria. Results are listed in Table 1.

- 5 o; Release force was less than 2,000 mN/20 mm.
 ×; Release force was 2,000 mN/20 mm or more.

[0088]

<Testing Example 3> (Evaluation of Releasability from Ceramic Green Sheet)

- 10 Ceramic slurry was prepared through adding 69 mass parts of toluene and 46 mass parts of ethanol to 100 mass parts of barium titanate (BaTiO_3 ; available from SAKAI CHEMICAL INDUSTRY CO., LTD., product name "BT-03"), 10 mass parts of polyvinyl butyral (available from SEKISUI CHEMICAL
- 15 CO., LTD., product name "S-LEC B·KBM-2"), and 5 mass parts of dioctyl phthalate (available from KANTO CHEMICAL CO., INC., product name "Dioctyl phthalate Cica first grade") and mixing and dispersing them using a ball mill.

[0089]

- 20 The release sheet according to each of Examples 1 to 11 and Comparative Example 2 for which the curability of the release agent layer was evaluated as "o" in Testing Example 1 was stored under an ordinary temperature for 24 hours after produced, then the release surface of the
- 25 release agent layer was uniformly coated with the above ceramic slurry using an applicator, and thereafter the ceramic slurry was dried at 80°C for one minute using a dryer. Through this operation, a ceramic green sheet having a thickness of 3 μm was obtained on the release
- 30 sheet. Thus, the release sheet with the ceramic green sheet was produced.

[0090]

The release sheet with the ceramic green sheet was

stationarily placed under an atmosphere of 23°C and 50% RH for 24 hours. Then, an acrylic pressure sensitive adhesive tape (available from Nitto Denko Corporation, product name "31B Tape") was attached to the surface of the ceramic green sheet opposite to the release sheet and, in this state, they were cut at a width of 20 mm. A measurement sample was thus obtained.

[0091]

The pressure sensitive adhesive tape side of the measurement sample was fixed to a flat plate and the release sheet was peeled off from the ceramic green sheet at a release angle of 180° and a release speed of 100 mm/min using a tensile tester (available from SHIMADZU CORPORATION, product name "AG-IS500N") to measure the force necessary for the peeling (release force; mN/20 mm).

[0092]

The releasability from the ceramic green sheet was evaluated on the basis of the obtained release force (mN/20 mm) in accordance with the following determination criteria. Results are listed in Table 1.

○; Release force was less than 100 mN/20 mm.

×; Release force was 100 mN/20 mm or more.

[0093]

Details of the simplified names listed in Table 1 and additional information are as follows.

<Isocyanate Group-containing Compound>

MFA-75B: Isocyanurate product of hexamethylene diisocyanate (available from Asahi Kasei Corporation, product name "MFA-75B")

MHG-80B: Isocyanurate product of hexamethylene diisocyanate (available from Asahi Kasei Corporation, product name "MHG-80B")

P301-75E: Adduct product of hexamethylene diisocyanate and

trimethylolpropane (available from Asahi Kasei Corporation,
product name "P301-75E")

TUL-100: Isocyanurate product of hexamethylene diisocyanate
(available from Asahi Kasei Corporation, product name "TUL-
5 100")

TPA-100: Isocyanurate product of hexamethylene diisocyanate
(available from Asahi Kasei Corporation, product name "TPA-
100")

WT30-100: Water-dispersed hexamethylene diisocyanate
10 (available from Asahi Kasei Corporation, product name
"WT30-100")

WB40-100: Water-dispersed hexamethylene diisocyanate
(available from Asahi Kasei Corporation, product name
"WB40-100")

15 [0094]

[Table 1]

	Hydroxyl group-containing acrylic-based compound (mass parts)	Acrylic-based compound free from hydroxyl groups (mass parts)	Polyorganosiloxane (mass parts)	Isocyanate group-containing compound (mass parts)						Photopolymerization initiator (mass parts)	Thermosetting catalyst (mass parts)	Evaluation of curability of release agent layer	Evaluation of releasability from pressure sensitive adhesive sheet	Evaluation of releasability from ceramic green sheet
				MFA -75B	MHG -80B	P301 -75E	TUL -100	TPA -100	WT30 -100	WB40 -100				
Example 1	100	0	0.75	20	0	0	0	0	0	0	1.0	○	○	○
Example 2	100	0	0.5	20	0	0	0	0	0	0	1.0	○	○	○
Example 3	100	0	1	20	0	0	0	0	0	0	1.0	○	○	○
Example 4	100	0	0.75	0	20	0	0	0	0	0	1.0	○	○	○
Example 5	100	0	0.75	0	0	20	0	0	0	0	1.0	○	○	○
Example 6	100	0	0.75	0	0	0	20	0	0	0	1.0	○	○	○
Example 7	100	0	0.75	0	0	0	0	20	0	0	1.0	○	○	○
Example 8	100	0	0.75	0	0	0	0	0	20	0	1.0	○	○	○
Example 9	100	0	0.75	0	0	0	0	0	0	20	1.0	○	○	○
Example 10	100	0	0.75	30	0	0	0	0	0	0	1.0	○	○	○
Example 11	100	0	0.75	40	0	0	0	0	0	0	1.0	○	○	○
Comparative Example 1	100	0	0.75	0	0	0	0	0	0	0	1.0	×	—	—
Comparative Example 2	100	0	0	20	0	0	0	0	0	0	1.0	○	×	×
Comparative Example 3	0	100	0.75	20	0	0	0	0	0	0	1.0	×	—	—

[0095]

As listed in Table 1, it has been found that the release sheets according to Examples are excellent in the curability of the release agent layers and exhibit good
5 releasability.

[Industrial applicability]

[0096]

The release sheet of the present invention can be suitably used as a release sheet on which the pressure
10 sensitive adhesive layer of a pressure sensitive adhesive sheet is laminated, a release sheet usable for the production of a ceramic green sheet, etc.

[Name of Document] Claims

1. A release sheet comprising a base material and a
release agent layer provided on at least one surface side
5 of the base material,
 the release agent layer being formed from a release
agent composition, the release agent composition containing
a hydroxyl group-containing acrylic-based compound,
polyorganosiloxane, and an isocyanate group-containing
10 compound.
2. The release sheet as recited in claim 1, wherein the
polyorganosiloxane has a reactive group capable of reacting
with an isocyanate group.
- 15 3. The release sheet as recited in claim 2, wherein the
reactive group is a hydroxyl group.
4. The release sheet as recited in any one of claims 1 to
20 3, wherein the hydroxyl group-containing acrylic-based
compound is at least one of pentaerythritol triacrylate and
dipentaerythritol pentaacrylate.
5. The release sheet as recited in any one of claims 1 to
25 4, wherein the isocyanate group-containing compound is an
isocyanurate product of polyisocyanate.
6. The release sheet as recited in claim 5, wherein the
polyisocyanate is hexamethylene diisocyanate.
- 30 7. The release sheet as recited in any one of claims 1 to
6, wherein the release agent composition contains a
photopolymerization initiator.

8. The release sheet as recited in any one of claims 1 to 7, wherein the release agent composition contains a thermosetting catalyst.

5

9. A method for producing the release sheet as recited in any one of claims 1 to 8, comprising:

a step of forming a coating film composed of the release agent composition on one surface side of the base material; and

10

a step of curing the coating film through heating and irradiation with active energy rays to form the release agent layer.