

Description

[Title of Invention] RELEASE SHEET

[Technical Field]

[0001]

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

[Background Art]

[0002]

Release sheets have heretofore been used in the production of pressure sensitive adhesive sheets. A
15 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 layer opposite to the base material (this surface may be referred to as a "release surface" in the present
20 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 sensitive adhesive sheet, and the coating liquid is dried to form the pressure sensitive adhesive layer. Then, a
25 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 sensitive adhesive sheet including the pressure sensitive adhesive layer and the base material can thereby be
30 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.

5 [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
10 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.

15 [0004]

In such a release sheet, the release agent layer is generally formed using a release agent composition that contains a release component. Patent Documents 1 to 5 disclose release sheets each formed with a release agent
20 layer using a cationically polymerizable silicone resin as the release component. The cationically polymerizable silicone resin is stimulated by ultraviolet rays or the like to cure in the presence of a cationic polymerization initiator. In the release sheets of Patent Documents 1 to
25 5, the release agent layer is formed through coating one surface side of a base material with a composition that contains the cationically polymerizable silicone resin and the cationic polymerization initiator and irradiating the coating film with ultraviolet rays to cure it.

30 [Prior Art Documents]

[Patent Documents]

[0005]

[Patent Document 1] JP4622079B

[Patent Document 2] JP5061405B

[Patent Document 3] JP4626055B

[Patent Document 4] JP2012-206509A

[Patent Document 5] JP5786798B

5 [Summary of the Invention]

[Problems to be solved by the Invention]

[0006]

A wide variety of objects are conceivable as those on which the release surface of a release sheet is laminated.
10 For such objects, an optimal release sheet is required to be used for each object. Therefore the development of a novel release sheet is in progress from the viewpoint of increasing the options of release sheets, etc.

[0007]

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

[Means for solving the Problems]

20 [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, wherein the release
25 agent layer is formed of a release agent composition that contains a cationically polymerizable compound, a release component, and a cationic polymerization initiator, wherein the cationically polymerizable compound contains no polysiloxane skeleton, wherein, in the release agent
30 composition, the compounding amount of the cationically polymerizable compound is larger than each of the compounding amount of the release component and the compounding amount of the cationic polymerization initiator, wherein, in the release agent composition, the compounding
35 amount of the cationically polymerizable compound is more than 50 mass% and 99.9 mass% or less

(Invention 1).

[0009]

In the release sheet according to the above invention (Invention 1), when the release agent layer is formed, the
5 cationically polymerizable compound contained as the primary agent in the release agent composition is cationically polymerized due to the action of the cationic polymerization initiator. Consequently, the release agent composition cures to well form the release agent layer
10 which contains the release component. Thus, the release component contained in the release agent layer allows the release sheet to exhibit good releasability.

[0010]

In the above invention (Invention 1), the cationically
15 polymerizable compound may preferably be an epoxy compound (Invention 2).

[0011]

In the above invention (Invention 2), the epoxy compound may preferably have three or more epoxy groups in
20 one molecule (Invention 3).

[0012]

In the above invention (Invention 1, 2), the epoxy compound may preferably have a molecular weight of 200 or more and 2,000 or less (Invention 4).

25 [0013]

In the above invention (Invention 1 to 4), the release component may preferably comprise at least one selected from the group consisting of a silicone-based release component, a fluorine-based release component, and a long-
30 chain alkyl-based release component (Invention 5).

[0014]

In the above invention (Invention 1 to 5), the release component may preferably have a reactive group that can

react with the cationically polymerizable compound (Invention 6).

[0015]

In the above invention (Invention 6), the release
5 component may preferably be reactive polyorganosiloxane (Invention 7).

[0016]

In the above invention (Invention 1 to 7), the surface
free energy as measured on the surface of the release agent
10 layer opposite to the base material may preferably be 25
mJ/m² or more and 35 mJ/m² or less (Invention 8).

[0017]

In the above invention (Invention 1 to 8), the release
sheet may preferably be used for a ceramic green sheet
15 production process (Invention 9).

[Advantageous Effect of the Invention]

[0018]

According to the present invention, a novel release
sheet that has good releasability is provided.

20 [Embodiments for Carrying out the Invention]

[0019]

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

The release sheet according to an embodiment of the
25 present invention is configured to include a base material
and a release agent layer provided on one surface side of
the base material.

[0020]

In the release sheet according to the present
30 embodiment, the release agent layer is formed of a release
agent composition that contains a cationically
polymerizable compound, a release component, and a cationic
polymerization initiator. The cationically polymerizable

compound contains no polysiloxane skeleton.

[0021]

In the release sheet according to the present embodiment, in the release agent composition, the
5 compounding amount of the cationically polymerizable compound is larger than each of the compounding amount of the release component and the compounding amount of the cationic polymerization initiator. That is, in the release sheet according to the present embodiment, the cationically
10 polymerizable compound may be compounded as the primary agent.

[0022]

The release agent layer of the release sheet according to the present embodiment may be formed by curing the
15 above-described release agent composition. This curing occurs through the cationic polymerization of the cationically polymerizable compound, which is contained as the primary agent, due to the action of the cationic polymerization initiator. The cationically polymerizable
20 compound can therefore be sufficiently polymerized to form a well-cured release agent layer. Furthermore, the release agent layer contains the release component and the release sheet can thereby exhibit good releasability.

[0023]

25 The cationic polymerization refers generally to a reaction in which the cation acts as an active species to progress the polymerization of the cationically polymerizable compound. This reaction may be initiated by the cationic polymerization initiator.

30 [0024]

1. Base Material

The base material of the release sheet according to 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, 5 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 is preferred, and a polyethylene 10 terephthalate film is 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 15 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 20 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. Examples of the above oxidation method include corona discharge treatment, plasma discharge treatment, chromium 25 oxidation treatment (wet type), flame treatment, hot-air treatment, ozone exposure treatment, and ultraviolet ray irradiation treatment. Examples of the roughening method include a sandblast method and a thermal spraying method. These surface treatment methods may be appropriately 30 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.

[0026]

The thickness of the base material may preferably be 10 μm or more, particularly preferably 15 μm or more, and further preferably 20 μm or more. From another aspect, the thickness may preferably be 300 μm or less, particularly
 5 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
 10 embodiment, the release agent layer is formed of a release agent composition that contains a cationically polymerizable compound, a release component, and a cationic polymerization initiator.

[0028]

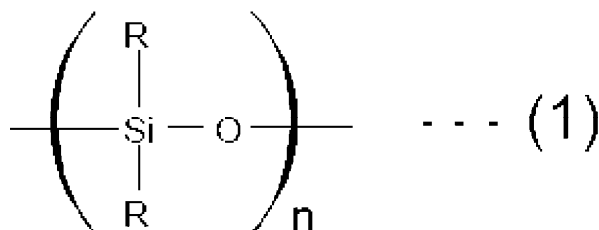
15 (1) Cationically Polymerizable Compound

A compound capable of forming a polymer by cationic polymerization can be used as the cationically polymerizable compound. This compound contains no polysiloxane skeleton.

20 [0029]

Here, the polysiloxane skeleton refers to a skeleton in which silicon atoms and oxygen atoms linked by covalent bonding are alternately present, and specifically to a structure represented by the following general formula (1).

25 [Chemical Formula 1]



(In the formula, each R is a hydrogen atom or an organic group and n is any positive integer.)

[0030]

Specific examples of the cationically polymerizable compound include compounds having cyclic ether such as an epoxy group or an oxetanyl group. In particular, it is preferred to use an epoxy compound having an epoxy group
5 because the types of polyfunctional compounds are abundant.

[0031]

The above epoxy compound may preferably have three or more epoxy groups in one molecule. From another aspect, the above epoxy compound may preferably have 10 or less
10 epoxy groups in one molecule, particularly preferably have 9 or less epoxy groups in one molecule, and further preferably have 8 or less epoxy groups in one molecule. When the number of epoxy groups in one molecule is three or more, the epoxy compound is likely to be cationically
15 polymerized, and it thereby becomes easy to form a release agent layer in which the release agent composition is well cured. As a result, the release agent layer exhibits excellent solvent resistance, and blocking is less likely to occur when rolling up the release sheet according to the
20 present embodiment. When the number of epoxy groups in one molecule is 10 or less, good compatibility with the release component can be obtained.

[0032]

The above epoxy compound may preferably have a
25 molecular weight of 200 or more, particularly preferably 250 or more, and further preferably 300 or more. From another aspect, the above epoxy compound may preferably have a molecular weight of 2,000 or less, particularly preferably 1,500 or less, and further preferably 1,250 or
30 less. When the molecular weight of the epoxy compound is 200 or more, crawling is less likely to appear on the coating surface when coating the base material with the release agent composition. When the molecular weight of

the epoxy compound is 2,000 or less, the release agent composition or the coating liquid containing the release agent composition can have a relatively low viscosity. The release agent composition or the coating liquid can
5 therefore be used to form a release agent layer having a surface on which the occurrence of streak defects and the like is suppressed, thus having excellent smoothness.

[0033]

Examples of the epoxy compound which can be used in
10 the release sheet according to the present embodiment include: glycidyl ethers of bisphenols such as bisphenol A and bisphenol F; glycidyl ethers of phenol resins such as resorcinol, phenyl novolac, and cresol novolac; glycidyl ethers of other polyalcohols; glycidyl esters of polyvalent
15 carboxylic acids such as phthalic acid, isophthalic acid, and tetrahydrophthalic acid; glycidylamine-type epoxy compounds composed of epichlorohydrin adducts of amines and anilines; and so-called alicyclic epoxides in which epoxy is introduced, for example, by oxidizing the carbon-carbon
20 double bond in the molecule, such as vinylcyclohexane diepoxide, 3,4-epoxycyclohexylmethyl-3,4-dicyclohexanecarboxylate, and 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexan-m-dioxane.

[0034]

25 Examples of the polyalcohols which constitute the glycidyl ethers of other polyalcohols include glycerin, diglycerol, sugar alcohols, butanediol, polyethylene glycol, polypropylene glycol, and polyalcohols having biphenyl skeletons, dicyclohexadiene skeletons, naphthalene
30 skeletons, and the like.

[0035]

Among these epoxy compounds, compounds having three or more epoxy groups in one molecule are preferred. As the

epoxy compounds having three or more epoxy groups in one molecule, glycidyl ethers of alcohols having trivalent or more hydroxyl groups are preferred. Examples of such alcohols include glycerin (trivalent), diglycerol
5 (tetraivalent), trimethylolpropane (trivalent), ditrimethylolpropane (tetraivalent), pentaerythritol (tetraivalent), dipentaerythritol (tetraivalent), sugar alcohols such as erythritol (tetraivalent), xylitol (pentavalent), arabitol (pentavalent), sorbitol
10 (hexavalent), mannitol (hexavalent), and galactitol (hexavalent), ring-opened compounds of the above epoxy compounds, such as bisphenol A diglycerol ether (tetraivalent).

[0036]

15 One type of the epoxy compound can be used alone, or two or more types of these epoxy compounds can also be used in combination. It is preferred to use diglycerol polyglycidyl ether, which is glycidyl ether of diglycerol, and/or sorbitol polyglycidyl ether among the above epoxy
20 compounds from the viewpoint of the high reactivity and the availability.

[0037]

As previously described, in the release agent composition according to the present embodiment, the
25 cationically polymerizable compound may be compounded as the primary agent. This allows the cationic polymerization of the cationically polymerizable compound to effectively progress. As a result, the release agent layer is well formed. Specifically, the compounding amount of the
30 cationically polymerizable compound in the release agent composition may preferably be more than 50 mass%, particularly preferably 75 mass% or more, and further preferably 90 mass% or more. From another aspect, the

compounding amount may preferably be 99.9 mass% or less, particularly preferably 99.75 mass% or less, and further preferably 99.5 mass% or less. When the compounding amount is more than 50 mass%, a polymer network (three-dimensional
5 network structure) of the cationically polymerizable compound is well formed with a sufficient amount of the cationically polymerizable compound, and the release agent layer which is sufficiently cured can readily be obtained. When the compounding amount is 99.9 mass% or less, the
10 compounding amounts of the cationic polymerization initiator and the release component can be relatively increased, so that the cationic polymerization is liable to progress and the desired releasability can readily be achieved.

15 [0038]

(2) Release Component

The release component is not particularly limited, provided that it allows the release agent layer to have releasability. For example, it is possible to use at least
20 one selected from the group consisting of a silicone-based release component, a fluorine-based release component, a long-chain alkyl-based release component, an alkyd-based release component, an olefin-based release component, an acrylic-based release component, and a rubber-based release
25 component. Among these, at least one selected from the group consisting of a silicone-based release component, a fluorine-based release component, and a long-chain alkyl-based release component may preferably be used, and a silicone-based release component may particularly
30 preferably be used, from the viewpoint of readily imparting the desired releasability to the release agent layer.

[0039]

The release component may preferably have a reactive

group that can react with the cationically polymerizable compound. This allows the release component to be fixed to the polymer, which is made by the cationic polymerization of the cationically polymerizable compound, in the release agent layer. As a result, the release agent layer can be formed with a better network to further improve the curability and it is possible to suppress migration of the release component from the release agent layer to an object on which the release surface of the release sheet according to the present embodiment is laminated.

[0040]

The above reactive group is not particularly limited, provided that it can react with the cationically polymerizable compound. Examples of the reactive group include an epoxy group, an amino group, a mercapto group, a carboxyl group, and an anhydrous carboxyl group. When the cationically polymerizable compound has a reactive group, the release component may preferably have the same reactive group as that of the cationically polymerizable compound. This allows the release component to have excellent reactivity with the cationically polymerizable compound, and the release component can readily be firmly incorporated into the previously-described network in the release agent layer via the chemical bond. In particular, when the cationically polymerizable compound has an epoxy group, it is preferred that the release component also have an epoxy group as the reactive group.

[0041]

The position of the above reactive group in the release component is not particularly limited. For example, when the release component has a linear structure or includes a main chain of a linear structure, the reactive group may be located at an end of the linear structure or

may also be located at a side chain of the linear structure. When located at an end, the reactive group may be located at one end of the linear structure or the reactive groups may be located at both ends. When located at a side chain,
5 the side chain itself may be a reactive group or a part of the side chain may be a reactive group. In an embodiment, the reactive groups may be located at both the end or ends and the side chain. Among others, the release component may preferably have a reactive group at least as a side
10 chain. This allows the three-dimensional network structure, which includes the release component, to readily be formed in the release agent layer and the release component is less likely to migrate from the release agent layer to an object on which the release surface of the release sheet
15 according to the present embodiment is laminated.

[0042]

In the release sheet according to the present embodiment, the release component may preferably be a silicone-based release component as previously described
20 and particularly preferably reactive polyorganosiloxane. The reactive polyorganosiloxane is excellent in the reactivity with the cationically polymerizable compound. By using the reactive polyorganosiloxane, more excellent releasability can be achieved. As a result, it is possible
25 to obtain a release sheet that is provided with a well-cured release agent layer and exhibits better releasability.

[0043]

The weight-average molecular weight of the above reactive polyorganosiloxane may preferably be 1,000 or more,
30 particularly preferably 1,500 or more, and further preferably 2,000 or more. From another aspect, the weight-average molecular weight may preferably be 100,000 or less, particularly preferably 50,000 or less, and further

preferably 25,000 or less. When the weight-average molecular weight is 1,000 or more, desired releasability can readily be achieved. When the weight-average molecular weight is 100,000 or less, the viscosity of the release agent composition or the coating liquid containing the release agent composition can be relatively low, and the release agent composition or the coating liquid can be used to form a release agent layer having a surface on which the occurrence of streak defects and the like is suppressed, thus having excellent smoothness.

[0044]

Preferred examples of the above reactive polyorganosiloxane include epoxy-modified polydimethylsiloxane. In particular, it is preferred to use epoxy-modified polydimethylsiloxane having an epoxy group at a side chain from the viewpoint that the coating film obtained using the release agent composition or the coating liquid containing the release agent composition can have an excellent surface state and excellent curability.

[0045]

As the above epoxy-modified polydimethylsiloxane, for example, a commercially available compound can be used. Examples of product names of such compounds as the epoxy compounds having epoxy groups at side chains include product name "X-22-343," product name "KF-101," product name "KF-1001," product name "X-22-2000," product name "KF-102," product name "X-22-4741," and product name "KF-1002," all of which are available from Shin-Etsu Chemical Co., Ltd. Examples of the epoxy compounds having epoxy groups at both ends include product name "X-22-163C" and product name "X-22-169B," both of which are available from Shin-Etsu Chemical Co., Ltd. Examples of the epoxy compounds having epoxy groups at one ends include product name "X-22-173DX,"

which is available from Shin-Etsu Chemical Co., Ltd. Examples of the epoxy compounds having epoxy groups at both ends and side chains include product name "X-22-9002," which is available from Shin-Etsu Chemical Co., Ltd. One
5 type of them can be used alone or two or more types can also be used in combination.

[0046]

As previously described, in the release sheet according to the present embodiment, the compounding amount
10 of the cationically polymerizable compound in the release agent composition is larger than the compounding amount of the release component. This allows the cationic polymerization of the cationically polymerizable compound, which is contained as the primary agent, to effectively
15 progress to result in the good formation of the release agent layer. In particular, the compounding amount of the release component in the release agent composition may preferably be 0.1 mass parts or more, particularly preferably 0.25 mass parts or more, and further preferably
20 0.5 mass parts or more with respect to 100 mass parts of the cationically polymerizable compound. From another aspect, the compounding amount of the release component in the release agent composition may preferably be 30 mass parts or less, particularly preferably 20 mass parts or
25 less, and further preferably 10 mass parts or less with respect to 100 mass parts of the cationically polymerizable compound. When the compounding amount of the release component is 0.1 mass parts or more, the release agent layer can exhibit more excellent releasability. When the
30 compounding amount of the release component is 30 mass parts or less, the compounding amount of the cationically polymerizable compound is relatively large, and a well-cured release agent layer can thereby be readily obtained.

[0047]

(3) Cationic Polymerization Initiator

The cationic polymerization initiator is not particularly limited, provided that it can initiate the
5 cationic polymerization of the cationically polymerizable compound. In particular, the cationic polymerization initiator may preferably be able to initiate the cationic polymerization of the cationically polymerizable compound by at least one of irradiation with active energy rays and
10 heating. By using such a cationic polymerization initiator, the initiation of the cationic polymerization can be controlled, so that a desired release agent layer can readily be formed. Comparing active energy rays with heat, it is preferred to use active energy rays from the
15 viewpoint that the uniform irradiation is easy and the initiation of the cationic polymerization can more readily be controlled. Ultraviolet rays, electron rays, or the like can be used as the active energy rays, among which ultraviolet rays may preferably be used because of easy
20 management.

[0048]

Preferred examples of the above cationic polymerization initiator include sulfonium salt-based, iodonium salt-based, phosphonium salt-based, diazonium
25 salt-based, ammonium salt-based, and ferrocenes-based photoreaction initiators. Any known one can be used as the cationic polymerization initiator. Specific examples will be exemplified below, but the present invention is not limited to using these compounds. One type of these
30 compounds may be used alone or two or more types may also be used in combination.

[0049]

Examples of the sulfonium salt-based photoreaction

initiators include bis[4-(diphenylsulfonio)phenyl] sulfide
 bishexafluorophosphate, bis[4-(diphenylsulfonio)phenyl]
 sulfide bishexafluoroantimonate, bis[4-
 (diphenylsulfonio)phenyl] sulfide bistetrafluoroborate,
 5 bis[4-(diphenylsulfonio)phenyl] sulfide
 tetrakis(pentafluorophenyl) borate, diphenyl-4-(phenylthio)
 phenylsulfonium hexafluorophosphate, diphenyl-4-
 (phenylthio) phenylsulfonium hexafluoroantimonate,
 diphenyl-4-(phenylthio) phenylsulfonium tetrafluoroborate,
 10 diphenyl-4-(phenylthio) phenylsulfonium
 tetrakis(pentafluorophenyl) borate, triphenylsulfonium
 hexafluorophosphate, triphenylsulfonium
 hexafluoroantimonate, triphenylsulfonium tetrafluoroborate,
 triphenylsulfonium tetrakis(pentafluorophenyl) borate,
 15 bis[4-(di(4-(2-hydroxyethoxy))phenylsulfonio)phenyl]
 sulfide bishexafluorophosphate, bis[4-(di(4-(2-
 hydroxyethoxy))phenylsulfonio)phenyl] sulfide
 bishexafluoroantimonate, bis[4-(di(4-(2-
 hydroxyethoxy))phenylsulfonio)phenyl] sulfide
 20 bistetrafluoroborate, and bis[4-(di(4-(2-
 hydroxyethoxy))phenylsulfonio)phenyl] sulfide
 tetrakis(pentafluorophenyl) borate.

[0050]

Preferred examples of the iodonium-based photoreaction
 25 initiators include diphenyliodonium hexafluorophosphate,
 diphenyliodonium hexafluoroantimonate, diphenyliodonium
 tetrafluoroborate, diphenyliodonium
 tetrakis(pentafluorophenyl) borate, bis(dodecylphenyl)
 iodonium hexafluorophosphate, bis(dodecylphenyl) iodonium
 30 hexafluoroantimonate, bis(dodecylphenyl) iodonium
 tetrafluoroborate, bis(dodecylphenyl) iodonium
 tetrakis(pentafluorophenyl) borate, 4-methylphenyl-4-(1-
 methylethyl) phenyliodonium hexafluorophosphate, 4-

methylphenyl-4-(1-methylethyl) phenyliodonium
 hexafluoroantimonate, 4-methylphenyl-4-(1-methylethyl)
 phenyliodonium tetrafluoroborate, and 4-methylphenyl-4-(1-
 methylethyl) phenyliodonium tetrakis(pentafluorophenyl)
 5 borate.

[0051]

Preferred examples of the phosphonium salt-based
 photoreaction initiators include ethyltriphenylphosphonium
 tetrafluoroborate, ethyltriphenylphosphonium
 10 hexafluorophosphate, ethyltriphenylphosphonium
 hexafluoroantimonate, tetrabutylphosphonium
 tetrafluoroborate, tetrabutylphosphonium
 hexafluorophosphate, and tetrabutylphosphonium
 hexafluoroantimonate.

15 [0052]

Preferred examples of the diazonium salt-based
 photoreaction initiators include phenyldiazonium
 hexafluorophosphate, phenyldiazonium hexafluoroantimonate,
 phenyldiazonium tetrafluoroborate, and phenyldiazonium
 20 tetrakis(pentafluorophenyl) borate.

[0053]

Preferred examples of the ammonium salt-based
 photoreaction initiators include 1-benzyl-2-cyanopyridinium
 hexafluorophosphate, 1-benzyl-2-cyanopyridinium
 25 hexafluoroantimonate, 1-benzyl-2-cyanopyridinium
 tetrafluoroborate, 1-benzyl-2-cyanopyridinium
 tetrakis(pentafluorophenyl) borate, 1-(naphthylmethyl)-2-
 cyanopyridinium hexafluorophosphate, 1-(naphthylmethyl)-2-
 cyanopyridinium hexafluoroantimonate, 1-(naphthylmethyl)-2-
 30 cyanopyridinium tetrafluoroborate, and 1-(naphthylmethyl)-
 2-cyanopyridinium tetrakis(pentafluorophenyl) borate.

[0054]

Preferred examples of the ferrocene-based

photoreaction initiators include (2,4-cyclopentadien-1-yl)[(1-methylethyl)benzene]-Fe(II) hexafluorophosphate, (2,4-cyclopentadiene-1-yl)[(1-methylethyl)benzene]-Fe(II) hexafluoroantimonate, (2,4-cyclopentadien-1-yl)[(1-methylethyl)benzene]-Fe(II) tetrafluoroborate, and (2,4-cyclopentadien-1-yl)[(1-methylethyl)benzene]-Fe(II) tetrakis(pentafluorophenyl) borate.

[0055]

Examples of commercial products of these photoreaction initiators include product names "SP-150," "SP-152," "SP-170," "SP-172," "CP-66," and "CP-77" available from ADEKA Corporation; product names "CYRACURE-UVI-6990," "CYRACURE-UVI-6974," and "CYRACURE-UVI-6992" available from Union Carbide Corporation; product names "CI-2855," "CI-2639," and "CI-2758" available from Nippon Soda Co., Ltd.; product names "San-Aid SI-60," "San-Aid SI-80," and "San-Aid SI-100" available from SANSHIN CHEMICAL INDUSTRY CO., LTD.; product names "IRGACURE 261" and "IRGACURE 250" available from Ciba Specialty Chemicals; product name "RHODORSIL 2074" available from Solvay Japan, Ltd.; product name "Bis(4-t-butylphenyl)iodonium hexafluorophosphate" available from Midori Kagaku Co., Ltd.; product names "CPI-100P," "CPI-101A," and "CPI-200K" available from San-Apro Ltd.; product names "ESACURE-1064" and "ESACURE-1187" available from Lamberti; and product name "Kayacure PCI-220" available from Nippon Kayaku Co., Ltd.

[0056]

Sulfonium salt-based or iodonium salt-based initiators may be preferred as the cationic polymerization initiator from the viewpoint of the curing speed, stability, and economic efficiency. It is therefore preferred to use, among the above commercial products, the product name "IRGACURE 250" available from Ciba Specialty Chemicals or

the product name "CPI-100P," "CPI-101A," or "CPI-200K" available from San-Apro Ltd. as the cationic polymerization initiator.

[0057]

- 5 One type of the cationic polymerization initiators may be used alone or two or more types may also be used in combination.

[0058]

- 10 In the release sheet according to the present embodiment, the compounding amount of the cationic polymerization initiator in the release agent composition may preferably be 0.1 mass parts or more, particularly preferably 1 mass part or more, and further preferably 2 mass parts or more with respect to 100 mass parts of the
- 15 cationically polymerizable compound. From another aspect, the compounding amount of the cationic polymerization initiator in the release agent composition may preferably be 100 mass parts or less, particularly preferably 50 mass parts or less, and further preferably 40 mass parts or less
- 20 with respect to 100 mass parts of the cationically polymerizable compound. When the compounding amount of the cationic polymerization initiator falls within the above range, the cationic polymerization effectively progresses and a well-cured release agent layer can thereby be readily
- 25 obtained.

[0059]

(4) Other Components

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

[0060]

(5) Production of Release Agent Composition

The release agent composition can be produced by mixing the previously-described cationically polymerizable compound, release component, and cationic polymerization initiator and, optionally, other components. The obtained
5 release agent composition may be diluted with a dilution solvent as necessary to obtain a coating liquid.

[0061]

Examples of the above dilution solvent include aliphatic hydrocarbons such as hexane, heptane, and
10 cyclohexane, aromatic hydrocarbons such as toluene and xylene, halogenated hydrocarbons such as methylene chloride and ethylene chloride, alcohols such as methanol, ethanol, propanol, butanol, and 1-methoxy-2-propanol, ketones such as acetone, methyl ethyl ketone, 2-pentanone, isophorone,
15 and cyclohexanone, esters such as ethyl acetate and butyl acetate, and cellosolve-based solvents such as ethyl cellosolve.

[0062]

The concentration and viscosity of the coating liquid
20 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
25 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.

[0063]

30 (6) Thickness of Release Agent Layer

In the release sheet according to the present embodiment, the thickness of the release agent layer may preferably be 10 nm or more and particularly preferably 50

nm or more. From another aspect, the thickness may preferably be 10,000 nm or less and particularly preferably 5,000 nm or less. When the thickness of the release agent layer is 10 nm or more, desired releasability can readily
 5 be achieved. When the thickness of the release agent layer is 10,000 nm or less, a well-cured release agent layer can readily be formed.

[0064]

3. Physical Properties of Release Sheet, etc.

10 In the release sheet according to the present embodiment, the surface free energy (γ_{total}) as measured on the surface of the release agent layer opposite to the base material may preferably be 25 mJ/m² or more and particularly preferably 27 mJ/m² or more. From another
 15 aspect, the surface free energy may preferably be 35 mJ/m² or less and particularly preferably 33 mJ/m² or less. When the free energy is 25 mJ/m² or more, bonding between the release component and the network occurs appropriately in the release agent layer, and the release component is
 20 suppressed from migrating to a pressure sensitive adhesive or a green sheet for which the release sheet according to the present embodiment is used. When the surface free energy is 35 mJ/m² or less, the release component is locally present near the surface of the release agent layer,
 25 and the releasability can be designed so as to effectively reduce the release force from a pressure sensitive adhesive or a green sheet for which the release sheet according to the present embodiment is used.

[0065]

30 In the release sheet according to the present embodiment, the maximum peak height R_p of the surface of the release agent layer opposite to the base material may preferably be less than 2,000 nm, particularly preferably

500 nm or less, and further preferably 50 nm or less. When the maximum peak height R_p is less than 2,000 nm, the release surface of the release sheet can have excellent smoothness. Accordingly, in a pressure sensitive adhesive sheet or a ceramic green sheet laminated on the release surface, the surface in contact with the release surface can also have excellent smoothness. As a result, it is possible to produce a pressure sensitive adhesive sheet exhibiting excellent performance and a laminated ceramic product exhibiting excellent performance. The lower limit of the maximum peak height R_p is not particularly limited, but may preferably be 10 nm or more and particularly preferably 20 nm or more.

[0066]

15 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 preferably be 100 mN/20 mm or more and particularly preferably 150 mN/20 mm or more. From another aspect, the release force may preferably be 2,000 mN/20 mm or less and particularly preferably 1,500 mN/20 mm or less.

25 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 method of measuring the release force when releasing the release sheet from a pressure sensitive adhesive sheet is as specified in the exemplary test, which will be described later.

[0067]

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 preferably be 5 mN/20 mm or more and particularly preferably 10 mN/20 mm or more. From another aspect, the release force may preferably be 100 mN/20 mm or less and particularly preferably 75 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 method of measuring the release force when releasing the release sheet from a ceramic green sheet is as specified in the exemplary test, which will be described later.

[0068]

4. Production Method for Release Sheet

The release sheet according to the present embodiment can be produced by a commonly-used method. For example, the release sheet can be obtained through coating one surface of the base material with a coating liquid of the previously-described release agent composition and then curing the obtained coating film to form the release agent layer.

[0069]

Examples of the coating method to be used 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.

[0070]

When the above coating film is heated to dry the solvent of the coating liquid, the temperature may preferably be 100°C or higher and particularly preferably

120°C or higher. From another aspect, the temperature may preferably be 180°C or lower and particularly preferably 150°C or lower. The heating time may preferably be 10 seconds or more and particularly preferably 15 seconds or more. From another aspect, the heating time may preferably be 60 seconds or less and particularly preferably 30 seconds or less.

[0071]

Curing of the above coating film can be carried out by progressing the cationic polymerization of the cationically polymerizable compound. Here, the cationic polymerization can be initiated by performing at least one of irradiation of the coating film with active energy rays and heating of the coating film, depending on the type of the cationic polymerization initiator.

[0072]

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

[0073]

Irradiation with ultraviolet rays can be performed using a high-pressure mercury lamp, xenon lamp, or the like. The irradiance level of ultraviolet rays may preferably be 50 mW/cm² or more and particularly preferably 200 mW/cm² or more as the illuminance. From another aspect, the illuminance may preferably be 5,000 mW/cm² or less and particularly preferably 3,000 mW/cm² or less. The light amount of ultraviolet rays may preferably be 10 mJ/cm² or more and particularly preferably 30 mJ/cm² or more. From another aspect, the light amount may preferably be 250 mJ/cm² or less and particularly preferably 150 mJ/cm² or less. When the irradiation with ultraviolet rays is

carried out under the condition according to the above range, the release agent composition can be well cured, and a satisfactory release agent layer can be effectively formed.

5 [0074]

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

[0075]

According to the above-described production method, it is possible to effectively progress the cationic
15 polymerization of the cationically polymerizable compound, and a well-cured release agent layer can be formed. Moreover, the release sheet can exhibit good releasability because the release agent layer thus obtained contains the release component.

20 [0076]

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.

25 [0077]

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
30 present embodiment may be coated with a coating liquid of a 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 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, 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 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.

[0078]

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 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.

[0079]

In the release sheet according to the present embodiment, the release agent layer is formed using the previously-described release agent composition. In

particular, when the release agent layer is formed, the cationically polymerizable compound contained as the primary agent in the release agent composition is cationically polymerized due to the action of the cationic polymerization initiator thereby to cure the release agent composition. This allows the release agent layer, which contains the release component, to be well formed. The release sheet according to the present embodiment can therefore exhibit good releasability.

10 [0080]

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.

[0081]

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]

25 [0082]

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.

30 [0083]

<Example 1>

A coating liquid of a release agent composition was obtained by mixing 100 mass parts (equivalent amount to the

solid content, here and hereinafter) of diglycerol polyglycidyl ether as the cationically polymerizable compound (product name "Denacol EX-421" available from Nagase ChemteX Corporation, number of epoxy groups in one
5 molecule: 3, molecular weight: 334), 1.0 mass parts of polydimethylsiloxane with an epoxy-modified side chain as the release component (product name "KF-101" available from Shin-Etsu Chemical Co., Ltd., weight-average molecular weight: 28,500), and 8.0 mass parts of diphenyl[4-
10 (phenylthio)phenyl]sulfonium hexafluorophosphate as the cationic polymerization initiator (product name "CPI-100P" available from San-Apro Ltd.) in methyl ethyl ketone. The solid content of the coating liquid was 18 mass%.

[0084]

15 One surface of a biaxially-stretched polyethylene terephthalate film as the base material (product name "Lumirror S10" available from Toray Industries, Inc., thickness: 23 μm , maximum peak height R_p on both surfaces: 452 nm) was coated with the obtained coating liquid of the
20 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 surface side to the base material to form a
25 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.

[0085]

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

[0086]

<Examples 2 to 6 and Comparative Examples 1 and 2>

Release sheets were obtained in the same manner as in Example 1 except that the compounding amounts of the release component and cationic polymerization initiator in the release agent composition were modified as listed in Table 1.

[0087]

<Exemplary Test 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 (smear) and drop-off (rub-off) was visually confirmed. Then, the curability of the release agent layer was evaluated in accordance with the criteria as below. Results are listed in Table 1.

o; Both smear and rub-off were unconfirmed.

x; At least one of smear and rub-off was confirmed.

[0088]

<Exemplary Test 2> (Evaluation of Releasability from Pressure Sensitive Adhesive Sheet)

An acrylic pressure sensitive adhesive tape having a width of 20 mm (product name "31B Tape" available from Nitto Denko Corporation) was attached, using a hand roller of 2 kg, to the release surface of the release sheet according to each of Examples 1 to 6 and Comparative Example 2 for which the curability of the release agent layer was evaluated as "o" in Exemplary Test 1.

[0089]

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 tensile tester (product name "AG-IS500N" available from SHIMADZU CORPORATION) to measure the force necessary for the peeling (release force; mN/20 mm).

5 [0090]

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

10 o; Release force was less than 500 mN/20 mm.

x; Release force was 500 mN/20 mm or more.

[0091]

<Exemplary Test 3> (Evaluation of Releasability from Ceramic Green Sheet)

15 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 ; product name "BT-03" available from SAKAI CHEMICAL INDUSTRY CO., LTD), 10 mass parts of polyvinyl butyral (product name "S-LEC B·KBM-2"

20 available from SEKISUI CHEMICAL CO., LTD.), and 5 mass parts of dioctyl phthalate (product name "Dioctyl phthalate Cica first grade" available from KANTO CHEMICAL CO., INC.) and mixing and dispersing them in a ball mill.

[0092]

25 The release sheet according to each of Examples 1 to 6 and Comparative Example 2 for which the curability of the release agent layer was evaluated as "o" in Exemplary Test 1 was stored under an ordinary temperature for 24 hours after produced, then the release surface of the release

30 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 sheet. Thus, the release sheet with the ceramic green sheet was produced.

[0093]

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 (product name "31B Tape" available from Nitto Denko Corporation) 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.

[0094]

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 (product name "AG-IS500N" available from SHIMADZU CORPORATION) to measure the force necessary for the peeling (release force; mN/20 mm).

[0095]

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

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

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

[0096]

<Exemplary Test 4> (Measurement of Surface Free Energy)

The surface free energy (γ_{total}) of the surface on the release agent layer side of the release sheet obtained in each of Examples and Comparative Examples was calculated. Specifically, the surface free energy (γ_{total}) and each component (dispersion component γ_{d} , polar component γ_{p} ,

hydrogen bond component γ_h) were obtained through using water, diiodomethane, and bromonaphthalene having known contact angles as probe liquids to measure the contact angle of each probe solution to the release agent layer with a contact angle meter and calculating the surface free energy and each component from the obtained contact angle in accordance with the Kitazaki/Hata method (see KITAZAKI Yasuaki et al., Journal of the Adhesion Society of Japan, Vol. 8, No. 3, 1972, pp. 131-141). The used contact angle meter was a contact angle meter (product name "Fully-automatic contact angle meter DM-701" available from Kyowa Interface Science Co., Ltd). Results are listed in Table 1.

[0097]

[Table 1]

	Cationically polymerizable compound (mass parts)	Release component (mass parts)	Cationic polymerization initiator (mass parts)	Evaluation of curability of release agent layer	Evaluation of releasability from pressure sensitive adhesive sheet	Evaluation of releasability from ceramic green sheet	Surface free energy (mJ/m ²)
Example 1	100	1.0	4.0	○	○	○	29
Example 2	100	0.5	4.0	○	○	○	28
Example 3	100	1.5	4.0	○	○	○	32
Example 4	100	2.0	4.0	○	○	○	32
Example 5	100	1.0	3.5	○	○	○	31
Example 6	100	1.0	4.5	○	○	○	32
Comparative Example 1	100	1.0	0.0	×	—	—	—
Comparative Example 2	100	0.0	4.0	○	×	×	42

[0098]

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 releasability as compared with the release sheets according to Comparative Examples.

[Industrial applicability]

[0099]

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

production of a ceramic green sheet, etc.

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,
wherein the release agent layer is formed of a release agent composition that contains a cationically polymerizable compound, a release component, and a cationic polymerization initiator, wherein the cationically
10 polymerizable compound contains no polysiloxane skeleton,
wherein, in the release agent composition, a compounding amount of the cationically polymerizable compound is larger than each of a compounding amount of the release component and a compounding amount of the cationic
15 polymerization initiator,
wherein, in the release agent composition, the compounding amount of the cationically polymerizable compound is more than 50 mass% and 99.9 mass% or less.
- 20 2. The release sheet as recited in claim 1, wherein the cationically polymerizable compound is an epoxy compound.
3. The release sheet as recited in claim 2, wherein the epoxy compound has three or more epoxy groups in one
25 molecule.
4. The release sheet as recited in claim 2 or 3, wherein the epoxy compound has a molecular weight of 200 or more and 2,000 or less.
- 30 5. The release sheet as recited in any one of claims 1 to 4, wherein the release component comprises at least one selected from the group consisting of a silicone-based

release component, a fluorine-based release component, and a long-chain alkyl-based release component.

6. The release sheet as recited in any one of claims 1 to
5 5, wherein the release component has a reactive group that can react with the cationically polymerizable compound.

7. The release sheet as recited in claim 6, wherein the release component is reactive polyorganosiloxane.
10

8. The release sheet as recited in any one of claims 1 to 7, wherein surface free energy as measured on a surface of the release agent layer opposite to the base material is 25 mJ/m² or more and 35 mJ/m² or less.

15 9. The release sheet as recited in any one of claims 1 to 8, wherein the release sheet is used for a ceramic green sheet production process.

Abstract

RELEASE SHEET

5 A release sheet is provided, comprising a base
material and a release agent layer provided on at least one
surface side of the base material. The release agent layer
is formed of a release agent composition that contains a
cationically polymerizable compound, a release component,
10 and a cationic polymerization initiator. The cationically
polymerizable compound contains no polysiloxane skeleton.
In the release agent composition, the compounding amount of
the cationically polymerizable compound is larger than each
of the compounding amount of the release component and the
15 compounding amount of the cationic polymerization initiator.
This release sheet is novel one that has good releasability.

[No Suitable Figure]