

[Name of Document] Description
[Title of Invention] RELEASE FILM FOR CERAMIC GREEN
SHEET PRODUCTION PROCESS
[Technical Field]

5 [0001]

The present invention relates to a release film that is used in a ceramic green sheet production process.

[Background Art]

[0002]

10 To produce multi-layer ceramic products such as multi-layer ceramic capacitors and multi-layer ceramic substrates, it has conventionally been performed to mold ceramic green sheets and laminate the obtained plural ceramic green sheets to be fired.

15 [0003]

A ceramic green sheet is molded by coating a release film with ceramic slurry that contains ceramic materials such as barium titanate and titanium oxide. As the release film, a film base material treated for release with
20 silicone-based compound such as polysiloxane may be used. Such a release film is required to have releasability such that a thin ceramic green sheet molded on the release film can be released from the release film without breakage and other troubles.

25 [0004]

In recent years, as electronic devices are reduced in size and enhanced in performance, the multi-layer ceramic capacitors and multi-layer substrates are also reduced in size and increased in the number of lamination, so that the
30 ceramic green sheet is more and more reduced in its thickness. If the ceramic green sheet is reduced in thickness and the thickness after drying becomes 3 μm or less, for example, defects such as pinholes and thickness

irregularity may readily occur in the ceramic green sheet when the ceramic slurry is coated and dried. In addition, when the molded ceramic green sheet is released from the release film, troubles may readily occur such as breakage
5 of the ceramic green sheet due to reduction in its strength.

[0005]

To solve the former problem, Patent Literature 1 proposes to use a carrier film (release film) having a surface to which ceramic slurry is applied and of which a
10 maximum height R_{max} as defined by JIS B0601 is 0.2 μm or less.

[Prior Art Literature]

[Patent Literature]

[0006]

15 [Patent Literature 1] JP2003-203822A

[Summary of the Invention]

[Problems to be solved by the Invention]

[0007]

However, even when a release film having a defined
20 maximum height R_{max} as in Patent Literature 1 is used, it may not be possible to effectively prevent the occurrence of defects such as pinholes and thickness irregularity in a ceramic green sheet having a reduced thickness. In addition, when a ceramic green sheet having a reduced
25 thickness is released from the release film, troubles such as breakage of the ceramic green sheet may still occur.

[0008]

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 film for a ceramic green sheet production process which can prevent/suppress the occurrence of defects such as pinholes and thickness irregularity in a ceramic green sheet and which has

excellent releasability of a ceramic green sheet.

[Means for solving the Problems]

[0009]

To achieve the above object, first, the present
5 invention provides a release film for a ceramic green sheet
production process, the release film being characterized by
comprising a base material and a release agent layer
provided at one side of the base material, wherein: the
release agent layer comprises a cured material of a release
10 agent composition that contains an active energy ray
curable component and a silicone-based component; a surface
of the release agent layer at an opposite side to the base
material has an arithmetic average roughness (Ra) of 8 nm
or less and a maximum projection height (Rp) of 50 nm or
15 less; an elastic modulus measured by a nanoindentation test
of the release agent layer is 4.0 GPa or more; and a
surface of the base material at an opposite side to the
release agent layer has an arithmetic average roughness
(Ra) of 5 to 50 nm and a maximum projection height (Rp) of
20 30 to 500 nm (Invention 1).

[0009a] In one aspect, there is provided a release
film for a ceramic green sheet production process, the
release film comprising a base material and a release agent
layer provided at one side of the base material, wherein:

25 the release agent layer comprises a cured material of
a release agent composition that contains (meth)acrylic
ester and a silicone-based component;

a surface of the release agent layer at an opposite
side to the base material has an arithmetic average
30 roughness (Ra) of 8 nm or less and a maximum projection
height (Rp) of 50 nm or less;

an elastic modulus measured by a nanoindentation test
of the release agent layer is 4.0 GPa or more; and

a surface of the base material at an opposite side to
35 the release agent layer has an arithmetic average roughness

(Ra) of 5 to 50 nm and a maximum projection height (Rp) of 30 to 500 nm.

[0010]

According to the above invention (Invention 1), the
5 surface of the release agent layer is highly smooth mainly
due to the cured material of the active energy ray curable
component. Therefore, it is possible to effectively
prevent/suppress the occurrence of defects such as pinholes
and thickness irregularity in a ceramic green sheet. In
10 addition, due to that the release agent layer contains the
silicone-based component or its cured material and that the
elastic modulus of the release agent layer is defined as
above, a ceramic green sheet can be released in a normal
way from the release film for a ceramic green sheet
15 production process. Furthermore, due to that the rear

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surface of the base material has a predetermined roughness, it is possible to suppress the occurrence of defects in a ceramic green sheet due to roughness at the rear surface of the base material while effectively suppressing troubles
5 such as the occurrence of blocking, meandering at the time of feeding, and winding deviation at the time of winding.

[0011]

In the above invention (Invention 1), it is preferable that a mass fraction of the silicone-based component in the
10 release agent composition to a total mass of the active energy ray curable component and the silicone-based component is 0.7 to 5 mass% (Invention 2).

[0012]

In the above invention (Inventions 1, 2), it is
15 preferable that the silicone-based component comprises polyorganosiloxane having a reactive functional group (Invention 3).

[0013]

In the above invention (Inventions 1 to 3), it is
20 preferable that the active energy ray curable component comprises (meth)acrylic ester (Invention 4).

[0014]

In the above invention (Invention 4), it is preferable that the (meth)acrylic ester comprises (meth)acrylic ester
25 that has a trifunctional or more functional (meth)acryloyl group (Invention 5).

[0015]

In the above invention (Invention 5), it is preferable that the release agent layer has a thickness of 0.3 to 2 μm
30 (Invention 6).

[Advantageous Effect of the Invention]

[0016]

According to the release film for a ceramic green

sheet production process of the present invention, the surface of the release agent layer is highly smooth, so that it is possible to effectively prevent/suppress the occurrence of defects such as pinholes and thickness irregularity in a ceramic green sheet, and the releasability from a ceramic green sheet is also excellent.

[Brief Description of Drawing(s)]

[0017]

[FIG. 1] FIG. 1 is a cross-sectional view of a release film according to one embodiment of the present invention.

[Embodiments for Carrying out the Invention]

[0018]

Embodiments of the present invention will hereinafter be described.

As shown in FIG. 1, a release film for a ceramic green sheet production process (which may be referred simply to as a "release film", hereinafter) 1 according to the present embodiment comprises a base material 11 and a release agent layer 12 laminated on a first surface (upper surface in FIG. 1) of the base material 11.

[0019]

The base material 11 to be used in the release film 1 according to the present embodiment is not particularly limited, and may appropriately be selected from any of conventionally known ones. Examples of such base material 11 include films formed of plastic, such as polyethylene terephthalate, polyethylene naphthalate and other polyester, polypropylene, polymethylpentene and other polyolefin, polycarbonate, and ethylene-vinyl acetate copolymer, which may be a single layer, or may be multilayer of two or more layers of the same type or different types. Among them, polyester film is preferable, polyethylene terephthalate film is particularly preferable, and biaxial stretched

polyethylene terephthalate film is further preferable. When being fabricated and used, polyethylene terephthalate film is unlikely to generate dust and the like, and can effectively prevent troubles, such as ceramic slurry coating failure, due to dust and the like, for example.

[0020]

A first surface of the base material 11 may be subjected to surface treatment such as using oxidation method or primer treatment for the purpose of improving the interfacial adhesion with the release agent layer 12 to be provided on the first surface. 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 irradiation treatment. These surface treatment methods may be appropriately selected depending on the type of the base material film, and the corona discharge treatment method may preferably be used in view of the effect and the operability in general.

[0021]

The thickness of the base material 11 may ordinarily be 10 to 300 μm , preferably 15 to 200 μm , and particularly preferably 20 to 125 μm .

[0022]

An arithmetic average roughness (Ra) at the first surface of the base material 11 may preferably be 2 to 50 nm, and particularly preferably 5 to 30 nm. A maximum projection height (Rp) at the first surface of the base material 11 may preferably be 10 to 700 nm, and particularly preferably 30 to 500 nm. Adjusting the arithmetic average roughness (Ra) and the maximum projection height (Rp) at the first surface of the base material 11 within the above ranges may allow the

arithmetic average roughness (Ra) and the maximum projection height (Rp) at the surface of the release agent layer 12 to easily fall within the ranges to be described later.

5 [0023]

An arithmetic average roughness (Ra) at a second surface (surface at the opposite side to the first surface; lower surface in FIG. 1; which may be referred to as a "rear surface") of the base material 11 is 5 to 50 nm, and
10 may preferably be 10 to 30 nm. A maximum projection height (Rp) at the second surface of the base material 11 is 30 to 500 nm, and may preferably be 50 to 300 nm.

[0024]

If the arithmetic average roughness (Ra) of the second
15 surface of the base material 11 is less than 5 nm, the second surface will be excessively smooth, so that the second surface of the base material 11 and the highly smooth release agent layer 12 may closely contact to each other to readily cause blocking when the release film 1 is
20 wound. If the arithmetic average roughness (Ra) of the second surface of the base material 11 exceeds 50 nm, it will be difficult to allow the maximum projection height (Rp) of the second surface of the base material 11 to fall within the above preferable range.

25 [0025]

If the maximum projection height (Rp) at the second surface of the base material 11 exceeds 500 nm, the ceramic green sheet will be partially thin because the irregular profile of the second surface of the base material 11 in
30 close contact with the ceramic green sheet may be transferred to the ceramic green sheet when the ceramic green sheet is wound after being molded. In this case, there may be a risk of troubles due to short circuit when

those ceramic green sheets are laminated to manufacture capacitors. If the maximum projection height (R_p) of the second surface of the base material 11 is less than 30 nm, the second surface of the base material 11 will have less
5 irregularity so as to be flat, so that air may readily be involved into a surface at which the base material 11 contacts with a roll, such as during a process for forming the release agent layer 12. This may result in troubles such as that the base material 11 being carried meanders
10 and winding deviation occurs when the base material is wound into a roll-shape.

[0026]

When the arithmetic average roughness (R_a) and the maximum projection height (R_p) at the second surface of the
15 base material 11 are adjusted within the above ranges, winding deviation at the time of winding can effectively be suppressed. Therefore, the winding tension need not be increased, and it is thereby possible to suppress the deformation of the core portion and its periphery due to
20 the winding tension.

[0027]

The same layer as the release agent layer 12 to be described later, or a different layer from the release agent layer 12, maybe provided on the opposite surface to
25 the first surface of the base material 11. In these cases, the second surface of the base material 11 refers to a surface at the opposite side to the base material 11 side among surfaces of these layers.

[0028]

30 To obtain a film in which both of the maximum projection height (R_p) of the first surface of the base material 11 and the maximum projection height (R_p) of the second surface of the base material 11 are within the above

preferable ranges, the base material 11 to be used may be such that the maximum projection height (R_p) of the first surface of the base material 11 and the maximum projection height (R_p) of the second surface of the base material 11 are different, i.e., the front and rear surfaces of different roughness degrees, or the base material 11 may be such that the maximum projection height (R_p) of the first surface and the maximum projection height (R_p) of the second surface are substantially the same, i.e., the front and rear surfaces of the same roughness degree.

[0029]

The release agent layer 12 in the release film 1 according to the present embodiment is a cured material obtained by curing a release agent composition that contains: an active energy ray curable component; and a silicone-based component (the release agent composition is referred hereinafter to as a "release agent composition C"). According to the release agent composition C, the surface of the release agent layer 12 to be obtained can be highly smooth because recess portions that are present between the protrusions on the first surface of the base material 11 may be effectively filled mainly with the cured material of the active energy ray curable component. In addition, the surface of the release agent layer 12 can be imparted with appropriate releasability due to the silicone-based component or its cured material. Furthermore, since the coated film of the release agent composition C can be cured by irradiation of active energy ray when the release film 1 is produced, it is possible to suppress the occurrence of damages such as shrinkage and deformation of the base material compared to a case of using a heat curable release agent composition, for example.

[0030]

Conventional silicone resin-based release agent may easily follow a shape of the surface of the base material 11, and smoothing effect as in the release agent composition C cannot be obtained. Heretofore, in a certain resin film, particularly in a polyester-based film, a filler material might have to be added in order to impart slipping property of the surface and/or mechanical strength, but there have been limitations in reducing the density of protrusions having a large height due to such fillers by improving a method of producing a film. In contrast, the cured material of the active energy ray curable component is used to highly smoothen the surface of the release agent layer 12, as described above, thereby to reduce the density of protrusions having a large height at the surface of the release agent layer 12, and a release film 1 having a highly smooth surface can thus be obtained. As is known, a release agent layer formed using a conventional silicone resin-based release agent has a low elastic modulus and is readily to deform. Accordingly, when the molded ceramic green sheet is released, the release agent layer may deform to follow the ceramic green sheet thereby to increase the releasing force, so that the ceramic green sheet may not be released in a normal way.

[0031]

The active energy ray curable component in the release agent composition C is not particularly limited as long as it does not hinder the effect of the present invention and it is a component that can be cured by irradiation of active energy ray. The active energy ray curable component may be any of a monomer, oligomer, polymer, or mixture thereof. This active energy ray curable component may preferably be (meth)acrylic ester. The (meth)acrylic ester as used herein means both acrylic ester and methacrylic

ester. The same applies to other similar terms. When the main component of the release agent layer 12 is a cured material of (meth)acrylic ester-based component, repellency to the ceramic slurry may not be caused on the release agent layer 12.

[0032]

The (meth)acrylic ester may preferably be at least one kind selected from polyfunctional (meth)acrylate monomers and (meth)acrylate oligomers, particularly preferably at least one kind selected from trifunctional or more functional (meth)acrylate monomers and (meth)acrylate oligomers, and further preferably at least one kind selected from trifunctional or more functional (meth)acrylate monomers. Being trifunctional or more functional allows the release agent composition C to have excellent curability and also allows the surface of the obtained release agent layer 12 to have more excellent releasability.

[0033]

Examples of the polyfunctional (meth)acrylate monomer include trimethylolpropane tri(meth)acrylate, dipentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, propionic acid-modified dipentaerythritol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, propylene oxide-modified trimethylolpropane tri(meth)acrylate, tris((meth)acryloxyethyl)isocyanurate, propionic acid-modified dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, and caprolactone-modified dipentaerythritol hexa(meth)acrylate. These may be solely used, or two or more kinds may be used in combination.

[0034]

Examples of the polyfunctional (meth)acrylate oligomer include polyester acrylate-based oligomer, epoxy acrylate-based oligomer, urethane acrylate-based oligomer, polyether acrylate-based oligomer, polybutadiene acrylate-based oligomer, and silicone acrylate-based oligomer.

[0035]

The polyester acrylate-based oligomer can be obtained, for example, by using polyester oligomer which is obtained by condensation of polycarboxylic acid and polyalcohol and has hydroxyl groups at both ends and esterifying the hydroxyl groups with (meth)acrylic acid, or using oligomer obtained by addition of alkylene oxide to polycarboxylic acid and esterifying the hydroxyl groups at ends of the oligomer with (meth)acrylic acid.

[0036]

The epoxy acrylate-based oligomer can be obtained, for example, by esterification of an oxirane ring of relatively low molecular weight bisphenol-type epoxy resin or novolak-type epoxy resin with (meth)acrylic acid. There may also be used carboxyl-modified-type epoxy acrylate-based oligomer which is partially modified epoxy acrylate-based oligomer with dibasic carboxylic acid anhydride.

[0037]

The urethane acrylate-based oligomer can be obtained, for example, by esterifying polyurethane oligomer with (meth)acrylic acid. The polyurethane oligomer may be obtained by reaction of polyether polyol or polyester polyol and polyisocyanate.

[0038]

The polyether acrylate-based oligomer can be obtained, for example, by esterifying hydroxyl groups of polyether polyol with (meth)acrylic acid.

[0039]

The above polyfunctional (meth)acrylate monomers and polyfunctional (meth)acrylate oligomers may be used solely in one kind, or two or more kinds may be used in combination. One or more polyfunctional (meth)acrylate
5 monomers and one or more polyfunctional (meth)acrylate oligomers may be used in combination.

[0040]

The release agent composition C may include one of the active energy ray curable components solely, or two or more
10 of them in combination.

[0041]

The silicone-based component in the release agent composition C is not particularly limited as long as it does not hinder the effect of the present invention and it
15 is a component that can impart desired releasability to the surface of the release agent layer 12. There may be used polyorganosiloxane, preferably polyorganosiloxane having a reactive functional group, and particularly preferably polydimethylsiloxane having a reactive functional group.
20 When the polyorganosiloxane having a reactive functional group is used, irradiation of active energy ray or other reaction step (e.g., heating step) may cause the reactive functional group to react so that the polyorganosiloxane (silicone-based component) will be incorporated in the
25 cross-linked structure and fixed. This suppresses the silicone-based component in the release agent layer 12 from transferring and migration to the ceramic green sheet molded on the release agent layer 12.

[0042]

30 The reactive functional group may be introduced to one end or to each of both ends of polyorganosiloxane or to a side chain. Examples of the reactive functional group include (meth)acryloyl group, vinyl group, maleimide group,

epoxy group, carboxyl group, isocyanate group, and hydroxyl group, among which (meth)acryloyl group, vinyl group and maleimide group are preferable because they can be cured concurrently with curing of the above active energy ray curable component (when active energy ray is irradiated). It may be preferable that at least two reactive functional groups are introduced in one molecule of polyorganosiloxane. Two or more kinds of these reactive functional groups may also be introduced in one molecule of polyorganosiloxane.

10 [0043]

The release agent composition C may include, one of the silicone-based components solely or two or more of them in combination.

[0044]

15 A mass fraction of the silicone-based component in the release agent composition C to a total mass of the active energy ray curable component and the silicone-based component may preferably be 0.7 to 5 mass%, and particularly preferably 1.0 to 2.5 mass%. By adjusting the mass fraction of the silicone-based component within the above range, ceramic slurry can be applied to the surface of the release agent layer 12 without being repelled, and the ceramic green sheet thus molded can readily be released without breakage, so that the release agent layer 12 has excellent releasability. If the mass fraction of the silicone-based component is less than 0.7 mass%, there may be a risk that the release agent layer 12 cannot exert sufficient releasing performance. If the mass fraction of the silicone-based component exceeds 5 mass%, there may be a risk that the release agent layer 12 is difficult to be cured and the elastic modulus of the release agent layer 12 is unduly low. There may also be a risk that, when ceramic slurry is applied to the surface of the release agent layer

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12, the ceramic slurry tends to be repelled. In addition, the release agent layer 12 will be difficult to be cured so that sufficient releasability may not be obtained.

[0045]

5 A mass fraction of the total mass of the active energy ray curable component and the silicone-based component to the whole mass of a solid content contained in the release agent composition C may preferably be 85 mass% or more, and particularly preferably 90 mass% or more. The mass
10 fraction of the total mass of the active energy ray curable component and the silicone-based component being within the above range allows the formed release agent layer 12 to have a highly smooth surface and also allows the release agent composition C to readily have sufficient curability.

15 [0046]

 When ultraviolet ray is used as the active energy ray to irradiate the release agent composition C, it may be preferable that the release agent composition C further contains photopolymerization initiator. Containing the
20 photopolymerization initiator may allow the active energy ray curable component (and the silicone-based component) to efficiently be cured; and may also reduce the time required for polymerization and curing, and the amount of irradiating light ray.

25 [0047]

 Specific examples of the photopolymerization initiator include benzophenone, acetophenones, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin benzoic acid, benzoin
30 methyl benzoate, benzoin dimethyl ketal, 2,4-diethylthioxanthone, 1-hydroxycyclohexyl phenyl ketone, benzyl diphenyl sulfide, tetramethyl thiuram monosulfide, azobisisobutyronitrile, benzyl, dibenzyl, diacetyl, β -

chloroanthraquinone, (2,4,6-trimethyl benzyl
diphenyl)phosphine oxide, and 2-benzothiazole-N,N-
diethyldithiocarbamate. In particular, preferable examples
for an excellent surface curability include 2-hydroxy-1-{4-
5 [4-(2-hydroxy-2-methyl-propionyl)-benzil]-phenyl}-2-
methylpropane-1-one, 1-hydroxy-cyclohexyl-phenyl-ketone, 2-
hydroxy-2-methyl-1-phenyl-propane-1-one, and 2-methyl-1-[4-
(methylthio)phenyl]-2-morpholinopropane-1-one. Among which
2-hydroxy-2-methyl-1-phenyl-propane-1-one and 2-methyl-1-
10 [4-(methylthio)phenyl]-2-morpholinopropane-1-one are
particularly preferable. These may be solely used, or two
or more kinds may be used in combination.

[0048]

The photopolymerization initiator may preferably be
15 used with an amount within a range of 1 to 20 mass parts,
in particular 3 to 15 mass parts, to the total 100 mass
parts of the active energy ray curable component and an
active energy ray curable silicone-based component (e.g.,
polyorganosiloxane having (meth)acryloyl group or groups,
20 vinyl group or groups or maleimide group or groups as
reactive functional group or groups).

[0049]

The release agent (including the release agent
composition C) that constitutes the release agent layer 12
25 may contain, as necessary, silica, antistatic agent, dye,
pigment and/or other additives. These additives may
preferably be used with an amount within a range of 0.1 to
50 mass parts to the total 100 mass parts of the active
energy ray curable component and the silicone component.

30 [0050]

The thickness of the release agent layer 12 may
preferably be 0.3 to 2 μm , and particularly preferably 0.5
to 1.5 μm . If the thickness of the release agent layer 12

is less than 0.3 μm , the smoothness of the surface of the release agent layer 12 will be insufficient, so that pinholes and/or thickness irregularity may readily occur in the ceramic green sheet. If the thickness of the release agent layer 12 exceeds 2 μm , there may be a risk that curling readily occurs in the release film 1 due to the cure shrinkage of the release agent layer 12. In addition, when the release film 1 is wound into a roll-shape, there may be a risk that winding failure is caused because blocking with the second surface of the base material 11 may readily occur and/or that the electrostatic charge amount increases at the time of unwinding so that foreign materials may easily be attached thereto.

[0051]

The release agent layer 12 can be formed by: applying a releasing agent solution, which contains the releasing agent and desired diluent and other additives, to the first surface of the base material 11; drying it as necessary; and curing it using irradiation of an active energy ray. When the reactive functional group or groups of the silicone-based component are those which react by heat, the drying at that time may cause the reaction so that the silicone-based component can be incorporated in the cross-linked structure. Examples of application method of the releasing agent solution to be used include gravure-coating method, bar-coating method, spray-coating method, spin-coating method, knife-coating method, roll-coating method, and die-coating method.

[0052]

As the active energy ray, there may ordinarily be used ultraviolet ray, electron ray or the like. The irradiation amount of the active energy ray differs depending on the type of energy ray, but may preferably be 50 to 1000 mJ/cm^2 ,

and particularly preferably 100 to 500 mJ/cm² as an amount of light in a case of ultraviolet ray. In a case of electron ray, the amount may preferably be about 0.1 to 50 kGy.

5 [0053]

The irradiation of the above active energy ray causes the active energy ray curable component in the release agent composition C to cure. When the silicone-based component in the release agent composition C has active
10 energy ray curable reactive group or groups, the silicone-based component is also cured. This allows the release agent layer 12 to be formed which is highly smooth and unlikely to repel ceramic slurry and has excellent releasability of ceramic green sheet.

15 [0054]

In the release film 1 according to the present embodiment, a surface of the release agent layer 12 (upper surface in FIG. 1; surface at the opposite side to the base material 11) on which ceramic slurry is to be molded has an
20 arithmetic average roughness (Ra) of 8 nm or less and a maximum projection height (Rp) of 50 nm or less. The arithmetic average roughness (Ra) and the maximum projection height (Rp) as used herein refer to values measured in conformity with JIS B0601-1994 (in an exemplary
25 test, measured using a surface roughness measuring machine SV3000S4 (stylus type) available from Mitutoyo Corporation).

[0055]

By adjusting the arithmetic average roughness (Ra) and the maximum projection height (Rp) of the surface of the
30 release agent layer 12 within such ranges as described above, the surface of the release agent layer 12 can sufficiently be highly smooth to exhibit good sheet moldability. For example, even when a thin film ceramic

green sheet having a thickness of less than 1 μm is molded on the surface of the release agent layer 12, defects such as pinholes and thickness irregularity are unlikely to occur in the thin film ceramic green sheet. In addition, by adjusting the arithmetic average roughness (Ra) and the maximum projection height (Rp) of the surface of the release agent layer 12 within such ranges as described above, the releasability of a ceramic green sheet can be excellent such that, even when a thin film ceramic green sheet having a thickness of less than 1 μm , for example, is released from the release agent layer 12, the ceramic green sheet is unlikely to be broken. These excellent effects cannot be obtained merely by defining the maximum height (Rmax) of the release agent layer 12 as in Patent Literature 1.

[0056]

The arithmetic average roughness (Ra) of the surface of the release agent layer 12 may preferably be 6 nm or less, and particularly preferably 4 nm or less. The maximum projection height (Rp) of the surface of the release agent layer 12 may preferably be 40 nm or less, and particularly preferably 30 nm or less.

[0057]

An elastic modulus measured by a nanoindentation test of the release agent layer 12 is 4.0 GPa or more, and may preferably be 4.2 GPa or more. Due to the elastic modulus of the release agent layer 12 is 4.0 GPa or more, the release agent layer 12 is difficult to deform, so that the release agent layer 12 is unlikely to follow the ceramic green sheet when the ceramic green sheet is released from the release agent layer 12. This allows the ceramic green sheet to be released in a normal way. If the elastic modulus of the release agent layer 12 is less than 4.0 GPa,

then, when the ceramic green sheet is released from the release agent layer 12, the release agent layer may deform to follow the ceramic green sheet thereby to increase the releasing force, so that the ceramic green sheet may not be released in a normal way. Such a high elastic modulus as described above can be achieved by using the release agent composition C to form the release agent layer 12 and appropriately selecting and setting the type and the compounding amount of the active energy ray curable component, but would not be achieved in a case of using a conventional silicone resin-based release agent.

[0058]

In the present description, measurement of the elastic modulus of the release agent layer may be performed by a nanoindentation test under an atmosphere of 23°C. Specifically, the nanoindentation test may be performed such that: the release film 1 is cut into a size of 10 mm×10 mm; a glass plate is adhered to an aluminum stage; the rear surface side of the base material of the release film 1 is fixed to the glass plate using two-component-type epoxy adhesive; and the elastic modulus is measured using a microhardness evaluation apparatus (in an exemplary test, measured using "Nano Indenter SA2" available from MTS Systems Corporation).

[0059]

By using the release film 1 as described above in a production process for a ceramic green sheet, it is possible to effectively prevent/suppress the occurrence of defects such as pinholes and thickness irregularity in the obtained ceramic green sheet. Moreover, also when the ceramic green sheet is released from the release film 1, it is possible to effectively prevent/suppress the occurrence of troubles such as breakage of the ceramic green sheet.

[0060]

It should be appreciated that the embodiments heretofore explained are described to facilitate understanding of the present invention and are not
5 described to limit the present invention. Therefore, it is 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.

[0061]

10 For example, one or more other layers may be present between the base material 11 and the release agent layer 12 and/or on the second surface of the base material 11.

[Examples]

[0062]

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

[0063]

20 <Example 1>

A polyethylene terephthalate (PET) film (thickness of 31 μm) having front and rear surfaces of the same roughness degree was prepared as a base material. Both surfaces of this PET film have the arithmetic average roughness (Ra) of
25 29 nm and the maximum projection height (Rp) of 257 nm. Measuring method of the arithmetic average roughness (Ra) and the maximum projection height (Rp) at both surfaces of the PET film is the same as the measuring method of the arithmetic average roughness (Ra) and the maximum
30 projection height (Rp) at the surface of the release agent layer to be described later (the same applies to the following examples).

[0064]

The release agent composition C, comprising: 99.0 mass parts of dipentaerythritol hexaacrylate (A-DPH, solid content of 100 mass%, available from Shin Nakamura Chemical Co., Ltd.) as the active energy ray curable component; 1.0 mass part of polyether-modified acryloyl group-containing polydimethylsiloxane (BYK-3500, solid content of 100 mass%, available from BYK Japan KK) as the silicone-based component; and 5.0 mass parts of 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one (IRGACURE907 available from BASF) as the photopolymerization initiator, was diluted using a mixed liquid of isopropyl alcohol and methyl ethyl ketone (mixture mass ratio of 3:1), and the diluted solution was used as a release agent solution (solid content of 20 mass%). This release agent solution was applied to one surface (first surface) of the above base material using a bar coater so that the thickness of the release agent layer after curing would be 0.97 μm , and dried at 80°C for 1 minute. Thereafter, ultraviolet ray was irradiated (accumulated light amount: 250 mJ/cm^2) to cure the release agent composition C to form the release agent layer, and the film thus obtained was used as a release film. The thickness of the release agent layer is a result measured using a method of measurement to be described later (the same applies to the following examples).

[0065]

<Example 2>

A release film was prepared in the same manner in Example 1 except that the active energy ray curable component was 15.0 mass parts of dipentaerythritol hexaacrylate (A-DPH, solid content of 100 mass%, available from Shin Nakamura Chemical Co., Ltd.) and 84.0 mass parts of trimethylolpropane triacrylate (A-TMPT, solid content of

100 mass%, available from Shin Nakamura Chemical Co., Ltd).

[0066]

<Examples 3 and 4>

Release films were prepared in the same manner in
5 Example 1 except that the release agent layer had a
thickness listed in Table 1.

[0067]

<Example 5>

A release film was prepared in the same manner in
10 Example 1 except that the release agent composition C
contained the silicone-based component in the mass ratio
listed in Table 1.

[0068]

<Comparative Example 1>

15 A release film was prepared in the same manner in
Example 1 except that the release agent composition C did
not contain a silicone-based component.

[0069]

<Comparative Examples 2 to 4>

20 Release films were prepared in the same manner in
Example 1 except that the release agent layer had a
thickness listed in Table 1.

[0070]

<Comparative Example 5>

25 A release film was prepared in the same manner in
Example 1 except that trimethylolpropane triacrylate (A-
TMPT, solid content of 100 mass%, available from Shin
Nakamura Chemical Co., Ltd) was used instead of the active
energy ray curable component in Example 1.

30 [0071]

<Comparative Example 6>

A release film was prepared in the same manner in
Example 1 except that the release agent composition C

contained the silicone-based component in the mass ratio listed in Table 1.

[0072]

<Comparative Example 7>

5 A release agent solution having a solid content of 5.0 mass% was prepared by diluting 100 mass parts of a heat curable addition reaction-type silicone (KS-847H available from Shin-Etsu Chemical Co., Ltd.) using toluene and mixing thereto 2 mass parts of platinum catalyst (CAT-PL-50T
10 available from Shin-Etsu Chemical Co., Ltd).

[0073]

The release agent solution thus obtained was applied uniformly to one surface (first surface) of the same base material as that in Example 1 so that the thickness of the
15 release agent layer to be formed after drying would be 0.3 μm , and dried at 140°C for 1 minute to form the release agent layer. The film thus obtained was used as a release film.

[0074]

20 <Comparative Examples 8 and 9>

Release films were prepared in the same manner in Comparative Example 7 except that the release agent layer had a thickness listed in Table 1.

[0075]

25 <Comparative Example 10>

A PET film (thickness of 38 μm) having front and rear surfaces of the same roughness degree was prepared as the base material. At both surfaces of this PET film, the arithmetic average roughness (Ra) was 42 nm and the maximum
30 projection height (Rp) was 619 nm. A release film was prepared in the same manner in Example 1 except for using the above base material as a base material.

[0076]

<Exemplary Test 1> (Measurement of thickness of release agent layer)

The thickness (μm) of the release agent layer of the release film obtained in each of the examples and the comparative examples was measured using a reflective film thickness meter (F20 available from Filmetrics, Inc). Specifically, the release film obtained in each of the examples and the comparative examples was cut into 100×100 mm; the release film was then installed on the film thickness meter so that the opposite surface to a surface to be measured would be at the side of a suction stage; thicknesses were measured at ten locations at the surface of the release agent layer; and the average value was calculated as the thickness of the release agent layer. Results are listed in Table 1.

[0077]

<Exemplary Test 2> (Measurement of surface roughness of release agent layer)

A double coated tape was applied to a glass plate, and the release film obtained in each of the examples and the comparative examples was fixed to the glass plate via the above double coated tape so that the opposite surface to a surface to be measured would be at the side of the glass plate. The arithmetic average roughness (R_a ; nm) and the maximum projection height (R_p ; nm) at the surface of the release agent layer of the release film were measured in conformity with JIS B0601-1994 using a surface roughness measuring machine (SV-3000S4, stylus type, available from Mitutoyo Corporation). Results are listed in Table 1.

[0078]

<Exemplary Test 3> (Measurement of elastic modulus)

The release film obtained in each of the examples and the comparative examples was cut into a size of 10 mm×10

mm; a glass plate was adhered to an aluminum stage; and the rear surface of the base material of the cut release film was then fixed to the glass plate using two-component-type epoxy adhesive. Thereafter, nanoindentation test was
5 performed to measure the elastic modulus of the release agent layer of the above release film using a microhardness evaluation apparatus (Nano Indenter SA2 available from MTS Systems Corporation) under a condition of a maximum indenting depth of an indenter of 100 nm, a strain speed of
10 0.05 sec^{-1} , a displacement amplitude of 2 nm, a vibration frequency of 45Hz, and an atmosphere of 23°C. Results are listed in Table 1.

[0079]

<Exemplary Test 4> (Evaluation of curability of release
15 agent layer)

For the release film obtained in each of the examples and the comparative examples, the surface of the release agent layer was polished reciprocally 10 times with a load of 1 kg/cm^2 using a waste cloth (BEMCOT AP-2 available from
20 OZU CORPORATION) involving 3 ml of methyl ethyl ketone. Thereafter, the surface of the release agent layer was visually observed, and the curability of the release agent layer was evaluated in accordance with the following criteria:

25 A... There was no dissolution and dropping off of the release agent layer;

B... There was observed partial dissolution of the release agent layer; and

C... The release agent layer was completely dissolved
30 and dropped off from the base material.

Results are listed in Table 1.

[0080]

<Exemplary Test 5> (Evaluation of curling)

The release film obtained in each of the examples and the comparative examples was cut into 200×200 mm and then placed on a flat glass plate so that the base material would be at the side of the glass plate. Subsequently,
5 another glass plate of 100×100 mm was placed on the center of the release agent layer of the release film. Thereafter, a height from the upper surface of the lower glass plate to the top of each corner portion of the release film was measured and evaluated in accordance with the following
10 criteria:

A... The sum of the heights of the corner portions was less than 50 mm;

B... The sum of the heights of the corner portions was 50 mm or more and less than 100 mm; and

15 C... The sum of the heights of the corner portions was 100 mm or more.

Results are listed in Table 1.

[0081]

<Exemplary Test 6> (Evaluation of blocking property)

20 The release film obtained in each of the examples and the comparative examples was wound up into a roll-shape having a width of 400 mm and a length of 5000 m. After this release film roll was kept under an environment of 40°C and a humidity of 50% or less for 30 days, the
25 appearance of the release film roll itself was visually observed, and the blocking property was evaluated in accordance with the following criteria:

A... There was no change from the time when the release film was wound up into a roll-shape (no blocking);

30 B... Change in color due to close contact between films was observed in a half region or less in the width direction (slight blocking occurred); and

C... Change in color due to close contact between films

was observed over a half region in the width direction (blocking occurred).

Results are listed in Table 1.

[0082]

- 5 <Exemplary Test 7> (Evaluation of coating ability of slurry)

Ceramic slurry was prepared by adding 135 mass parts of a mixed liquid of toluene and ethanol (mass ratio of 6:4) to 100 mass parts of barium titanate powder (BaTiO_3 ; 10 BT-03 available from SAKAI CHEMICAL INDUSTRY CO., LTD), 8 mass parts of polyvinyl butyral (S-LEC B·K BM-2 available from SEKISUI CHEMICAL CO., LTD.) as binder, and 4 mass parts of dioctyl phthalate (dioctyl phthalate Cica first grade available from KANTO CHEMICAL CO., INC.) as 15 plasticizer, and mixing and dispersing them using a ball mill.

[0083]

The above ceramic slurry was coated on the surface of the release agent layer of the release film obtained in 20 each of the examples and comparative examples across a width of 250 mm and a length of 10 m using a die coater so that the film thickness after drying would be 1 μm , and thereafter dried at 80°C for one minute using a dryer. For the release film thus molded thereon with the ceramic green 25 sheet, the whole surface of the coated ceramic green sheet was visually examined under fluorescent light illuminated from the side of the release film, and the coating ability of slurry was evaluated in accordance with the following criteria:

- 30 A... No pinhole occurred in the ceramic green sheet;
B... One to five pinholes occurred in the ceramic green sheet; and
C... Six or more pinholes occurred in the ceramic green

sheet.

Results are listed in Table 1.

[0084]

<Exemplary Test 8> (Evaluation of releasability)

5 A ceramic green sheet was molded on the surface of the
release agent layer of the release film in the same
procedure as that in Exemplary Test 7, and the ceramic
green sheet was punched out into 200 mm×200 mm so that the
release film would not be punched out. Subsequently, the
10 sheet release mechanism of a green sheet laminator was
utilized to suction the green sheet thus punched out onto a
vacuum suction stage to release it from the release film.
The releasability of the ceramic green sheet at that time
was evaluated in accordance with the following criteria:

15 A... The ceramic green sheet was able to be smoothly
released without being broken, and the ceramic green sheet
did not remain on the release agent layer;

 B... The ceramic green sheet was able to be released,
but less smoothly, without break, and the ceramic green
20 sheet did not remain on the release agent layer; and

 C... The ceramic green sheet was broken, or was not able
to be released.

Results are listed in Table 1.

[0085]

25 <Exemplary Test 9> (Evaluation of defects at surface of
release agent layer)

 A coating liquid was prepared by dissolving a
polyvinyl butyral resin into a mixed liquid of toluene and
ethanol (mass ratio of 6:4). The coating liquid was coated
30 on the release agent layer of the release film obtained in
each of the examples and comparative examples so that the
thickness after drying would be 1 μm , and dried at 80°C for
one minute to form a polyvinyl butyral resin layer.

Thereafter, a polyester tape was applied to the surface of the polyvinyl butyral resin layer.

[0086]

Subsequently, the polyester tape was used to remove
5 the release film from the polyvinyl butyral resin layer,
and the number of recesses at the surface of the polyvinyl
butyral resin layer that had been in contact with the
release agent layer of the release film was counted.
Specifically, observation was performed at $\times 50$ magnitude in
10 PSI mode using an optical interferometry-type surface
profile observation apparatus (WYKO-1100 available from
Veeco Instruments Inc.); the number of recesses having a
depth of 150 nm or more was counted on the basis of the
obtained surface profile image within a coverage of
15 $91.2 \times 119.8 \mu\text{m}$; and evaluation of defects at the surface of
the release agent layer was performed in accordance with
the following criteria:

A... The number of recesses was zero;

B... The number of recesses was 1 to 5; and

20 C... The number of recesses was 6 or more.

With regard to those of which the evaluation was "C" in the
previously-described test for evaluation of releasability,
this test was not performed because a sample sufficient to
perform this test was not able to be obtained.

25 Results are listed in Table 1.

[0087]

If a capacitor is produced using a ceramic green sheet
having recesses as above, the obtained capacitor will be
such that a short circuit due to deterioration in
30 withstanding voltage may readily occur.

[0088]

<Exemplary Test 10> (Evaluation of defects at rear surface
of base material)

A coating liquid was prepared by dissolving a polyvinyl butyral resin into a mixed liquid of toluene and ethanol (mass ratio of 6:4). The coating liquid was coated on a PET film having a thickness of 50 μm so that the
5 thickness after drying would be 1 μm , and dried at 80°C for one minute to form a polyvinyl butyral resin layer. The release film obtained in each of the examples and comparative examples was laminated to the surface of the polyvinyl butyral resin layer so that the rear surface of
10 the base material of the release film would be in contact with the above polyvinyl butyral resin layer. This laminate was cut into 100 mm×100 mm and thereafter pressed under a load of 5 kg/cm², so that the shape of projection at the rear surface of the base material of the release
15 film was transferred to the polyvinyl butyral resin layer.

[0089]

Subsequently, the release film was removed from the polyvinyl butyral resin layer, and the number of recesses at the surface of the polyvinyl butyral resin layer that
20 had been in contact with the rear surface of the base material of the release film was counted. Specifically, observation was performed at ×50 magnitude in PSI mode using an optical interferometry-type surface profile observation apparatus (WYKO-1100 available from Veeco
25 Instruments Inc.); the number of recesses having a depth of 500 nm or more was counted on the basis of the obtained surface profile image within a coverage of 91.2×119.8 μm ; and evaluation of defects at the rear surface of the base material was performed in accordance with the following
30 criteria:

- A... The number of recesses was zero;
- B... The number of recesses was 1 to 5; and
- C... The number of recesses was 6 or more.

Results are listed in Table 1.

[0090]

If a capacitor is produced using a ceramic green sheet having recesses as above, the obtained capacitor will be such that a short circuit due to deterioration in withstanding voltage may readily occur.

[0091]

[Table 1]

	Thickness of release agent layer (μm)	Mass ratio of silicone-based component (mass%)	Surface roughness (nm)				Elastic modulus of release agent layer (GPa)	Evaluation of curability	Evaluation of curling	Evaluation of blocking property	Evaluation of coating ability of slurry	Evaluation of releasability	Evaluation of defects at surface of release agent layer	Evaluation of defects at rear surface of base material
			Surface of release agent layer		Rear surface of base material									
			Ra	Rp	Ra	Rp								
Example 1	0.97	1.0	3	17	29	257	5.4	A	A	A	A	A	A	A
Example 2	0.97	1.0	3	17	29	257	4.2	A	A	A	A	A	A	A
Example 3	0.48	1.0	5	49	29	257	5.4	A	A	A	A	A	A	A
Example 4	3.00	1.0	3	11	29	257	5.4	A	C	A	A	A	A	A
Example 5	0.97	0.5	3	17	29	257	5.4	A	A	A	A	B	A	A
Comparative Example 1	0.97	-	4	19	29	257	5.5	A	A	A	A	C	-	A
Comparative Example 2	0.10	1.0	13	147	29	257	5.4	A	A	A	A	B	C	A
Comparative Example 3	0.20	1.0	11	102	29	257	5.4	A	A	A	A	B	C	A
Comparative Example 4	0.25	1.0	9	62	29	257	5.4	A	A	A	A	B	C	A
Comparative Example 5	0.97	1.0	3	17	29	257	3.8	A	A	A	A	C	-	A
Comparative Example 6	0.97	7.5	3	17	29	257	3.6	C	A	B	B	B	A	A
Comparative Example 7	0.30	-	29	241	29	257	0.4	A	A	B	B	B	C	A
Comparative Example 8	0.60	-	26	219	29	257	0.4	A	A	C	C	C	-	A
Comparative Example 9	1.00	-	24	202	29	257	0.4	A	A	C	C	C	-	A
Comparative Example 10	0.97	1.0	7	49	42	619	5.4	A	A	A	A	A	A	C

10

[0092]

As apparent from Table 1, the release films obtained in the examples were such that no defect occurred due to the surface of the release agent layer and no defect occurred due to the rear surface of the base material, and had excellent releasability of ceramic green sheets.

[Industrial Applicability]

[0093]

The release film for a ceramic green sheet production

15

process according to the present invention is suitable for molding a thin film ceramic green sheet, in particular, having a thickness of 1 μm or less.

[Description of Reference Numerals]

5 [0094]

1... Release film

11... Base material

12... Release agent layer

[Name of Document] Claims

[Claim 1]

5 A release film for a ceramic green sheet production process, the release film comprising a base material and a release agent layer provided at one side of the base material, wherein:

 the release agent layer comprises a cured material of a release agent composition that contains (meth)acrylic ester and a silicone-based component;

10 a surface of the release agent layer at an opposite side to the base material has an arithmetic average roughness (Ra) of 8 nm or less and a maximum projection height (Rp) of 50 nm or less;

 an elastic modulus measured by a nanoindentation test
15 of the release agent layer is 4.0 GPa or more; and

 a surface of the base material at an opposite side to the release agent layer has an arithmetic average roughness (Ra) of 5 to 50 nm and a maximum projection height (Rp) of 30 to 500 nm.

20 [Claim 2]

 The release film for a ceramic green sheet production process as recited in claim 1, wherein a mass fraction of the silicone-based component in the release agent composition to a total mass of the (meth)acrylic ester and
25 the silicone-based component is 0.7 to 5 mass%.

[Claim 3]

 The release film for a ceramic green sheet production process as recited in claim 1 or 2, wherein the silicone-based component comprises polyorganosiloxane having a
30 reactive functional group.

[Claim 4]

The release film for a ceramic green sheet production process as recited in any one of claims 1 to 3, wherein the (meth)acrylic ester comprises (meth)acrylic ester that has
5 a trifunctional or more functional (meth)acryloyl group.

[Claim 5]

The release film for a ceramic green sheet production process as recited in any one of claims 1 to 4, wherein the release agent layer has a thickness of 0.3 to 2 μm .

RELEASE FILM FOR CERAMIC GREEN SHEET PRODUCTION PROCESS

Abstract

A release film (1) for a ceramic green sheet
5 production process is provided. The release film (1)
comprises a base material (11) and a release agent layer
(12) provided at one side of the base material (11). The
release agent layer (12) comprises a cured material of a
release agent composition. The release agent composition
10 contains an active energy ray curable component and a
silicone-based component. A surface of the release agent
layer (12) at the opposite side to the base material (11)
has an arithmetic average roughness (Ra) of 8 nm or less
and a maximum projection height (Rp) of 50 nm or less. An
15 elastic modulus measured by a nanoindentation test of the
release agent layer (12) is 4.0 GPa or more. A surface of
the base material (11) at the opposite side to the release
agent layer (12) has an arithmetic average roughness (Ra)
of 5 to 50 nm and a maximum projection height (Rp) of 30 to
20 500 nm. According to the release film (1) for a ceramic
green sheet production process, it is possible to
effectively prevent/suppress the occurrence of defects such
as pinholes and thickness irregularity in a ceramic green
sheet, and the releasability of a ceramic green sheet is
25 also excellent.

Fig. 1