

[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 process for producing a ceramic green sheet.

[Background Art]

[0002]

10 To produce laminated ceramic products such as laminated ceramic capacitors and multilayer ceramic substrates, it has conventionally been performed to form ceramic green sheets, laminate the obtained ceramic green sheets, and fire them.

15 [0003]

Each ceramic green sheet may be formed by coating a release film with a ceramic slurry that contains ceramic materials such as barium titanate and titanium oxide. The release film is required to have releasability such that
20 the release film can be released from the thin ceramic green sheet, which is formed on the release film, by moderate release force without crack, breakage, and other troubles in the ceramic green sheet.

[0004]

25 The release film is generally composed of a base material and a release agent layer provided on one surface of the base material. Materials of existing release agent layers include ultraviolet curable compounds. Such a release agent layer may be formed by coating a base
30 material with a release agent composition that contains an ultraviolet curable compound and irradiating the composition with ultraviolet rays to cure it. However, some types of ultraviolet curable compounds may be

inhibited from curing due to oxygen. When such a type of ultraviolet curable compound is used, curing may be insufficient in the vicinity of the surface of the release agent layer opposite to the base material (surface in
5 contact with the ceramic slurry/ceramic green sheet, which may be referred to as a "release surface," hereinafter). Insufficient curing of the release agent layer will deteriorate the elasticity of the release agent layer. This may result in the increased release force required
10 when the release film is released from the ceramic green sheet which is formed on the release surface.

[0005]

Patent Literature 1 discloses a release film provided with a release agent layer that contains a thermoset
15 compound, such as a melamine resin, and a polysiloxane (polyorganosiloxane). In this release film, the release agent layer contains polyorganosiloxane and the above release force can therefore be reduced to some extent. Moreover, the release agent layer can be cured without
20 inhibition due to oxygen as described above because the melamine resin is condensed by heating. It is thus possible to avoid the previously-described problems which are specific to the case of using an ultraviolet curable compound.

25 [0006]

In general, the "melamine resin" refers to a mixture that contains at least either of two or more types of melamine compounds and a polynuclear substance obtained by condensing one or more types of melamine compounds. In the
30 present description, the term "melamine resin" shall refer to the above mixture or an aggregate of one type of a melamine compound. In the present description, a product obtained by curing the melamine resin shall be referred to

as a "melamine cured product."

[Prior Art Literature]

[Patent Literature]

[0007]

5 [Patent Literature 1] JP2004-82370A

[Summary of the Invention]

[Problems to be solved by the Invention]

[0008]

When a laminated ceramic product is produced,
10 misalignment may occur in the plane direction in the
laminated ceramic green sheets. Such misalignment appears
to occur, for example, due to accumulation of misalignment
of the lamination position in a lamination process,
misalignment caused by thermocompression bonding in a
15 thermocompression bonding process, misalignment caused by
contraction in a firing process, and other misalignment.

[0009]

When a ceramic green sheet is formed using a release
film comprising a release agent layer that contains
20 polyorganosiloxane as described in Patent Literature 1,
migration of the polyorganosiloxane from the release agent
layer to the ceramic green sheet may readily occur. If a
laminated ceramic product is produced by laminating a
number of ceramic green sheets to which the
25 polyorganosiloxane has migrated, interfacial adhesion
between the ceramic green sheets may deteriorate to cause
misalignment as previously described. This may result in a
poor yield in the production of laminated ceramic products.
Thus, demands exist for release films from which
30 polyorganosiloxane is less likely to migrate to ceramic
green sheets.

[0010]

The present invention has been made in consideration

of such actual circumstances and an object of the present invention is to provide a release film for a ceramic green sheet production process which exhibits good releasability and is suppressed from the occurrence of migration of polyorganosiloxane from the release agent layer to the ceramic green sheet.

[Means for solving the Problems]

[0011]

To achieve the above object, first, the present invention provides a release film for a ceramic green sheet production process, the release film comprising a base material and a release agent layer provided on one side of the base material, the release agent layer being formed of a release agent composition that contains a polyorganosiloxane and a melamine resin, the polyorganosiloxane having at least one hydroxyl group in one molecule, the melamine resin having a total acid value of 0.030 to 0.154 mgKOH/g (Invention 1).

[0012]

According to the above invention (Invention 1), the release agent layer is formed of a release agent composition that contains a polyorganosiloxane having at least one hydroxyl group in one molecule and a melamine resin having a total acid value of 0.030 to 0.154 mgKOH/g. Good releasability is thereby exhibited and the occurrence of migration of polyorganosiloxane from the release agent layer to the ceramic green sheet is suppressed.

[0013]

In the above invention (Invention 1), the polyorganosiloxane may preferably have at least one organic group in one molecule, wherein the at least one organic group is selected from a polyester group and a polyether group (Invention 2).

[0014]

In the above invention (Invention 1, 2), at least one of the hydroxyl groups may preferably be present at an end of the polyorganosiloxane (Invention 3).

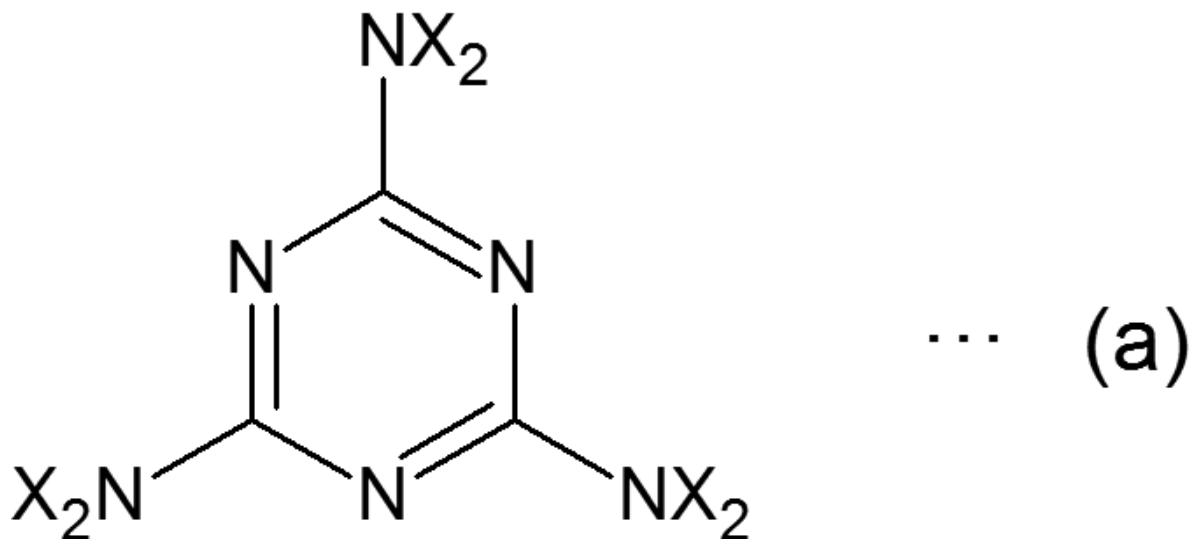
5 [0015]

In the above invention (Invention 1 to 3), the polyorganosiloxane may preferably have a weight-average molecular weight of 1,000 to 300,000 (Invention 4).

[0016]

10 In the above invention (Invention 1 to 4), the melamine resin may preferably contain a compound represented by general formula (a) below or a polynuclear substance obtained by condensing two or more molecules of the compound,

15 [Chemical Formula 1]



where each X represents -H, -CH₂-OH, or -CH₂-O-R and may be the same or different, each R represents an alkyl group having a carbon number of 1 to 8 and may be the same or different, and at least one X is -CH₂-OH (Invention 5).

[0017]

In the above invention (Invention 1 to 5), the release agent composition may preferably further contain an acid catalyst (Invention 6).

[0018]

5 In the above invention (Invention 1 to 6), the release agent layer may preferably have a thickness of 0.1 to 3 μm (Invention 7).

[0019]

10 In the above invention (Invention 1 to 7), the release film for a ceramic green sheet production process may preferably further comprise a resin layer located between the base material and the release agent layer (Invention 8).
[Advantageous Effect of the Invention]

[0020]

15 The release film for a ceramic green sheet production process according to the present invention exhibits good releasability and is suppressed from the occurrence of migration of polyorganosiloxane from the release agent layer to the ceramic green sheet.

20 [Brief Description of Drawings]

[0021]

[FIG. 1] FIG. 1 is a cross-sectional view of a release film for a ceramic green sheet production process according to an embodiment of the present invention.

25 [FIG. 2] FIG. 2 is a cross-sectional view of a release film for a ceramic green sheet production process according to another embodiment of the present invention.

[Embodiments for Carrying out the Invention]

[0022]

30 Hereinafter, embodiments of the present invention will be described.

<Release Film for Ceramic Green Sheet Production Process>

As illustrated in FIG. 1, a release film for a ceramic

green sheet production process 1A according to a first embodiment (which may be simply referred to as a "release film 1A," hereinafter) is configured to include a base material 11 and a release agent layer 12 laminated on one surface (upper surface in FIG. 1) of the base material 11.

[0023]

As illustrated in FIG. 2, a release film for a ceramic green sheet production process 1B according to a second embodiment (which may be simply referred to as a "release film 1B," hereinafter) is configured to include a base material 11, a resin layer 13 laminated on one surface (upper surface in FIG. 2) of the base material 11, and a release agent layer 12 laminated on a surface (upper surface in FIG. 2) of the resin layer 13 opposite to the base material 11.

[0024]

1. Release Agent Layer

The release agent layer 12 of the release film 1A, 1B is formed of a release agent composition that contains a polyorganosiloxane having at least one hydroxyl group in one molecule and a melamine resin having a total acid value of 0.030 to 0.154 mgKOH/g.

[0025]

In the release film 1A, 1B, the release agent composition for forming the release agent layer 12 contains polyorganosiloxane. The surface free energy at the release surface of the release agent layer 12 is therefore moderately reduced. The release agent composition further contains a melamine resin. The release agent composition can therefore be sufficiently cured by heating and the formed release agent layer 12 has sufficient elasticity. Owing to these features, when the release film 1A, 1B is released from the ceramic green sheet formed on the release

surface of the release film 1A, 1B, the release force is moderately reduced and good releasability is exhibited.

[0026]

In the release film 1A, 1B, the total acid value of
5 the melamine resin contained in the release agent
composition for forming the release agent layer 12 is 0.030
to 0.154 mgKOH/g. This means that the melamine resin has a
relatively large amount of acidic functional groups. The
acidic functional groups originate mainly from hydroxyl
10 groups of methylol groups ($-\text{CH}_2-\text{OH}$) in the melamine resin.
On the other hand, the polyorganosiloxane contained in the
release agent composition also has at least one hydroxyl
group in one molecule. When such a release agent
composition is cured to form the release agent layer 12,
15 the melamine resin and the polyorganosiloxane are
chemically bonded at their hydroxyl groups to form a
structure in which the polyorganosiloxane is fixed to the
melamine cured product. This restricts the
polyorganosiloxane from freely moving in the release agent
20 layer 12. When a ceramic green sheet is formed on the
release surface of the release film 1A, 1B, therefore,
migration of the polyorganosiloxane from the release agent
layer 12 to the ceramic green sheet is suppressed. This
can enhance the interfacial adhesion between ceramic green
25 sheets each formed using the release film 1A, 1B and
suppress the occurrence of misalignment between the ceramic
green sheets when they are laminated on one another.

[0027]

(1) Melamine Resin

30 In the release agent composition for forming the
release agent layer 12, the total acid value of the
melamine resin is 0.030 to 0.154 mgKOH/g and may be
preferably 0.032 to 0.100 mgKOH/g and particularly

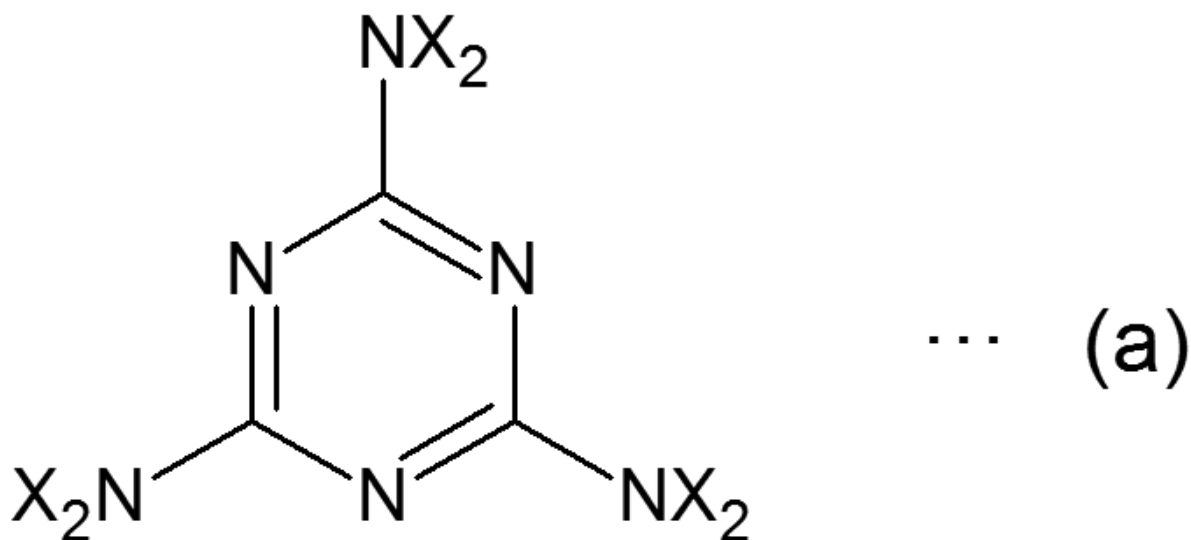
preferably 0.035 to 0.070 mgKOH/g. The total acid value of a melamine resin refers to a mass (mg) of potassium hydroxide necessary to completely react groups that are able to react with potassium hydroxide contained in 1 g of the melamine resin. In the present description, the total acid value of a melamine resin shall be represented by an actual measurement value rather than by a theoretical value. Here, the groups which are able to react with potassium hydroxide refer to methylol groups ($-\text{CH}_2-\text{OH}$). Imino groups ($-\text{NH}-$) and alkyl ether groups ($-\text{CH}_2-\text{OR}$) do not react with potassium hydroxide. A specific method of measuring the total acid value of a melamine resin will be described in the exemplary test, which will be described later. If the total acid value is less than 0.030 mgKOH/g, the number of hydroxyl groups in the melamine resin will be insufficient and the reaction between the polyorganosiloxane and the melamine resin will not sufficiently progress. Consequently, in the formed release agent layer 12, the amount of polyorganosiloxane that is not fixed to the melamine cured product will be large and the migration of polyorganosiloxane to the ceramic green sheet may readily occur. If, on the other hand, the total acid value exceeds 0.154 mgKOH/g, acid groups that are not involved in the previously-described condensation reaction and the condensation reaction between melamine resins may be excessively present and it will be difficult to control the crosslinking speed. This may possibly result in the quality deterioration of a ceramic green sheet formed on the release surface.

[0028]

Specifically, the above melamine resin may preferably contain a melamine compound represented by general formula (a) below or a polynuclear substance obtained by condensing

two or more molecules of the melamine compound.

[Chemical Formula 2]



5

[0029]

In the formula (a), each X represents -H, -CH₂-OH, or -CH₂-O-R. These groups may constitute reactive groups in the condensation reaction between molecules of the above melamine compound. Specifically, an -NH group in which X is H can undergo condensation reactions with an -N-CH₂-OH group and an -N-CH₂-R group. An -N-CH₂-OH group in which X is -CH₂-OH and an -N-CH₂-R group in which X is -CH₂-R can both undergo condensation reactions with an -NH group, an -N-CH₂-OH group, and an -N-CH₂-O-R group. In the formula (a), at least one X is -CH₂-OH. The existence of at least one -CH₂-OH group allows the reaction between the hydroxyl group contained in the group and the hydroxyl group of polyorganosiloxane, and the migration of polyorganosiloxane can be suppressed as previously described. When the melamine resin contains a polynuclear substance obtained by condensing two or more molecules of the above melamine compound, the polynuclear substance itself may have at

20

least one $-\text{CH}_2\text{-OH}$ group.

[0030]

In the above $-\text{CH}_2\text{-O-R}$ group, R represents an alkyl group having a carbon number of 1 to 8. The carbon number
5 may be preferably 1 to 6 and particularly preferably 1 to 3. Examples of the alkyl group having a carbon number of 1 to 8 include a methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, and octyl group, among which the methyl group may be preferred.

10 [0031]

In the above, each X may be the same or different and each R may be the same or different.

[0032]

In general, melamine compounds may be classified into
15 those of a full ether type in which all of Xs are $-\text{CH}_2\text{-O-R}$, those of an imino-methylol type in which at least one X is $-\text{CH}_2\text{-OH}$ and at least one X is H, those of a methylol type in which at least one X is $-\text{CH}_2\text{-OH}$ and no X exists as H, and those of an imino type in which at least one X is H and
20 no X exists as $-\text{CH}_2\text{-OH}$. In the release film 1A, 1B, the above melamine resin may preferably contain a melamine compound of the imino-methylol type or the methylol type from the viewpoint of easy suppression of curling and the viewpoint of readily achieving the property that the total
25 acid value is 0.030 to 0.154 mgKOH/g. In particular, in the formula (a), it is preferred for a more number of Xs to be $-\text{CH}_2\text{-OH}$. Specifically, the number of Xs as $-\text{CH}_2\text{-OH}$ may be preferably at least two and particularly preferably at least three.

30 [0033]

The above melamine resin may contain a polynuclear substance in which 2 to 50 molecules of the compound represented by the above formula (a) are condensed in an

embodiment, contain a polynuclear substance in which 2 to 30 molecules of the compound are condensed in another embodiment, contain a polynuclear substance in which 2 to 10 molecules of the compound are condensed in a particular
5 embodiment, and contain a polynuclear substance in which 2 to 5 molecules of the compound are condensed in a further embodiment.

[0034]

In the release agent composition for forming the
10 release agent layer 12, the weight-average molecular weight of the melamine resin may be preferably 350 to 10,000, particularly preferably 700 to 5,000, and further preferably 1,000 to 4,000. The weight-average molecular weight being 350 or more may stabilize the crosslinking
15 speed and allows a more smooth release surface to be formed. The weight-average molecular weight being 10,000 or less can suppress the viscosity of the release agent composition from being excessively high. This enables good coating properties when the base material 11 is coated with the
20 release agent composition. As used in the present description, the weight-average molecular weight refers to a value that is measured as a standard polystyrene equivalent value using the gel permeation chromatography (GPC) method.

25 [0035]

(2) Polyorganosiloxane

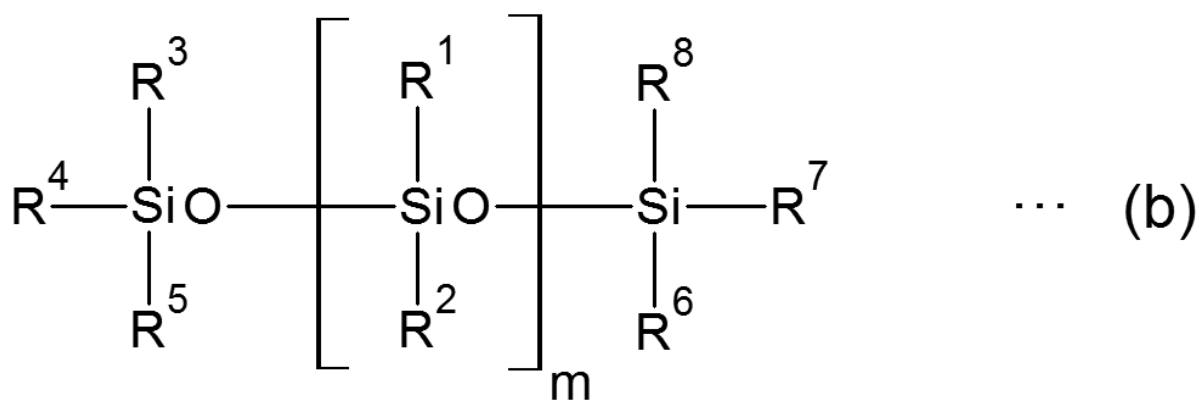
The polyorganosiloxane may preferably have at least one hydroxyl group in one molecule. The upper limit of the number of hydroxyl groups in one molecule of
30 polyorganosiloxane is not particularly limited, but may be, for example, 20. When the release agent layer 12 of the release film 1A, 1B is formed of a release agent composition that contains polyorganosiloxane, the release

surface of the release agent layer 12 can exhibit good releasability. Moreover, the polyorganosiloxane having the above hydroxyl group can be fixed to the melamine cured product by the condensation reaction with the melamine resin. This can suppress the migration of polyorganosiloxane from the release agent layer 12 to the ceramic green sheet.

[0036]

The structure other than the above hydroxyl group in the polyorganosiloxane is not particularly limited unless it inhibits the previously-described releasability, the condensation reaction between the polyorganosiloxane and the melamine resin, and the condensation reaction between melamine compounds contained in the melamine resin. A polymer of a silicon-containing compound represented by general formula (b) below can be used as the polyorganosiloxane.

[Chemical Formula 3]



[0037]

In the formula (b), m is an integer not smaller than one. At least one of R^1 to R^8 may be a hydroxyl group or an organic group having a hydroxyl group. In particular, it is preferred that at least one of R^3 to R^8 be a hydroxyl

group or an organic group having a hydroxyl group. That is, it is preferred that at least one of hydroxyl groups or organic groups having hydroxyl groups be present at an end or ends of the polyorganosiloxane. The hydroxyl group or groups being present at an end or ends allows the polyorganosiloxane to readily undergo the condensation reaction with the melamine resin and the migration of polyorganosiloxane can be effectively suppressed.

[0038]

10 In the formula (b), at least one of R^1 to R^8 other than a hydroxyl group is preferably an organic group. Here, when at least one of R^1 to R^8 in the formula (b) is a hydroxyl group, the organic group included in other R^1 to R^8 may be an organic group having a hydroxyl group or may also be an organic group having no hydroxyl group. When all of R^1 to R^8 in the formula (b) are not a hydroxyl group, the organic group included in other R^1 to R^8 is an organic group having a hydroxyl group. In the present description, examples of the "organic group" do not include an alkyl group, which will be described later. The polyorganosiloxane represented by the formula (b) preferably has at least one organic group that has a hydroxyl group or does not have a hydroxyl group, particularly preferably has 1 to 10 such organic groups, and further preferably has 1 to 5 such organic groups, in one molecule. Here, the organic groups are preferably one or more types of organic groups selected from a polyester group and a polyether group. Both the polyester group and the polyether group may be present in one molecule. When the polyester group or polyether group includes a hydroxyl group, the hydroxyl group may be present at an end of the organic group or may also be present at a side chain of the organic group. When the polyorganosiloxane has the above

organic group or groups, the polyorganosiloxane and the melamine resin are mixed well in the release agent composition to suppress significant phase separation between them when the release agent composition is cured.

5 This allows the condensation reaction between the polyorganosiloxane and the melamine resin as previously described to progress well and the migration of polyorganosiloxane can also be effectively suppressed.

[0039]

10 In the formula (b), a group of R^1 to R^8 other than the above-described groups is preferably an alkyl group having a carbon number of 1 to 12. Examples of the alkyl group having a carbon number of 1 to 12 include a methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl
15 group, and octyl group, among which the methyl group may be preferred.

[0040]

Each of R^1 to R^8 may be the same or different. When a plurality of R^1 and a plurality of R^2 are present, each of
20 R^1 and R^2 may be the same or different.

[0041]

The weight-average molecular weight of the above polyorganosiloxane may be preferably 1,000 to 300,000, particularly preferably 3,000 to 100,000, and further
25 preferably 4,000 to 50,000. When the weight-average molecular weight of the polyorganosiloxane is 1,000 or more, the surface free energy at the release surface of the release agent layer 12 moderately decreases to allow the release force to be effectively reduced when the release
30 film 1A, 1B is released from the ceramic green sheet. The weight-average molecular weight of the polyorganosiloxane being 300,000 or less can suppress the viscosity of the release agent composition from being excessively high, and

the base material 11 may be readily coated with the release agent composition.

[0042]

The content of the polyorganosiloxane in the release agent composition may be preferably 0.05 to 15 mass parts, particularly preferably 0.1 to 10 mass parts, and further preferably 0.5 to 8 mass parts, to 100 mass parts of the melamine resin. The content of the polyorganosiloxane in the release agent composition being 0.05 mass parts or more can sufficiently reduce the surface free energy at the release surface of the release agent layer 12 to achieve the moderate release force. The content of the polyorganosiloxane in the release agent composition being 15 mass parts or less can ensure the content of the melamine resin. This can enhance the elasticity of the release agent layer 12 to achieve the moderate release force. In the release film 1A, 1B, migration of the polyorganosiloxane is suppressed due to the reaction between the polyorganosiloxane and the melamine resin as previously described. Migration of the polyorganosiloxane can therefore be sufficiently suppressed even when the release agent composition contains a relatively large amount of polyorganosiloxane.

[0043]

25 (3) Other Components

The release agent composition may preferably further contain an acid catalyst. Preferred examples of the acid catalyst include hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, phosphorus acid, and p-toluenesulfonic acid, among which the p-toluenesulfonic acid is particularly preferred. The release agent composition containing an acid catalyst allows the condensation reaction to efficiently progress in the above

melamine resin.

[0044]

The content of the acid catalyst in the release agent composition may be preferably 0.1 to 30 mass parts, particularly preferably 0.5 to 20 mass parts, and further preferably 1 to 15 mass parts, to 100 mass parts of the melamine resin.

[0045]

The release agent composition may contain other additives, such as a crosslinker and reaction inhibitor, in addition to the above components.

[0046]

(4) Thickness of Release Agent Layer

The thickness of the release agent layer 12 may be preferably 0.1 to 3 μm , particularly preferably 0.2 to 2 μm , and further preferably 0.3 to 1.5 μm . The thickness of the release agent layer 12 being 0.1 μm or more allows the release agent layer 12 to effectively exhibit its function. In particular, the thickness of the release agent layer 12 which contains the melamine cured product is thicker than an ordinary thickness and the elasticity of the release agent layer 12 is thereby enhanced to improve the releasability. The thickness of the release agent layer 12 being 3 μm or less can suppress the occurrence of blocking when the release film 1A, 1B is wound up into a roll-like shape. The thickness of the release agent layer 12, such as within a range of 0.1 to 3 μm , is thicker than the thickness of an ordinary release agent layer 12. In general, as the thickness of the release agent layer 12 increases, the amount of migration of the polyorganosiloxane tends to be large, but in the release agent layer 12 of the release film 1A, 1B, the reaction between the polyorganosiloxane and the melamine resin

occurs and the migration of polyorganosiloxane can thus be sufficiently suppressed even when the thickness of the release agent layer 12 is thick.

[0047]

5 2. Base Material

The base material 11 of the release film 1A, 1B is not particularly limited, provided that the release agent layer 12 or the resin layer 13 can be laminated on the base material 11. Examples of the base material 11 include
10 films formed of plastics, such as polyethylene terephthalate, polyethylene naphthalate and other polyesters, polypropylene, polymethylpentene and other polyolefins, polycarbonate, and polyvinyl acetate. These films may be in a single layer or may also be in a
15 multilayer of two or more layers of the same type or different types. Among these, a polyester film is preferred, a polyethylene terephthalate film is particularly preferred, and a biaxially stretched polyethylene terephthalate film is further preferred. The
20 polyethylene terephthalate film is less likely to generate dust and the like during the work and use and can therefore effectively prevent troubles, such as ceramic slurry coating failure, due to dust and the like, for example. The polyethylene terephthalate film may be treated with an
25 antistatic thereby to prevent firing due to static electrical charge at the time of coating with the ceramic slurry, which uses an organic solvent, and to enhance the effect of preventing the coating failure and the like.

[0048]

30 For the purpose of improving the interfacial adhesion property of the base material 11 with the release agent layer 12 or resin layer 13 provided on the surface of the base material 11, one surface or both surfaces of the base

material 11 may be subjected to surface treatment, such as using an oxidation method and roughening method, or primer treatment, as necessary. Examples of the above oxidation method include corona discharge treatment, plasma discharge
5 treatment, chromium 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 thermal spraying method. These surface treatment methods may be
10 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.

[0049]

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

[0050]

3. Resin Layer

20 The resin layer 13 provided in the release film 1B is located, as illustrated in FIG. 2, between the base material 11 and the release agent layer 12. Providing the resin layer 13 between the base material 11 and the release agent layer 12 can absorb irregularities on the surface of
25 the base material 11 at the release agent layer 12 side to reduce the roughness of the release surface of the release film 1B.

[0051]

The resin which constitutes the resin layer 13 is not
30 particularly limited. Examples of the resin include a melamine resin, epoxy resin, phenol resin, urea resin, polyester resin, urethane resin, acrylic resin, polyimide resin, and benzoxazine resin. Among these, the melamine

resin is preferably used to form the resin layer 13. Forming the resin layer 13 using a melamine resin enhances the interfacial adhesion between the resin layer 13 and the base material 11 and between the resin layer 13 and the release agent layer 12. Moreover, the elasticity of the release film 1B at the release surface side is improved to moderately reduce the release force when releasing the release film 1B from the ceramic green sheet.

[0052]

The melamine resin for forming the resin layer 13 is not particularly limited. From the viewpoint of suppressing the contraction of the resin layer 13 itself, however, it may be preferred to use the previously-described melamine resin, which is used for forming the release agent layer 12, as the melamine resin for the resin layer 13. That is, it may be preferred to form the resin layer 13 using a composition that contains the previously-described melamine resin.

[0053]

The resin layer 13 may contain other components than the melamine resin, in addition to the melamine resin. For example, the resin layer 13 may contain other resins than the melamine resin, such as an epoxy resin, phenol resin, urea resin, polyester resin, urethane resin, acrylic resin, polyimide resin, and benzoxazine resin. When the resin layer 13 contains such other resins, the content may be preferably 1 to 200 mass parts, particularly preferably 10 to 150 mass parts, and preferably 30 to 100 mass parts in an embodiment, to 100 mass parts of the melamine resin. In an embodiment, the resin layer 13 may contain additives, such as a crosslinker, reaction inhibitor, and an agent for improving the interfacial adhesion.

[0054]

The thickness of the resin layer 13 may be ordinarily 0.1 to 3 μm , preferably 0.2 to 2 μm , and particularly preferably 0.3 to 1.5 μm .

[0055]

5 4. Physical Properties of Release Film for Ceramic Green Sheet Production Process

The release force required when releasing the release film 1A, 1B from the ceramic green sheet formed on the release surface of the release film 1A, 1B can be
10 appropriately set, but may be preferably 2.5 to 50 mN/20 mm and particularly preferably 5 to 25 mN/20 mm. The release agent layer of the release film 1A, 1B is formed using the release agent composition which contains the above melamine resin and polyorganosiloxane. It is therefore possible to
15 appropriately set the release force, such as within a range of 2.5 to 50 mN/20 mm.

[0056]

When a ceramic green sheet is formed using the release film 1A, 1B, migration of the polyorganosiloxane from the
20 release agent layer 12 to the ceramic green sheet is suppressed. Specifically, when the ceramic green sheet is formed on the release surface of the release film 1A, 1B and the ceramic green sheet is thereafter released from the release film 1A, 1B, the amount of migration of the
25 polyorganosiloxane decreases at the surface of the ceramic green sheet which has been in contact with the release surface. In particular, when the ceramic green sheet is formed using the release film 1A, 1B, the silicon atomic ratio obtained by measuring the surface of the ceramic
30 green sheet having been in contact with the release surface may be preferably less than 1.0 at%, particularly preferably less than 0.5 at%, and further preferably less than 0.3 at%. The silicon atomic ratio may be calculated

in accordance with the equation below on the basis of the amounts (XPS counts) of silicon atoms (Si), carbon atoms (C), and oxygen atoms (O) which are measured by X-ray photoelectron spectroscopy (XPS).

5 Silicon atomic ratio (at%)=[(Si element amount)/{(C element amount)+(O element amount)+(Si element amount)}]×100

[0057]

10 A ceramic green sheet from which silicon is not detected by XPS (i.e. which does not contain a silicon compound) may be appropriately selected from ceramic green sheets for measurement and the silicon atomic ratio thereof may be utilized as a reference for evaluating the amount of migration of the polyorganosiloxane from the release agent layer 12.

[0058]

5. Production Method for Release Film for Ceramic Green Sheet Production Process

20 When the release film 1A is produced, one surface of the base material 11 may be coated with a coating liquid that contains the previously-described release agent composition and may further contain an organic solvent, if desired, and the coating liquid may then be dried and heated to cure the release agent composition, thus forming the release agent layer 12. The release film 1A can thereby be obtained. Examples of the coating method to be used include a gravure-coating method, bar-coating method, spray-coating method, spin-coating method, knife-coating method, roll-coating method, and die-coating method.

30 [0059]

When the release film 1B is produced, one surface of the base material 11 may be coated with a coating liquid that contains a melamine resin as the raw material therefor,

for example, and the coating liquid may then be dried and heated to form the resin layer 13. A surface of the resin layer 13 opposite to the base material 11 may be coated with a coating liquid that contains the previously-described release agent composition and may further contain an organic solvent, if desired, and the coating liquid may then be dried and heated to cure the release agent composition, thus forming the release agent layer 12. The release film 1B can thereby be obtained. The same methods as the above-described coating method can be used as those in this case.

[0060]

The above organic solvent is not particularly limited and various types can be used. Examples of the organic solvent to be used include hydrocarbon compounds, such as toluene, hexane and heptane, isopropyl alcohol, isobutyl alcohol, acetone, ethyl acetate, methyl ethyl ketone, methyl isobutyl ketone, and a mixture thereof. In particular, it may be preferred to use a mixture liquid of methyl ethyl ketone and isopropyl alcohol.

[0061]

The release agent composition after coating as the above may preferably be thermally cured. The heating temperature in this case may be preferably 90°C to 140°C and particularly preferably 110°C to 130°C. The heating time may be preferably about 10 to 120 seconds and particularly preferably about 50 to 70 seconds.

[0062]

6. Method of using Release Film for Ceramic Green Sheet Production Process

The release film 1A, 1B can be used for producing a ceramic green sheet. Specifically, the release surface of the release agent layer 12 may be coated with a ceramic

slurry that contains a ceramic material, such as barium titanate and titanium oxide, and the ceramic slurry can then be dried to obtain a ceramic green sheet. The coating can be performed, for example, using an appropriate scheme,
5 such as a slot die coating scheme and doctor blade scheme.

[0063]

Examples of binder components contained in the ceramic slurry include a butyral-based resin and acrylic-based resin. Examples of a solvent contained in the ceramic
10 slurry include an organic solvent and water-based solvent.

[0064]

In the release film 1A, 1B, the release agent layer 12 is formed of a release agent composition that contains the previously-described melamine resin and polyorganosiloxane,
15 and excellent releasability can thereby be exhibited. Moreover, the release agent layer 12 is formed with a structure in which the polyorganosiloxane is fixed to the melamine resin, and the migration of polyorganosiloxane from the release agent layer 12 to the ceramic green sheet
20 can therefore be suppressed. This can enhance the interfacial adhesion between ceramic green sheets each formed using the release film 1A, 1B and suppress the occurrence of misalignment between the ceramic green sheets when they are laminated on one another.

25 [0065]

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
30 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.

[0066]

For example, one or more other layers such as an antistatic layer may be provided on the surface of the base material 11 opposite to the release agent layer 12, between the base material 11 and the release agent layer 12 in the release film 1A, or between the base material 11 and the resin layer 13 or between the resin layer 13 and the release agent layer 12 in the release film 1B.

[Examples]

[0067]

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.

[0068]

<Example 1>

A coating liquid of a release agent composition was obtained through mixing 100 mass parts (equivalent amount to the solid content, here and hereinafter) of an imino-type methylated melamine resin (trade name: MX-730, available from NIPPON CARBIDE INDUSTRIES CO., INC., weight-average molecular weight of 1,508), 0.5 mass parts of polyether-modified hydroxyl group-containing polydimethylsiloxane (b1) (trade name: BYK-377, available from BYK Japan KK, number-average molecular weight (Mn) of 5,078, weight-average molecular weight (Mw) of 5,993, molecular weight distribution (Mw/Mn) of 1.18), and 4.0 mass parts of p-toluenesulfonic acid (trade name: Dryer 900, available from Hitachi Chemical Company, Ltd.) as an acid catalyst using a mixed solvent of methyl ethyl ketone, isopropyl alcohol, and isobutyl alcohol. The solid content of the coating liquid was 20 mass%.

[0069]

A surface of a biaxially stretched polyethylene

terephthalate film (thickness: 25 μm) as a base material was uniformly coated with the obtained coating liquid using a Meyer bar #6. The maximum peak height R_p on the surface was 452 nm. Then, the coating liquid was dried at 120°C
5 for one minute to cure the release agent composition and a release film was obtained in which a release agent layer having a thickness of 1.2 μm was laminated on the base material.

[0070]

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

[0071]

<Examples 2 to 4>

15 Release films were obtained in the same manner as in Example 1 except that the mass parts of the polyether-modified hydroxyl group-containing polydimethylsiloxane (b1) were modified as listed in Table 1.

[0072]

20 <Example 5>

A release film was obtained in the same manner as in Example 1 except that the 0.5 mass parts of the polyether-modified hydroxyl group-containing polydimethylsiloxane (b1) were substituted by 1.0 mass part of polyester-
25 modified hydroxyl group-containing polydimethylsiloxane (b2) (trade name: BYK-370, available from BYK Japan KK, number-average molecular weight (M_n) of 2,689, weight-average molecular weight (M_w) of 4,283, molecular weight distribution (M_w/M_n) of 1.59).

30 [0073]

<Example 6>

A release film was obtained in the same manner as in Example 5 except that the mass parts of the polyester-

modified hydroxyl group-containing polydimethylsiloxane (b2) were modified as listed in Table 1.

[0074]

<Comparative Example 1>

5 A release film was obtained in the same manner as in Example 1 except that the 0.5 mass parts of the polyether-modified hydroxyl group-containing polydimethylsiloxane (b1) were substituted by 1.0 mass part of polyether-modified polydimethylsiloxane (b3) (trade name: BYK-345,
10 available from BYK Japan KK, number-average molecular weight (Mn) of 1,194, weight-average molecular weight (Mw) of 1,563, molecular weight distribution (Mw/Mn) of 1.31).

[0075]

<Comparative Example 2>

15 A release film was obtained in the same manner as in Comparative Example 1 except that the mass parts of the polyether-modified polydimethylsiloxane (b3) were modified as listed in Table 1.

[0076]

20 <Exemplary Test 1> (Measurement of Total Acid Value)

 The melamine resin used in each of the examples and comparative examples was diluted by isopropyl alcohol so that the solid content concentration would be 50 mass%. Then, 10 g of the diluted liquid was sampled into a 200 mL
25 beaker. This was added with 125 mL of a solution obtained by mixing toluene, deionized water, and 2-propanol at a mass ratio of 500:5:495, and a measurement sample was thus obtained. When each commercial product of the melamine resin used in the examples and comparative examples was one
30 that used other solvent than isopropyl alcohol, the commercial product was dried to remove the solvent and diluted with isopropyl alcohol so that the solid content concentration would be 50 mass%.

[0077]

The measurement sample was titrated with a potassium hydroxide 2-propanolic standard solution using a potential difference automatic titrator (product name: AT-610 EBU-
5 610-20B, available from Kyoto Electronics Manufacturing Co., Ltd.) to measure the amount of the potassium hydroxide 2-propanolic standard solution required for neutralization. The measurement was performed three times and the average value was calculated. The average value was used as the
10 basis to calculate the amount (mg) of potassium hydroxide required to neutralize one gram of the melamine resin, and the calculated amount was used as the total acid value (mgKOH/g). Results are listed in Table 1.

[0078]

15 <Exemplary Test 2> (Measurement of Release Force)

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 , trade name: BT-03, available from SAKAI CHEMICAL INDUSTRY CO., LTD), 10 mass
20 parts of polyvinyl butyral (trade name: S-LEC B·K BM-2, available from SEKISUI CHEMICAL CO., LTD.), and 5 mass parts of dioctyl phthalate (trade name: dioctyl phthalate Cica first grade, available from KANTO CHEMICAL CO., INC.), and mixing and dispersing them in a ball mill.

25 [0079]

In the release film stored under an ordinary temperature for 48 hours after produced in each of the examples and comparative examples, the release surface of the release agent layer was uniformly coated with the above
30 ceramic slurry using an applicator. 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 film. Thus,

the release film with the ceramic green sheet was produced.

[0080]

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

[0081]

The pressure sensitive adhesive tape side of the measurement sample was fixed to a flat plate and the release film was peeled off from the ceramic green sheet at
15 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). Results are listed in Table 1.

20 [0082]

<Exemplary Test 3> (Evaluation of Migration Property of Polyorganosiloxane)

In the release film stored under an ordinary temperature for 48 hours after produced in each of the
25 examples and comparative examples, the release surface of the release agent layer was uniformly coated with the above ceramic slurry using a 35 µm applicator. Thereafter the ceramic slurry was dried at 60°C for one minute using a dryer. Through this operation, a ceramic green sheet
30 having a thickness of 4 µm was obtained on the release film. Thus, the release film with the ceramic green sheet was produced.

[0083]

The above ceramic green sheet was released from the release film. For the surface of the ceramic green sheet which had been in contact with the release agent layer surface, the silicon atomic ratio (at%) was calculated in accordance with the equation below on the basis of the amounts (XPS counts) of silicon atoms (Si), carbon atoms (C), and oxygen atoms (O) which were measured by X-ray photoelectron spectroscopy (XPS).

$$\text{Silicon atomic ratio (at\%)} = \frac{(\text{Si element amount})}{\{(\text{C element amount}) + (\text{O element amount}) + (\text{Si element amount})\}} \times 100$$

[0084]

Then, the migration property of polyorganosiloxane was evaluated in accordance with the criteria below. Results of the silicon atomic ratio and evaluation are listed in Table 1.

A; The silicon atomic ratio was less than 0.3 at%.

B; The silicon atomic ratio was 0.3 at% or more and less than 0.75 at%.

C; The silicon atomic ratio was 0.75 at% or more.

[0085]

Details of reference characters or the like in Table 1 are as follows.

<Polyorganosiloxane>

b1: polyether-modified hydroxyl group-containing polydimethylsiloxane (trade name: BYK-377, available from BYK Japan KK, number-average molecular weight (Mn) of 5,078, weight-average molecular weight (Mw) of 5,993, molecular weight distribution (Mw/Mn) of 1.18)

b2: polyester-modified hydroxyl group-containing polydimethylsiloxane (trade name: BYK-370, available from BYK Japan KK, number-average molecular weight (Mn) of 2,689, weight-average molecular weight (Mw) of 4,283, molecular

weight distribution (Mw/Mn) of 1.59)

b3: polyether-modified polydimethylsiloxane (trade
name: BYK-345, available from BYK Japan KK, number-average
molecular weight (Mn) of 1,194, weight-average molecular
5 weight (Mw) of 1,563, molecular weight distribution (Mw/Mn)
of 1.31)

[0086]

[Table 1]

	Melamine resin (mass parts)	Polyorganosiloxane (mass parts)			Acid catalyst (mass parts)	Thickness of release agent layer (μ m)	Total acid value (mgKOH/g)	Release force (mN/20mm)	Migration property of polyorganosiloxane	
		b1	b2	b3					Silicon atomic ratio (at%)	Evaluation result
Example 1	100	0.5	—	—	4.0	1.2	0.038	15.5	0.11	A
Example 2	100	1.0	—	—	4.0	1.2	0.038	12.5	0.25	A
Example 3	100	2.0	—	—	4.0	1.2	0.038	14.7	0.25	A
Example 4	100	3.0	—	—	4.0	1.2	0.038	15.6	0.24	A
Example 5	100	—	1.0	—	4.0	1.2	0.038	19.5	0.23	A
Example 6	100	—	2.0	—	4.0	1.2	0.038	17.3	0.26	A
Comparative Example 1	100	—	—	1.0	4.0	1.2	0.038	31.2	0.50	B
Comparative Example 2	100	—	—	3.0	4.0	1.2	0.038	25.3	0.83	C

[0087]

As apparent from Table 1, when the release film obtained in each of the examples is released from the ceramic green sheet, the release is possible with moderate
5 release force. Moreover, in the ceramic green sheet formed using the release film obtained in each of the examples, the silicon atomic ratio is small and it has thus been found that the migration of polyorganosiloxane is effectively suppressed. In particular, it can be found
10 that the migration of polyorganosiloxane is suppressed even when the compounding amount of polyorganosiloxane in the release agent composition is large. It has also been confirmed that the release film obtained in each of the examples has a relatively low maximum peak height R_p on the
15 release surface and is thus excellent in the smoothness.

[0088]

On the other hand, it has been found that the release film obtained in each of the comparative examples requires strong release force when released from the ceramic green
20 sheet. In the ceramic green sheet formed using the release film obtained in each of the comparative examples, the silicon atomic ratio is large and it has thus been found that the migration of polyorganosiloxane is not sufficiently suppressed.

25 [Industrial Applicability]

[0089]

The release film for a ceramic green sheet production process of the present invention is suitable for forming a ceramic green sheet.

30 [Description of Reference Numerals]

[0090]

1A, 1B... Release film for a ceramic green sheet production process

- 11... Base material
- 12... Release agent layer
- 13... Resin layer

[Name of Document] Claims

[Claim 1]

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

the release agent layer being formed of a release agent composition that contains a polyorganosiloxane and a melamine resin,

10 the polyorganosiloxane having at least one hydroxyl group in one molecule,

the melamine resin having a total acid value of 0.030 to 0.154 mgKOH/g,

a content of the polyorganosiloxane in the release
15 agent composition being 0.05 to 15 mass parts to 100 mass parts of the melamine resin.

[Claim 2]

A release film for a ceramic green sheet production process, the release film comprising a base material and a
20 release agent layer provided on one side of the base material,

the release agent layer being formed of a release agent composition that contains a polyorganosiloxane and a melamine resin,

25 the polyorganosiloxane having at least one hydroxyl group in one molecule,

the melamine resin having a total acid value of 0.030 to 0.154 mgKOH/g,

the release agent composition containing neither an
30 alkyd resin nor an acrylic resin.

[Claim 3]

The release film for a ceramic green sheet production process as recited in claim 1 or 2, wherein the polyorganosiloxane has at least one organic group in one
5 molecule, wherein the at least one organic group is selected from a polyester group and a polyether group.

[Claim 4]

The release film for a ceramic green sheet production process as recited in any one of claims 1 to 3~~claim 1 or 2~~,
10 wherein at least one of the hydroxyl groups is present at an end of the polyorganosiloxane.

[Claim 5]

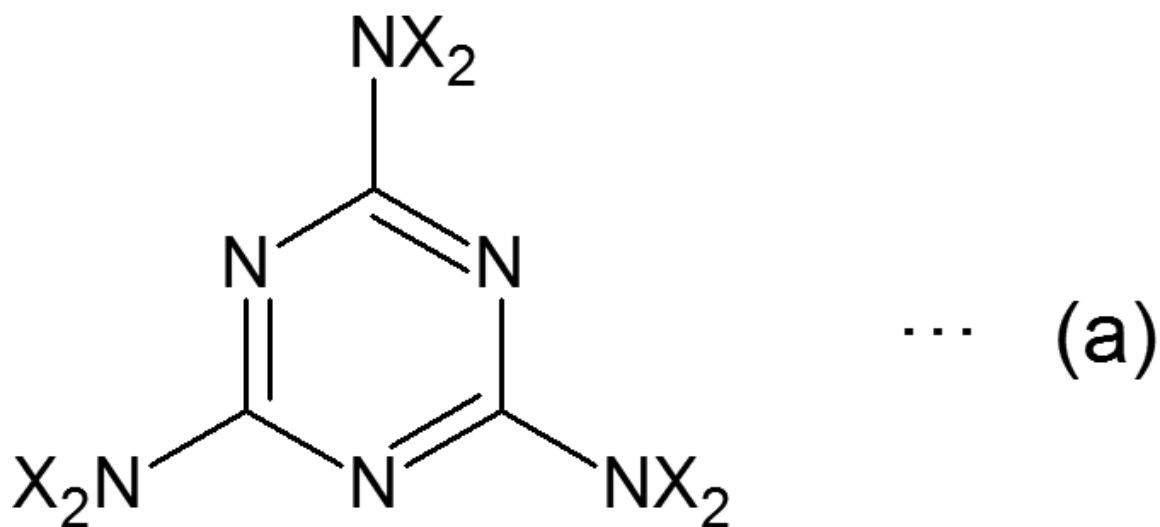
The release film for a ceramic green sheet production process as recited in any one of claims 1 to ~~3~~4, wherein
15 the polyorganosiloxane has a weight-average molecular weight of 1,000 to 300,000.

[Claim 6]

The release film for a ceramic green sheet production process as recited in any one of claims 1 to ~~4~~5, wherein
20 the melamine resin contains a compound represented by general formula (a) below or a polynuclear substance obtained by condensing two or more molecules of the compound,

[Chemical Formula 1]

36a



where each X represents $-\text{H}$, $-\text{CH}_2-\text{OH}$, or $-\text{CH}_2-\text{O}-\text{R}$ and may be same or different, each R represents an alkyl group having a carbon number of 1 to 8 and may be same or different, and
5 at least one X is $-\text{CH}_2-\text{OH}$.

[Claim 7]

The release film for a ceramic green sheet production process as recited in any one of claims 1 to 56, wherein
10 the release agent composition further contains an acid catalyst.

[Claim 8]

The release film for a ceramic green sheet production process as recited in any one of claims 1 to 67, wherein
15 the release agent layer has a thickness of 0.1 to 3 μm .

[Claim 9]

The release film for a ceramic green sheet production process as recited in any one of claims 1 to 78, further comprising a resin layer located between the base material
20 and the release agent layer.