

[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 and 2 each disclose a release film formed with a release agent layer using a melamine resin
15 which is one type of a thermoset compound. In this release film, a base material is coated with a release agent composition that contains a melamine resin and the release agent composition is heated to form a release agent layer that contains a cured product of the melamine resin. In
20 such a release agent layer, the previously-described specific problems when using the ultraviolet curable compound will not occur.

[0006]

In general, the "melamine resin" refers to a mixture
25 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 present description, the term "melamine resin" shall refer to the above mixture or an aggregate of one type of a
30 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]

[Patent Literature 1] JP11-300896A

[Patent Literature 2] JP2006-7568A

5 [Summary of the Invention]

[Problems to be solved by the Invention]

[0008]

In the release film as described in Patent Literature
1 and 2, however, curling may readily occur at the stage in
10 which the release agent layer is formed from the melamine
resin. In particular, when the release agent layer is
produced under a high-temperature condition, the occurrence
of curling may be accelerated. The release film in which
such curling occurs therefore has poor handling ability and
15 is not suitable for the production of ceramic green sheets.

[0009]

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
20 sheet production process which exhibits good releasability
and is suppressed from the occurrence of curling.

[Means for solving the Problems]

[0010]

To achieve the above object, first, the present
25 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 melamine resin
30 and a polyorganosiloxane, the melamine resin having a total
acid value of 0.030 to 0.154 mgKOH/g and a weight-average
molecular weight of 1,000 to 10,000 (Invention 1).

[0011]

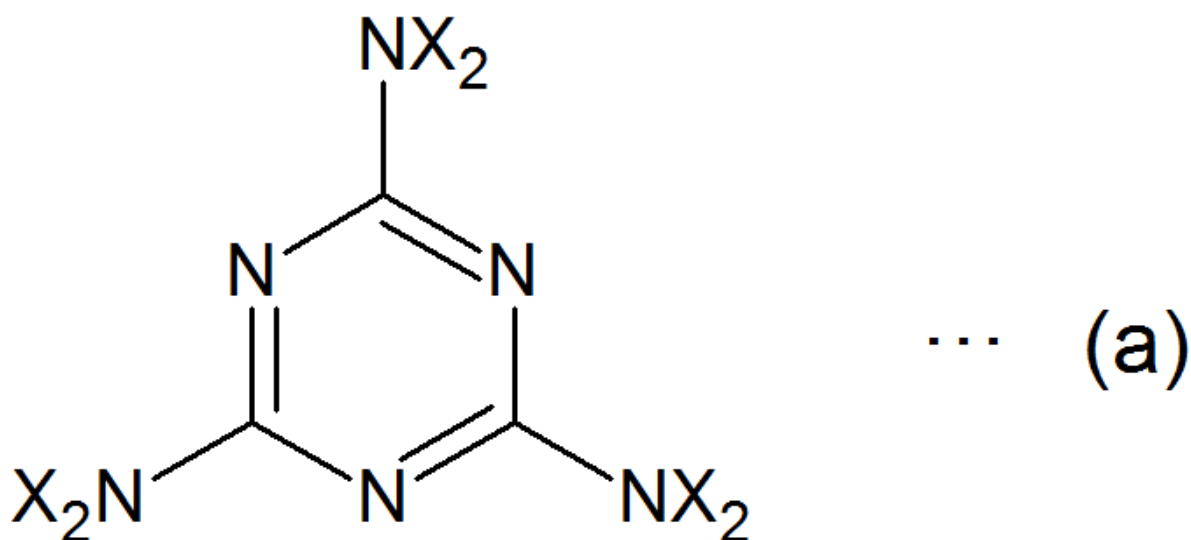
According to the above invention (Invention 1), the release agent layer is formed of a release agent composition that contains a melamine resin, which has a weight-average molecular weight of 1,000 to 10,000 and a total acid value of 0.030 to 0.154 mgKOH/g, and a polyorganosiloxane. Good releasability is thereby exhibited and the occurrence of curling is suppressed.

[0012]

In the above invention (Invention 1), 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,

[Chemical Formula 1]

15



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 2).

[0013]

In the above invention (Invention 1, 2), the

20

polyorganosiloxane may preferably have at least one hydroxyl group in one molecule (Invention 3).

[0014]

In the above invention (Invention 1 to 3), the
5 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 4).

[0015]

10 In the above invention (Invention 1 to 4), the polyorganosiloxane may preferably have a weight-average molecular weight of 1,000 to 300,000 (Invention 5).

[0016]

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

[0017]

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

[0018]

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
25 the base material and the release agent layer (Invention 8).

[0019]

In the above invention (Invention 8), the resin layer
may preferably be formed of a composition that contains a
melamine resin having a total acid value of 0.030 to 0.154
30 mgKOH/g and a weight-average molecular weight of 1,000 to
10,000 (Invention 9).

[Advantageous Effect of the Invention]

[0020]

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 curling.

5 [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.

10 [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]

15 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
20 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]

25 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
30 (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
5 melamine resin having a total acid value of 0.030 to 0.154 mgKOH/g and a weight-average molecular weight of 1,000 to 10,000 and a polyorganosiloxane.

[0025]

In the release film 1A, 1B, the release agent layer 12
10 is formed of the release agent composition which contains polyorganosiloxane. The surface free energy at the release surface is therefore moderately reduced. Moreover, the release agent layer 12 is formed of the release agent composition which contains a melamine resin. The release
15 agent composition can therefore be sufficiently cured when being heated. Thus, 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,
20 1B, the release force is moderately reduced and good releasability is exhibited.

[0026]

In general, crosslinking reaction of a melamine resin eliminates alcohol (R-OH), ether (R-O-R), or water in
25 accordance with the type of a functional group used in the reaction. The eliminated components are discharged from the release agent layer 12 when the release agent layer 12 is formed. In particular, crosslinking reaction under a high-temperature condition accelerates the discharge. Such
30 discharge appears to cause volume contraction of the release agent layer 12 so that the curling occurs in the release film.

[0027]

In the release agent composition for forming the release agent layer 12 of the release film 1A, 1B, the total acid value of the melamine resin is 0.030 to 0.154 mgKOH/g. This means that the amount of methanol groups (-CH₂-OH) in the melamine resin is relatively large. When such a melamine resin undergoes a condensation reaction, the ratio of water as an eliminated component will be large. This allows the release agent layer 12 formed of the melamine resin to have a small degree of volume contraction as compared with a release agent layer formed of a melamine resin in which the content of methanol groups is small. The occurrence of curling in the release film 1A, 1B can thus be suppressed.

[0028]

In the release agent composition for forming the release agent layer 12 of the release film 1A, 1B, the weight-average molecular weight of the melamine resin is 1,000 to 10,000. This means that the melamine resin contains a large amount of a polynuclear substance of a melamine compound. The polynuclear substance of a melamine compound has a chemical structure in which the condensation reaction progresses to some extent, as compared with a mononuclear substance. When curing the release agent composition which contains a melamine resin that contains a large amount of such a polynuclear substance of a melamine compound, the volume contraction will be small as the amount of eliminated components decreases. Also in this regard, the occurrence of curling in the release film 1A, 1B can be further suppressed.

[0029]

(1) Melamine Resin

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 methanol 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 ratio of imino groups and alkyl ether groups in the melamine resin will be relatively large and the ratio of elimination of components having a large molecular volume will also be large during the condensation reaction. This may increase the extent of volume contraction due to the condensation reaction and the curling will occur in the obtained release agent layer. If, on the other hand, the total acid value exceeds 0.154 mgKOH/g, acid groups that are not involved in the condensation reaction 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.

[0030]

In the release agent composition for forming the release agent layer 12, the weight-average molecular weight of the melamine resin is 1,000 to 10,000 and may be preferably 1,000 to 5,000 and particularly preferably 1,000

to 4,000. If the weight-average molecular weight is less than 1,000, the melamine resin contains a large amount of a mononuclear substance and the amount of eliminated components due to the condensation reaction will be large.

5 This may readily cause the volume contraction when the release agent composition is cured, and the curling is likely to occur in the obtained release film 1A, 1B. If the weight-average molecular weight exceeds 10,000, the viscosity of the release agent composition will be high and

10 the coating properties may deteriorate when the base material 11 is coated with the 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

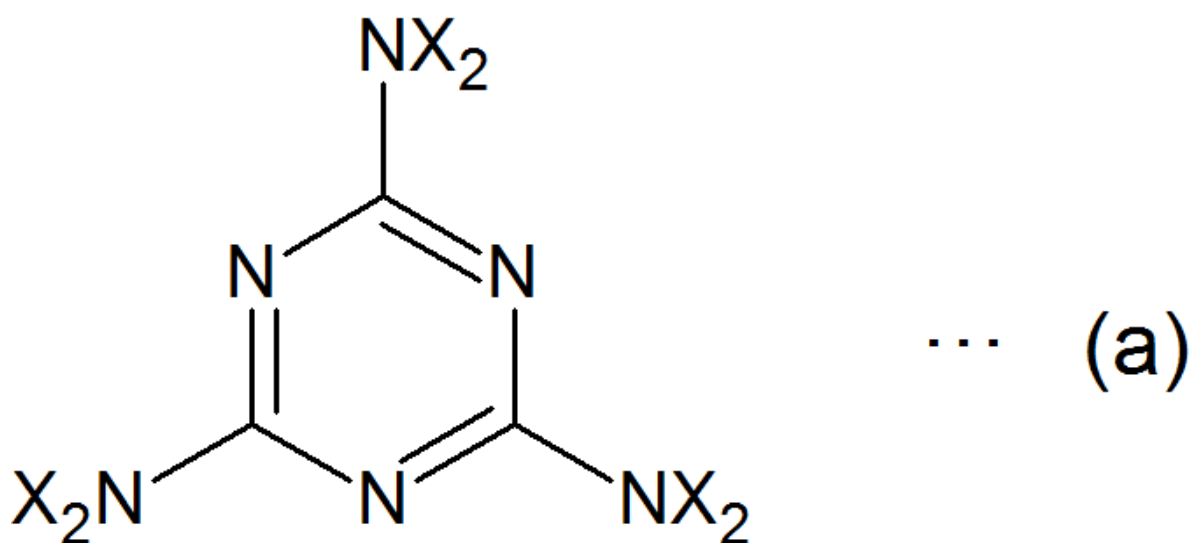
15 permeation chromatography (GPC) method.

[0031]

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

20 two or more molecules of the melamine compound.

[Chemical Formula 2]



[0032]

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. When the condensation reaction occurs in the -CH₂-OH group, the effect of suppressing volume contraction will be high and the curling in the release film 1A, 1B can be further suppressed. 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 least one -CH₂-OH group. When the polyorganosiloxane has a reactive group such as a hydroxyl group, the -CH₂-OH group and the -CH₂-O-R group may be given to the chemical bond with the reactive group.

[0033]

In the above -CH₂-O-R group, R represents an alkyl group having a carbon number of 1 to 8. The carbon number 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.

[0034]

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

[0035]

In general, melamine compounds may be classified into those of a full ether type in which all of Xs are $-\text{CH}_2-\text{O}-\text{R}$, 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 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 the curling and the viewpoint of readily achieving the property that the total 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 one and particularly preferably at least three.

[0036]

From the viewpoint of easy suppression of the curling in the release film 1A, 1B and the viewpoint of readily achieving the property that the weight-average molecular weight is 1,000 to 10,000, the melamine resin may be preferably a polynuclear substance in which 2 to 10 molecules of the compound represented by the above formula (a) are condensed, particularly preferably a polynuclear substance in which 3 to 9 molecules of the compound are condensed, and further preferably a polynuclear substance in which 4 to 7 molecules of the compound are condensed.

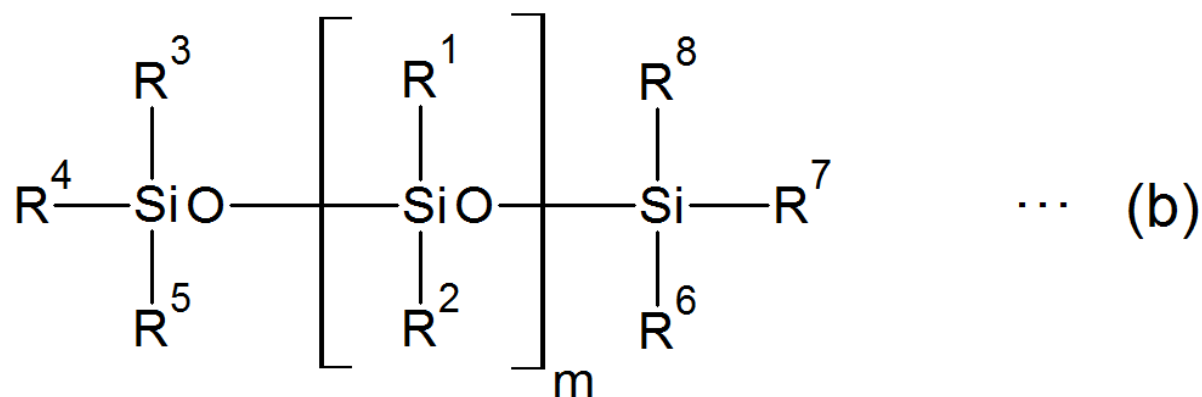
[0037]

(2) Polyorganosiloxane

The polyorganosiloxane is not particularly limited. When the release agent layer 12 of the release film 1A, 1B is formed of a release agent composition that contains

polyorganosiloxane, the release film 1A, 1B can exhibit good releasability. A polymer of a silicon-containing compound represented by general formula (b) below can be used as the polyorganosiloxane.

5 [Chemical Formula 3]



[0038]

10 In the formula (b), m is an integer not smaller than one. At least one of R^1 to R^8 is preferably a hydroxyl group or an organic group having a hydroxyl group. That is, the polyorganosiloxane represented by the formula (b) preferably contains at least one hydroxyl group or an

15 organic group having a hydroxyl group, in one molecule. The upper limit of the number of hydroxyl groups or organic groups having hydroxyl groups in one molecule of the above polyorganosiloxane may be, but is not limited to being, for example 20. When the polyorganosiloxane contains a

20 hydroxyl group or an organic group having a hydroxyl group, a condensation reaction occurs between the hydroxyl group and the $-CH_2-OH$ or $-CH_2-O-R$ group of the melamine resin to form a structure in which the polyorganosiloxane is linked to the melamine cured product. This can suppress migration

25 of the polyorganosiloxane from the release agent layer 12 to a ceramic green sheet formed on the release surface of

the release film 1A, 1B. 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 be present at an end or ends of the polyorganosiloxane. At least one of hydroxyl groups being present at an end or ends allows the polyorganosiloxane to readily undergo the condensation reaction with the melamine resin and the above migration can be effectively suppressed.

10 [0039]

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 preferably 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
5 between them when the release agent composition is cured.

[0040]

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
10 having a carbon number of 1 to 12 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.

[0041]

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
15 R^1 and R^2 may be the same or different.

[0042]

The weight-average molecular weight of the above
20 polyorganosiloxane may be preferably 1,000 to 300,000, particularly preferably 3,000 to 100,000, and further 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
25 release agent layer 12 moderately decreases to allow the release force to be effectively reduced when the release 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
30 release agent composition from being excessively high, and the base material 11 may be readily coated with the release agent composition.

[0043]

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.

[0044]

(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.

[0045]

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.

[0046]

The release agent composition may contain other

additives, such as a crosslinker and reaction inhibitor, in addition to the above components.

[0047]

(4) Thickness

5 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.

10 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

15 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

20 general, as the thickness of the release agent layer 12 increases, curling is more likely to occur. In the release film 1A, 1B, however, the release agent layer 12 is formed of the release agent composition which contains the previously-described melamine resin, and the occurrence of

25 curling can thereby be suppressed even when the thickness of the release agent layer 12 is thick.

[0048]

2. Base Material

30 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 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 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 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 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.

[0049]

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 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 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.

[0050]

5 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 .

[0051]

3. Resin Layer

10 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
15 the base material 11 at the release agent layer 12 side to reduce the roughness of the release surface of the release film 1B.

[0052]

20 The resin which constitutes the resin layer 13 is not 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.
25 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
30 moderately reduce the release force when releasing the release film 1B from the ceramic green sheet.

[0053]

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.

[0054]

10 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.

[0055]

25 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 .

[0056]

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

30 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 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
5 appropriately set the release force, such as within a range of 2.5 to 50 mN/20 mm.

[0057]

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

10 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
15 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
20 method, roll-coating method, and die-coating method.

[0058]

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,
25 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
30 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.

[0059]

The above organic solvent is not particularly limited
5 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
10 particular, it may be preferred to use a mixture liquid of methyl ethyl ketone and isopropyl alcohol.

[0060]

The release agent composition after coating as the above may preferably be thermally cured. The heating
15 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.

[0061]

20 In the release film 1A, 1B, the release agent layer 12 is formed using the release agent composition which contains the previously-described melamine resin and polyorganosiloxane, thereby to suppress the occurrence of curling while exhibiting good releasability. In particular,
25 the occurrence of curling can be effectively suppressed even when the release agent layer 12 is formed under a high-temperature condition.

[0062]

6. Method of using Release Film for Ceramic Green Sheet
30 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, 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 slurry include an organic solvent and water-based solvent.

[0064]

As previously described, the release film 1A, 1B exhibits good releasability and the occurrence of curling is suppressed. When the ceramic green sheet is formed using the release film 1A, 1B, therefore, the release film 1A, 1B can be released from the ceramic green sheet with moderate release force. Moreover, a flat ceramic green sheet can be obtained without curvature.

[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 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
5 further specifically with reference to examples, etc., but
the scope of the present invention is not limited to these
examples, etc.

[0068]

<Example 1>

10 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 (a1) (trade name: MX-730,
available from NIPPON CARBIDE INDUSTRIES CO., INC., weight-
15 average molecular weight of 1,508), 1.0 mass part of
polyether-modified hydroxyl group-containing
polydimethylsiloxane (b1) (trade name: BYK-377, available
from BYK Japan KK), and 4.0 mass parts of p-toluenesulfonic
acid (trade name: Dryer 900, available from Hitachi
20 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]

25 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
30 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]

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).

5 [0071]

<Examples 2 to 4>

Release films were obtained in the same manner as in Example 1 except that the polyether-modified hydroxyl group-containing polydimethylsiloxane (b1) (trade name: 10 BYK-377, available from BYK Japan KK) was substituted with a polyester-modified hydroxyl group-containing polydimethylsiloxane (b2) (trade name: BYK-370, available from BYK Japan KK) and the mass parts of the b2 were varied as listed in Table 1.

15 [0072]

<Example 5>

A release film was obtained in the same manner as in Example 2 except that the mass parts of the acid catalyst were modified as listed in Table 1.

20 [0073]

<Example 6>

A release film was obtained in the same manner as in Example 2 except that the imino-type methylated melamine resin (a1) (trade name: MX-730, available from NIPPON 25 CARBIDE INDUSTRIES CO., INC., weight-average molecular weight of 1,508) was substituted with an imino-methylol-type methylated melamine resin (a2) (trade name: MS-001, available from NIPPON CARBIDE INDUSTRIES CO., INC., weight-average molecular weight of 3,987, molecular weight 30 distribution (Mw/Mn) of 1.51).

[0074]

<Examples 7 and 8>

Release films were obtained in the same manner as in

Example 2 except that the thicknesses of the release agent layers were modified as listed in Table 1.

[0075]

<Example 9>

5 A release film was obtained in the same manner as in Example 1 except that the polyether-modified hydroxyl group-containing polydimethylsiloxane (b1) (trade name: BYK-377, available from BYK Japan KK) was substituted with a polyether-modified polymethylalkylsiloxane (b3) (trade
10 name: BYK-325, available from BYK Japan KK).

[0076]

<Example 10>

 A release film was obtained in the same manner as in Example 1 except that the polyether-modified hydroxyl
15 group-containing polydimethylsiloxane (b1) (trade name: BYK-377, available from BYK Japan KK) was substituted with a polyether-modified acrylic group-containing polydimethylsiloxane (b4) (trade name: BYK-UV3500, available from BYK Japan KK).

20 [0077]

<Comparative Example 1>

 A release film was obtained in the same manner as in Example 2 except that the imino-type methylated melamine resin (a1) (trade name: MX-730, available from NIPPON
25 CARBIDE INDUSTRIES CO., INC., weight-average molecular weight of 1,508) was substituted with a full ether-type methylated melamine resin (a3) (trade name: MW-30, available from NIPPON CARBIDE INDUSTRIES CO., INC., weight-average molecular weight of 608, molecular weight
30 distribution (Mw/Mn) of 1.01).

[0078]

<Comparative Example 2>

 A release film was obtained in the same manner as in

Example 2 except that the imino-type methylated melamine resin (a1) (trade name: MX-730, available from NIPPON CARBIDE INDUSTRIES CO., INC., weight-average molecular weight of 1,508) was substituted with a full ether-type
5 methylated melamine resin (a4) (trade name: L-105-60, available from DIC Corporation, weight-average molecular weight of 684, molecular weight distribution (Mw/Mn) of 1.52).

[0079]

10 <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
15 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
20 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%.

[0080]

25 The measurement sample was titrated with a potassium hydroxide 2-propanolic standard solution using a potential difference automatic titrator (product name: AT-610 EBU-610-20B, available from Kyoto Electronics Manufacturing Co., Ltd.) to measure the amount of the potassium hydroxide 2-
30 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 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.

[0081]

5 <Exemplary Test 2> (Measurement of Curling Amount)

The release film produced in each of the examples and comparative examples was cut out into 10 cm square and a measurement sample was thus obtained. The measurement sample was stationarily placed in a constant temperature oven of 70°C for two hours. Thereafter the measurement sample was placed on flat glass. When the measurement sample was curved, it was placed on the glass with the convex surface facing the glass. Heights of four corners of the measurement sample from the glass were measured and
10 the total value was used as a measured value (mm) of the curling amount. Results are listed in Table 1.

[0082]

<Exemplary Test 3> (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 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.),
20 and mixing and dispersing them in a ball mill.

[0083]

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 ceramic slurry using an applicator. Thereafter the ceramic
30

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.

5 [0084]

The release film with the ceramic green sheet was stationarily placed under an atmosphere of a room temperature of 23°C and humidity of 50% for 24 hours. Then, an acrylic pressure sensitive adhesive tape (trade name:
10 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 width of 20 mm. A measurement sample was thus obtained.

[0085]

15 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 a release angle of 180° and a release speed of 100 mm/min using a tensile tester (product name: AG-IS500N, available
20 from SHIMADZU CORPORATION) to measure the force necessary for the peeling (release force; mN/20 mm). Results are listed in Table 1.

[0086]

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

<Melamine Resin>

a1: imino-type methylated melamine resin (trade name: MX-730, available from NIPPON CARBIDE INDUSTRIES CO., INC., weight-average molecular weight of 1,508, molecular weight
30 distribution (M_w/M_n) of 1.18)

a2: imino-methylol-type methylated melamine resin (trade name: MS-001, available from NIPPON CARBIDE INDUSTRIES CO., INC., weight-average molecular weight of

3,987, molecular weight distribution (Mw/Mn) of 1.51)

a3: full ether-type methylated melamine resin (trade name: MW-30, available from NIPPON CARBIDE INDUSTRIES CO., INC., weight-average molecular weight of 608, molecular weight distribution (Mw/Mn) of 1.01)

a4: full ether-type methylated melamine resin (trade name: L-105-60, available from DIC Corporation, weight-average molecular weight of 684, molecular weight distribution (Mw/Mn) of 1.52)

10 <Polyorganosiloxane>

b1: polyether-modified hydroxyl group-containing polydimethylsiloxane (trade name: BYK-377, available from BYK Japan KK)

15 b2: polyester-modified hydroxyl group-containing polydimethylsiloxane (trade name: BYK-370, available from BYK Japan KK)

b3: polyether-modified polymethylalkylsiloxane (trade name: BYK-325, available from BYK Japan KK)

20 b4: polyether-modified acrylic group-containing polydimethylsiloxane (trade name: BYK-UV3500, available from BYK Japan KK)

[0087]

[Table 1]

	Melamine resin (mass parts)				Polyorganosiloxane (mass parts)				Acid catalyst (mass parts)	Weight-average molecular weight of melamine resin	Molecular weight distribution of melamine resin	Thickness of release agent layer (μm)	Total acid value (mgKOH/g)	Measured value of curling amount (mm)	Release force ($\text{mN}/20\text{mm}$)
	a1	a2	a3	a4	b1	b2	b3	b4							
Example 1	100	—	—	—	1.0	—	—	—	4.0	1508	1.18	1.20	0.038	1	12.5
Example 2	100	—	—	—	—	1.0	—	—	4.0	1508	1.18	1.20	0.038	1	19.5
Example 3	100	—	—	—	—	3.0	—	—	4.0	1508	1.18	1.20	0.038	0	21.6
Example 4	100	—	—	—	—	5.0	—	—	4.0	1508	1.18	1.20	0.038	6	23.5
Example 5	100	—	—	—	—	1.0	—	—	12.0	1508	1.18	1.20	0.038	5	14.1
Example 6	—	100	—	—	—	1.0	—	—	4.0	3987	1.51	1.20	0.062	1	20.1
Example 7	100	—	—	—	—	1.0	—	—	4.0	1508	1.18	0.84	0.038	0	20.3
Example 8	100	—	—	—	—	1.0	—	—	4.0	1508	1.18	1.50	0.038	3	17.5
Example 9	100	—	—	—	—	—	1.0	—	4.0	1508	1.18	1.20	0.038	1	24.7
Example 10	100	—	—	—	—	—	—	1.0	4.0	1508	1.18	1.20	0.038	2	13.4
Comparative Example 1	—	—	100	—	—	1.0	—	—	4.0	608	1.01	1.20	0.024	50	14.0
Comparative Example 2	—	—	—	100	—	1.0	—	—	4.0	684	1.52	1.20	0.022	74	20.0

[0088]

As apparent from Table 1, the occurrence of curling is suppressed in the release film obtained in each of the examples. Moreover, when the release film is released from
5 the ceramic green sheet, the release is possible with moderate release force. 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 release surface and is thus excellent in the smoothness.

10 [0089]

On the other hand, large curling occurs in the release film obtained in each of the comparative examples.

[Industrial Applicability]

[0090]

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

[Description of Reference Numerals]

[0091]

20 1A, 1B... Release film for a ceramic green sheet production process

11... Base material

12... Release agent layer

13... Resin layer

25

[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 melamine resin and a polyorganosiloxane,

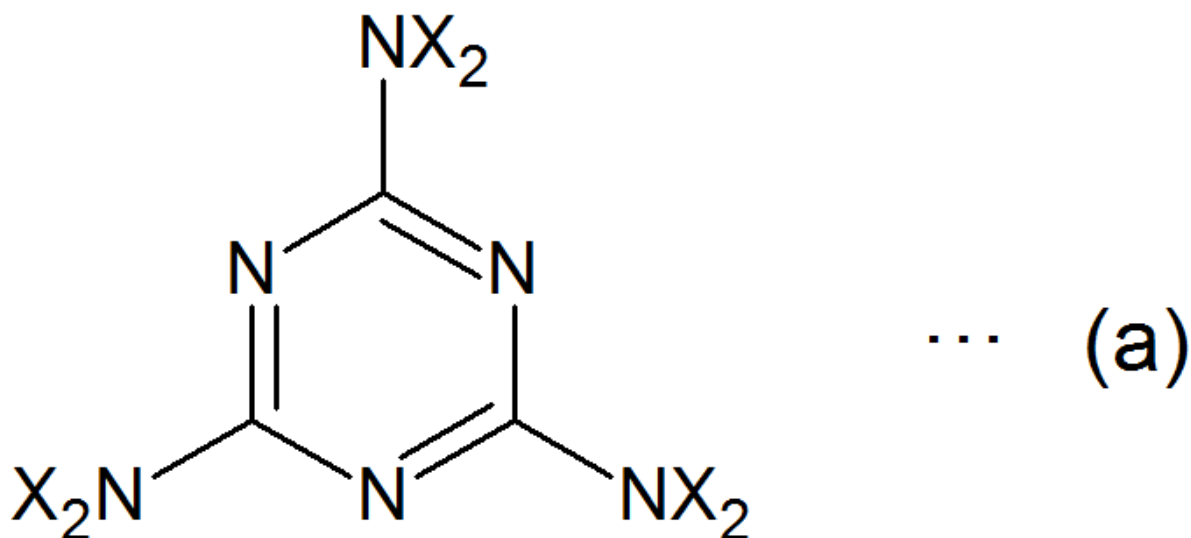
10 the melamine resin having a total acid value of 0.030 to 0.154 mgKOH/g and a weight-average molecular weight of 1,000 to 10,000.

[Claim 2]

The release film for a ceramic green sheet production
15 process as recited in claim 1, wherein 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]

20



where each X represents -H, -CH₂-OH, or -CH₂-O-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 at least one X is -CH₂-OH.

[Claim 3]

5 The release film for a ceramic green sheet production process as recited in claim 1 or 2, wherein the polyorganosiloxane has at least one hydroxyl group in one molecule.

[Claim 4]

10 The release film for a ceramic green sheet production process as recited in any one of claims 1 to 3, wherein the polyorganosiloxane has 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.

15 [Claim 5]

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

20 [Claim 6]

 The release film for a ceramic green sheet production process as recited in any one of claims 1 to 5, wherein the release agent composition further contains an acid catalyst.

[Claim 7]

25 The release film for a ceramic green sheet production process as recited in any one of claims 1 to 6, wherein the release agent layer has a thickness of 0.1 to 3 μm.

[Claim 8]

30 The release film for a ceramic green sheet production process as recited in any one of claims 1 to 7, further comprising a resin layer located between the base material and the release agent layer.

[Claim 9]

The release film for a ceramic green sheet production process as recited in claim 8, wherein the resin layer is formed of a composition that contains a melamine resin having a total acid value of 0.030 to 0.154 mgKOH/g and a
5 weight-average molecular weight of 1,000 to 10,000.