DESCRIPTION

TITLE OF THE INVENTION: RELEASE FILM FOR MANUFACTURING CERAMIC GREEN SHEET

TECHNICAL FIELD

[0001]

The present invention relates to a release film for manufacturing a ceramic green sheet, including a polyester film and a release layer, and the release film for manufacturing a ceramic green sheet can be suitably used for manufacturing an ultrathin ceramic green sheet and the like.

BACKGROUND ART

[0002]

Conventionally, a release film in which a polyester film is used as a substrate and a release layer is laminated thereon has been used as various process films. Among them, the release film for manufacturing a ceramic green sheet is also used as a process film for manufacturing a ceramic green sheet for which high smoothness is required, such as a multilayer ceramic capacitor and a ceramic substrate.

[0003]

In recent years, the thickness of the ceramic green

sheet has tended to also be reduced with reduction in the size of the laminated ceramic capacitor and an increase in the capacity thereof. The ceramic green sheet is formed by coating a slurry containing a ceramic component such as barium titanate and a binder resin on a release film and drying the slurry. On the formed ceramic green sheet, an electrode is printed, and the ceramic green sheet is peeled off from the release film. Another ceramic green sheet is then laminated on the ceramic green sheet, followed by pressing, firing, and applying an external electrode, to manufacture a laminated ceramic capacitor.

[0004]

In recent years, as the thickness of the ceramic green sheet is reduced, the peelability of the release film at the time of peeling the ceramic green sheet from the release film becomes more important. When the peeling force is large and nonuniform, damage is applied to the ceramic green sheet in a peeling step, and therefore sheet defects and thickness unevenness and the like occur, which have a problem that troubles such as pinholes and sheet cracking occur. Therefore, it is required to peel off the ceramic green sheet with a lower uniform force.

[0005]

As a measure for lightly peeling the release layer, as in Patent Document 1 and the like, there has been

proposed a release film in which polydimethylsiloxane having an alkenyl group, polydimethylsiloxane having a hydrosilyl group, and a platinum catalyst are used, and a silicone film formed by an addition reaction by heat or the like is used as a release layer.

[0006]

As a measure for enhancing the curability of the release layer, Patent Document 2 proposes a release film including a release layer obtained by curing a radically curable composition containing a polyorganosiloxane having a reactive functional group such as an acryloyl group and a polyfunctional (meth)acrylic acid ester.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0007]

Patent Document 1: JP-B-6619200

Patent Document 2: JP-B-5492352

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008]

However, in the invention of Patent Document 1, there is a tendency that it is difficult to achieve both the adhesion of the release layer to a substrate film and the

releasability of the surface, and there has been a concern that the silicone film fragment falls off from the release layer in the step of manufacturing the ceramic green sheet and contaminates in the step.

[0009]

In the invention of Patent Document 2, if the curability is enhanced to such an extent that the transfer of the release layer and the like can be prevented, there is a problem that sufficient releasability cannot be obtained when ceramic green sheet is peeled off.

[0010]

Therefore, an object of the present invention is to provide a release film for manufacturing a ceramic green sheet, which is excellent in releasability and is less likely to cause transfer/falling off of a release layer and poor adhesion. Another object of the present invention is to provide a method for manufacturing a ceramic green sheet using the release film.

MEANS FOR SOLVING THE PROBLEMS

[0011]

As a result of intensive studies to solve the above problems, the present inventors have found that the above problems can be solved particularly by controlling the ratio of a hydrogen bond component γSVh in surface free

energy γS within a predetermined range for a release layer cured by further adding an adhesion imparting agent, and have completed the present invention.

[0012]

That is, the present invention includes the following contents.

[0013]

[1] A release film for manufacturing a ceramic green sheet, including a polyester film and a release layer,

wherein the release layer is a layer obtained by curing a curable composition containing a polysiloxane A having two or more alkenyl groups in a molecule, a polysiloxane B having two or more hydrosilyl groups in a molecule, and an adhesion imparting agent C, and

surface free energy γS (mJ/m^2) of a surface of the release layer and a hydrogen bond component γSVh (mJ/m^2) of γS satisfy the following formulas (a) and (b):

$$1.0 \leq \gamma SVh/\gamma S*100 \leq 6.5 \quad (a)$$

$$\gamma S \leq 30 \quad (b)$$

[0014]

[2] The release film for manufacturing a ceramic green sheet according to [1], wherein the adhesion imparting agent C is a silane coupling agent having one or more functional groups selected from the group consisting of a vinyl group, an epoxy group, an acrylic group, and a

methacrylic group.

[0015]

[3] The release film for manufacturing a ceramic green sheet according to [1] or [2], wherein the polysiloxane A has a weight average molecular weight of 300,000 or more and 600,000 or less.

[0016]

[4] The release film for manufacturing a ceramic green sheet according to any one of [1] to [3], wherein a molar ratio between an amount of hydrosilyl groups of the polysiloxane B and an amount of alkenyl groups of the polysiloxane A in the curable composition satisfies the following formula (c):

$$1.0 \leq Si\text{-}H/Si\text{-}A \leq 3.8 \quad (c)$$

where Si-H represents a molar amount of the hydrosilyl groups, and Si-A represents a molar amount of the alkenyl groups.

[0017]

[5] The release film for manufacturing a ceramic green sheet according to any one of [1] to [4], wherein the curable composition contains the adhesion imparting agent C in an amount of 1% by mass or more and 10% by mass or less with respect to a total amount of the polysiloxane A and the polysiloxane B.

[0018]

[6] The release film for manufacturing a ceramic green sheet according to any one of [1] to [5], wherein the polyester film has a surface layer A that does not substantially contain inorganic particles, the release layer having a thickness of 0.005 μm or more and 0.1 μm or less is laminated on the surface layer A, and a maximum protrusion height (Sp) of a surface of the release layer is 100 nm or less.

[0019]

[7] A method for manufacturing a ceramic green sheet, the method including forming the ceramic green sheet using the release film for manufacturing a ceramic green sheet according to any one of [1] to [6], wherein the formed ceramic green sheet has a thickness of 0.2 μm to 1.0 μm.

EFFECT OF THE INVENTION

[0020]

According to the present invention, it is possible to provide a release film for manufacturing a ceramic green sheet, which is excellent in releasability and is less likely to cause transfer/falling off of a release layer and poor adhesion.

MODE FOR CARRYING OUT THE INVENTION

[0021]

[Release film for manufacturing ceramic green sheet]

A release film for manufacturing a ceramic green sheet of the present invention (hereinafter, may be simply referred to as “release film”) includes a polyester film and a release layer, and the release layer may be provided on at least one surface of the polyester film.

[0022]

An easily adhesive layer, an antistatic layer, and a smoothing layer and the like may be provided between the release layer and the polyester film, but in the present invention, good adhesion is easily obtained even if the easily adhesive layer and the like are not interposed. That is, as a preferred aspect, a release film in which a release layer is directly provided on a polyester film is exemplified.

[0023]

The release layer is a layer obtained by curing a curable composition containing a polysiloxane A having two or more alkenyl groups in a molecule, a polysiloxane B having two or more hydrosilyl groups in a molecule, and an adhesion imparting agent C.

[0024]

In the release film of the present invention, the surface free energy γS (mJ/m^2) of the surface of the release layer, that is, the surface of the release layer on

the opposite side of the polyester film and the hydrogen bond component γSVh (mJ/m^2) of γS satisfy the following formulas (a) and (b).

$$1.0 \leq \gamma SVh/\gamma S*100 \leq 6.5 \quad (a)$$

$$\gamma S \leq 30 \quad (b)$$

First, the surface characteristics of the release layer specified by the formulas (a) and (b) will be described.

[0025]

(Surface characteristics of release layer)

The above formulas (a) and (b) include the surface free energy γS and the hydrogen bond component γSVh thereof, and how to determine these will be described. The surface free energy can be determined by adding dropwise each solvent of water, methylene iodide, and ethylene glycol onto the release layer and measuring an angle (contact angle) formed by the droplet and the release layer after a certain period of time. From the contact angle of each solvent, the surface free energy γS of the release layer and the hydrogen bond component γSVh thereof are calculated using the Kitazaki-Hata formula.

[0026]

More specifically, a release film is fixed on a flat glass substrate, and 1.9 μL of water is added dropwise onto the release film. An angle formed by the droplet and the

release layer is measured 60 seconds after the droplet stops, and is taken as θ_1. Similarly, 0.9 μL of methylene iodide is added dropwise onto the release film. An angle formed by the droplet and the release layer is measured 30 seconds after the droplet stops, and is defined as θ_2. Furthermore, 0.9 μL of ethylene glycol is added dropwise onto the release film. An angle formed by the droplet and the release layer is measured 30 seconds after the droplet stops, and is defined as θ_3.

[0027]

From θ_1, θ_2, and θ_3 described above and $\gamma LVnd$, $\gamma LVnp$, $\gamma LVnh$, and γLn (with the proviso that n = 1, 2, or 3, and corresponds to water, methylene iodide, or ethylene glycol) of water, methylene iodide, and ethylene glycol described in Table 1, a dispersion component γSVd, a dipole component γSVp, and a hydrogen bond component γSVh of the surface free energy of the release layer were calculated by the following Kitazaki–Hata formula, and the total thereof was defined as the surface free energy γs of the release layer. That is, $\gamma SVd + \gamma SVp + \gamma SVh = \gamma s$ is set. The unit of the surface free energy and each component is "mJ/m^2".

[0028]

[Table 1]

	Dispersion component	Dipole component	Hydrogen bonding component	Total
	γLVnd	γLVnp	γLVnh	γLn
Water	29.1	1.3	42.4	72.8
Methylene iodide	46.8	4.0	0.0	50.8
Ethylene glycol	30.1	0.0	17.6	47.7

[0029]

[Math 1]

$$\sqrt{\gamma_{SV}{}^{d}\gamma_{LV1}{}^{d}} + \sqrt{\gamma_{SV}{}^{p}\gamma_{LV1}{}^{p}} + \sqrt{\gamma_{SV}{}^{h}\gamma_{LV1}{}^{h}} = \frac{\gamma_{L1}(1+\cos\Theta_1)}{2}$$

$$\sqrt{\gamma_{SV}{}^{d}\gamma_{LV2}{}^{d}} + \sqrt{\gamma_{SV}{}^{p}\gamma_{LV2}{}^{p}} + \sqrt{\gamma_{SV}{}^{h}\gamma_{LV2}{}^{h}} = \frac{\gamma_{L2}(1+\cos\Theta_2)}{2}$$

$$\sqrt{\gamma_{SV}{}^{d}\gamma_{LV3}{}^{d}} + \sqrt{\gamma_{SV}{}^{p}\gamma_{LV3}{}^{p}} + \sqrt{\gamma_{SV}{}^{h}\gamma_{LV3}{}^{h}} = \frac{\gamma_{L3}(1+\cos\Theta_3)}{2}$$

[0030]

The present inventors have found that when the surface free energy obtained by measuring the release layer under the above conditions satisfies the formulas (a) and (b), extremely good peelability is obtained when a ceramic green sheet formed by applying and drying a ceramic slurry to the release layer is peeled off. It has been found that when the inequality on the lower limit side of the formula (a) is satisfied, the curability of the coating film is improved, so that the release layer tends to have

sufficient strength, and thus problems such as falling off of the release layer are less likely to occur.

[0031]

It is considered that the excellent peelability to the ceramic green sheet is contributed by the small amount of the hydrogen bond component of the surface free energy in the release layer. That is, it is considered that preventing the hydroxyl group component in the binder contained in the ceramic green sheet from forming a hydrogen bond with a hydrogen component which is an unreacted component of the release layer contributes to the light peelability of the ceramic green sheet.

[0032]

The ratio ($\gamma SVh/\gamma S*100$) of the hydrogen bond component contained in the surface free energy of the release layer is preferably 6.5% or less, more preferably 6.0% or less, and still more preferably 5.0% or less. When the ratio is 6.5% or less, the peeling force is improved, and thus the ceramic green sheet is less likely to be deformed or damaged during peeling.

[0033]

Meanwhile, the lower limit of the ratio ($\gamma SVh/\gamma S*100$) is preferably 1.0% or more, and more preferably 1.2% or more. When this ratio is 1.0% or more, there are few unreacted vinyl groups, the coating film tends to have

sufficient strength, and problems such as falling off of the release layer hardly occur.

[0034]

The surface free energy γs of the release layer is also desirably low. This is considered to be because when the surface free energy of the release layer is close to the surface free energy of the ceramic green sheet, the energy required for peeling off the ceramic green sheet and the release layer increases, resulting in deterioration in peelability. The surface free energy γs is desirably 30 mJ/m^2 or less, more preferably 25 mJ/m^2 or less, and still more preferably 20 mJ/m^2 or less.

[0035]

The lower limit value of the surface free energy γs is not particularly limited, but the surface free energy γs is preferably 12 mJ/m^2 or more, and more preferably 14 mJ/m^2 or more, from the viewpoint of the coatability of the ceramic slurry and the like.

[0036]

[Release Layer]

As a material constituting the release layer of the release film, it is preferable to use the following curable composition in order to form a release layer satisfying the above-mentioned physical properties. That is, the release layer is preferably formed of a layer obtained by curing a

curable composition to be described below.

[0037]

The curable composition contains a polysiloxane A having two or more alkenyl groups in a molecule, a polysiloxane B having two or more hydrosilyl groups in a molecule, and an adhesion imparting agent C.

[0038]

(Polysiloxane A)

The polysiloxane A may have two or more alkenyl groups at the side chain and/or the terminal, and is preferably a polyorganosiloxane having an alkenyl group at least at the side chain, and more preferably a polyorganosiloxane having an alkenyl group only at the side chain. A copolymer containing a siloxane unit having an alkenyl group and a dialkylsiloxane unit or an alkylphenylsiloxane unit is preferable because it is easy to adjust the amount of the alkenyl group in one molecule while exhibiting releasability. A silicon atom at the terminal preferably has a trialkylsilane structure such as trimethylsilane.

[0039]

Examples of the alkenyl group include an alkenyl group having 2 or more and 10 or less carbon atoms. By having such an alkenyl group, the strength of the release layer becomes excellent. The alkenyl group is preferably

an alkenyl group having 2 or more and 8 or less carbon atoms, more preferably an alkenyl group having 2 or more and 6 or less carbon atoms, and particularly preferably a vinyl group or a hexenyl group. A plurality of alkenyl groups may be bonded to the silicon atom to which the alkenyl group is bonded, but it is preferable that the alkenyl group and the alkyl group are bonded. The alkyl group in this case is preferably a methyl group or the like.

[0040]

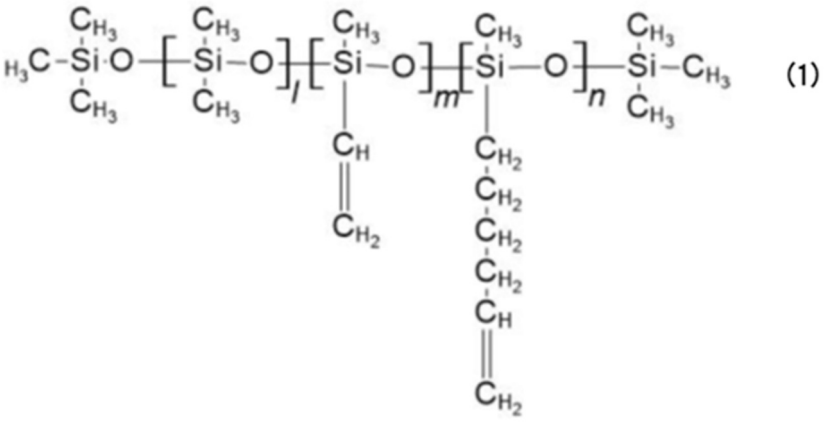
Preferred examples of the dialkylsiloxane unit and the like contained in the polysiloxane A besides the siloxane unit having an alkenyl group include a dimethylsiloxane unit and a phenylmethylsiloxane unit.

[0041]

Examples of the polysiloxane as described above include polysiloxanes represented by the following structural formula (1).

[0042]

[Formula 1]



(1)

[0043]

In the above formula (1), l, m, and n are integers of 0 or more (provided that m + n is 2 or more), but when l is in a range of 1000 or more and 10,000 or less and m + n is in a range of 2 or more and 100 or less, the crosslinking reaction suitably proceeds while sufficient releasability is exhibited, and thus strength of the release layer is improved, which is preferable. From the same viewpoint, (m + n)/(l + m + n + 2) is preferably 0.006 or more and 0.03 or less, and more preferably 0.01 or more and 0.024 or less.

[0044]

Note that the above formula does not mean an aspect of a block copolymer, but merely indicates that the total number of units is l, m, or n. Therefore, the polysiloxane in the above formula may be a random copolymer or a block copolymer.

[0045]

In the present invention, as the polysiloxane A, one of the above-mentioned polysiloxanes may be used alone, a polysiloxane having two or more different alkenyl groups in one molecule may be used, or two or more polysiloxanes having different structures, such as having different alkenyl groups, may be used in combination.

[0046]

The weight average molecular weight of the polysiloxane A is preferably 300,000 or more and 600,000 or less, and particularly preferably 400,000 or more and 550,000 or less. The weight average molecular weight in the present specification is a value in terms of standard polystyrene measured by a gel permeation chromatography (GPC) method.

[0047]

When the weight average molecular weight of the polysiloxane A is 300,000 or more, the release layer after crosslinking has appropriate coating film strength, and thus the falling off of the coating film can be more effectively prevented. When the weight average molecular weight is 600,000 or less, the flatness of the coating film after drying is improved.

[0048]

(Polysiloxane B)

The polysiloxane B only needs to have two or more

hydrosilyl groups (groups in which a hydrogen atom is directly bonded to a silicon atom) at the side chain and/or the terminal, and hydrogen polysiloxane having a hydrosilyl group at least at the side chain is preferable, and hydrogen polysiloxane having a hydrosilyl group only at the side chain is more preferable. A copolymer containing a siloxane unit having a hydrosilyl group and a dialkylsiloxane unit or an alkylphenylsiloxane unit is preferable because it is easy to adjust the amount of the hydrosilyl groups in one molecule while exhibiting releasability. A plurality of hydrogen atoms may be directly bonded to the silicon atom to which the hydrogen atom is directly bonded, but it is preferable that the hydrogen atom and the alkyl group are bonded. The alkyl group in this case is preferably a methyl group or the like. A silicon atom at the terminal preferably has a trialkylsilane structure such as trimethylsilane.

[0049]

Preferred examples of the dialkylsiloxane unit and the like contained in the polysiloxane B besides the siloxane unit having a hydrosilyl group include a dimethylsiloxane unit and a phenylmethylsiloxane unit.

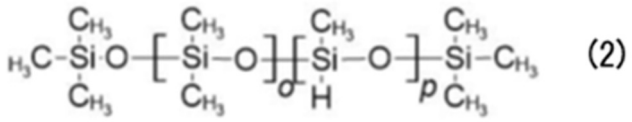
[0050]

Examples of the hydrogen polysiloxane include polysiloxanes represented by the following structural

formula (2).

[0051]

[Formula 2]



(2)

[0052]

In the above formula (2), o is an integer of 0 or more, and p is an integer of 2 or more, but when o is in a range of 0 or more and 120 or less, p is in a range of 2 or more and 120 or less, and o + p is in a range of 2 or more and 240 or less, the crosslinking reaction suitably proceeds, and thus the strength of the release layer is improved, which is preferable. From the same viewpoint, (p)/(o + p + 2) is preferably 0.3 or more and 1 or less.

[0053]

Note that the above formula does not mean an aspect of a block copolymer, but merely indicates that the total number of units is o or p. Therefore, the hydrogen polysiloxane in the above formula may be a random copolymer or a block copolymer.

[0054]

As the polysiloxane B, one of the hydrogen polysiloxanes as described above may be used alone, or two or more hydrogen polysiloxanes having different structures

such as different numbers of hydrosilyl groups in one molecule may be used in combination.

[0055]

The weight average molecular weight of the polysiloxane B is preferably 5000 or more and 100,000 or less, and particularly preferably 7000 or more and 20,000 or less. When the weight average molecular weight of the polysiloxane B is 5000 or more, the release layer after crosslinking has appropriate coating film strength, and the falling off of the coating film can be prevented. When the weight average molecular weight is 100,000 or less, the flatness of the coating film after drying is improved.

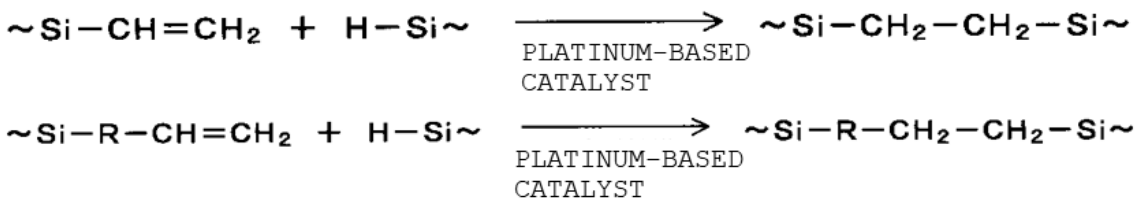
[0056]

In the present invention, a product obtained by the addition polymerization of the polysiloxane A and the polysiloxane B preferably in the presence of a platinum-based catalyst or the like to be described later is a main component of the release layer. The addition polymerization referred to herein is a reaction in which a functional group at a molecular terminal or in a molecular side chain in the polysiloxane A represented by $-Si-CH=CH_2$ or $-Si-R-CH=CH_2$ and a functional group at a molecular terminal or in a molecular side chain in the polysiloxane B represented by H-Si- become $-Si-CH_2CH_2-Si-$ or $-Si-R-CH_2CH_2-Si-$. However, "-" in the functional group indicates that

the molecules are further connected. When the reaction at this time is expressed as a reaction formula, the reaction is represented as the following formula. Here, R represents an alkylene group having 1 or more and 8 or less carbon atoms.

[0057]

[Formula 3]



[0058]

(Content of polysiloxane)

The molar ratio between the amount of the hydrosilyl groups of the polysiloxane B and the amount of the alkenyl groups of the polysiloxane A preferably satisfies the following formula (c) in the curable composition.

$$1.0 \leq Si\text{-}H/Si\text{-}A \leq 3.8 \quad (c)$$

(wherein Si-H represents a molar amount of the hydrosilyl groups, and Si-A represents a molar amount of the alkenyl groups.)

[0059]

That is, the release layer satisfies the formula (a), and in order to satisfy this formula, it is preferable to adjust the amount of the hydrosilyl groups of the

polysiloxane B in the curable composition. It is desirable that the amount of the hydrosilyl groups of the polysiloxane B is a molar amount from equal to the amount of the alkenyl groups of the polysiloxane A to 3.8 times. When the amount of the hydrosilyl groups of the polysiloxane B is equal to or more than the amount of the alkenyl groups of the polysiloxane A, the coating film tends to have sufficient strength, and thus problems such as the falling off of the release layer hardly occur. From such a viewpoint, the molar ratio is more preferably 1.5 or more, and still more preferably more than 2.0.

[0060]

Meanwhile, when the amount of the hydrosilyl groups of the polysiloxane B is 3.8 times or less the amount of the alkenyl groups of the polysiloxane A, the amount of the hydrogen bond component contained in the surface free energy of the release layer becomes appropriate, and thus the releasability is improved. From such a viewpoint, the molar ratio is more preferably 3.5 or less, and still more preferably 3.0 or less.

[0061]

In the present invention, the formula (c) is preferably satisfied by setting the mixing mass ratio (B/A) of the polysiloxane A and the polysiloxane B to preferably 0.5 or more and 5 or less, and more preferably 0.9 or more

and 3 or less, in the curable composition. By setting the mixing mass ratio (B/A) as described above, it is possible to prevent the polysiloxane A and the polysiloxane B from appropriately reacting and any component from precipitating on the surface of the release layer.

[0062]

(Adhesion imparting agent C)

The release layer of the present invention contains an adhesion imparting agent C as an essential component. The adhesion imparting agent tends to move to an interface between the polyester film and the release layer in the stage of forming the release layer, and improves adhesion between the polyester film and the release layer. This makes it possible to prevent the release layer from falling off from the polyester film in the process of processing the ceramic green sheet using the release film, which leads to a reduction in the defect rate in the manufacture of the ceramic green sheet.

[0063]

The adhesion imparting agent desirably has a functional group that reacts with at least one of the polysiloxane A and the polysiloxane B in order to have adhesion with a silicone resin that is a release layer. Specifically, it is preferable to have one or more functional groups selected from the group consisting of a

vinyl group, an epoxy group, an acrylic group, and a methacrylic group that react with a hydrosilyl group.

[0064]

The adhesion imparting agent is desirably a silane coupling agent in order to impart adhesion to the polyester film. When the silane coupling agent is used, the silane coupling agent can favorably impart adhesion (for example, an effect by hydrogen bonding) to the polyester film while having compatibility with the polysiloxane.

[0065]

As the silane coupling agent, those represented by the following general formula are preferable.

[0066]

[Formula 4]

$$X^1{}_a Si R^1{}_{(4-a)}$$

[0067]

In the general formula, X^1 represents the functional group, and a represents an integer of 1 or more and 3 or less. In particular, a is preferably 1.

[0068]

R^1 represents a hydrolyzable group selected from an alkoxy group, an acyloxy group, and a halogen, or an alkyl group. Among them, an alkoxy group and an acyloxy group are preferable. The alkoxy group is preferably an alkoxy

group having 1 to 10 carbon atoms, more preferably an alkoxy group having 1 to 6 carbon atoms, and particularly preferably a methoxy group or an ethoxy group. The acyloxy group is preferably an acyloxy group having 2 to 11 carbon atoms, more preferably an acyloxy group having 2 to 7 carbon atoms, and particularly preferably an acetoxy group. The halogen is preferably a chloro group. The alkyl group is preferably an alkyl group having 1 to 6 carbon atoms.

[0069]

When R^1 is as described above, the adhesion between the substrate film and the release layer is excellent.

[0070]

In the above general formula, (4-a) of R^1s are bonded to Si, but these R^1s may be of the same kind or of different kinds. In the present invention, an aspect in which at least one of the (4-a) of R^1s is an alkoxy group or an acyloxy group is preferable, and an aspect in which all R^1s are an alkoxy group or an acyloxy group is more preferable.

[0071]

As the silane coupling agent as in the general formula, one kind or two or more kinds may be used in combination, and it is also possible to use a reactant obtained by reacting two or more kinds of silane coupling agents.

[0072]

In order to improve adhesion between the silane coupling agent and the polyester film, acetic acid or p-toluenesulfonic acid or the like may be added to the silane coupling agent.

[0073]

The addition amount of the adhesion imparting agent in the curable composition is desirably 1% by mass or more and 10% by mass or less, and more desirably 2.0% by mass or more and 8.0% by mass or less, with respect to the total amount of the polysiloxane A and the polysiloxane B. When the addition amount is 1% by mass or more, the adhesion between the release layer and the substrate is improved, and when the addition amount is 10% by mass or less, an excessive adhesion imparting agent is less likely to adversely affect the release layer, and thus flatness and peelability are improved.

[0074]

(Catalyst D)

The curable composition for forming the release layer preferably further contains a catalyst D. The catalyst is not particularly limited as long as the catalyst can accelerate the curing reaction of the curable composition, and among them, a platinum group metal-based compound is preferable.

[0075]

Examples of the platinum group metal-based compound include particulate platinum, particulate platinum adsorbed on a carbon powder carrier, chloroplatinic acid, alcohol-modified chloroplatinic acid, an olefin complex of chloroplatinic acid, palladium, and rhodium. When the curable composition contains such a catalyst, the curing reaction of the curable composition can be more efficiently advanced.

[0076]

From the viewpoint of adjusting the curing reaction rate to a suitable range, the content of the catalyst D in the curable composition according to the present embodiment is preferably about 1 ppm or more and 1000 ppm or less with respect to the total amount of solid contents other than the catalyst D.

[0077]

(Optional components)

In addition to the above components, the curable composition may contain a reaction inhibitor, a solvent, a silicone resin having no reactive functional group, and an anti-static agent and the like.

[0078]

(Physical properties of release layer)

The thickness of the release layer is preferably

0.005 μm or more and 0.1 μm or less, and particularly preferably 0.01 μm or more and 0.05 μm or less. When the thickness of the release layer is 0.005 μm or more, the thickness is sufficient to exhibit a function as the release layer. Meanwhile, when the thickness of the release layer is 0.1 μm or less, the falling off of the coating film from the release layer hardly occurs.

[0079]

The release layer surface is desirably flat so as not to cause defects in the ceramic green sheet applied and formed thereon. It is preferable that the average area surface roughness (Sa) is 7 nm or less, and the maximum protrusion height (Sp) is 100 nm or less. More preferably, the average area surface roughness is 5 nm or less, and the maximum protrusion height is 80 nm or less. For example, the maximum protrusion height (Sp) may be 45 nm or less.

[0080]

If the average area surface roughness is 7 nm or less, and the maximum protrusion height is 100 nm or less, the defects such as pinholes do not occur when the ceramic green sheet is formed, and the yield is good, which is preferable. It can be said that it is more preferable as the average area surface roughness (Sa) is smaller, but the average area surface roughness (Sa) may be 0.1 nm or more or may be 0.3 nm or more. It also can be said that it is

more preferable as the maximum protrusion height (Sp) is smaller, but the maximum protrusion height (Sp) may be 1 nm or more or may be 3 nm or more.

[0081]

[Polyester film]

The polyester film used as the substrate film (hereinafter, sometimes referred to as substrate) of the present invention is a film containing polyester as a resin component, and is preferably a film containing polyester in the largest amount (for example, 90% by mass or more) in the resin component.

[0082]

Polyester constituting the polyester film is not particularly limited, and film-formed polyester which is generally used as a substrate for a release film can be used. The polyester is preferably crystalline linear saturated polyester composed of an aromatic dibasic acid component and a diol component, and for example, polyethylene terephthalate, polyethylene-2,6-naphthalate, polybutylene terephthalate, polytrimethylene terephthalate, or a copolymer containing constituent components of these resins as main components is more suitable.

[0083]

In particular, polyester films formed from polyethylene terephthalate are particularly suitable. In

polyethylene terephthalate, the content of repeating units of ethylene terephthalate is preferably 90 mol% or more, more preferably 95 mol% or more, and other dicarboxylic acid components and diol components may be copolymerized in small amounts. For example, from the viewpoint of cost, a copolymer manufactured from only terephthalic acid and ethylene glycol is preferable. Known additives such as an antioxidant, a light stabilizer, an ultraviolet absorber, and a crystallization agent may be added as long as the effect of the release film of the present invention is not impaired. The polyester film is preferably a biaxially oriented polyester film because of its elastic modulus in both directions, and the like.

[0084]

The intrinsic viscosity of the polyethylene terephthalate film is preferably 0.50 dl/g or more and 0.70 dl/g or less, and more preferably 0.52 dl/g or more and 0.62 dl/g or less. When the intrinsic viscosity is 0.50 dl/g or more, breakage does not often occur in a stretching step, which is preferable. Conversely, when the intrinsic viscosity is 0.70 dl/g or less, the cuttability of the polyethylene terephthalate film at the time of being cut into a predetermined product width is good and dimensional failure does not occur, which is preferable. In addition, it is preferable that the raw material pellets are

sufficiently vacuum-dried.

[0085]

In the present specification, the term "polyester film" may simply mean a polyester film including a surface layer A and a surface layer B (in which the surface layer A and the surface layer B are laminated).

[0086]

The method for manufacturing the polyester film of the present invention is not particularly limited, and methods generally used conventionally can be used. For example, the polyester film can be obtained by melting the polyester with an extruder, extruding the melted product into a film form, cooling the extruded product with a rotary cooling drum to obtain an un-stretched film, and biaxially stretching the un-stretched film. A biaxially stretched film can be obtained by a method in which a film uniaxially stretched in a machine direction or a transverse direction is sequentially stretched biaxially in the transverse direction or the machine direction, or a method in which the un-stretched film is simultaneously stretched biaxially in the machine direction and the transverse direction.

[0087]

In the present invention, a stretching temperature when stretching the polyester film is preferably set to be

equal to or higher than a secondary transition point (Tg) of the polyester. The polyester film is stretched in each of the machine and transverse directions preferably by once or more and 8 times or less and particularly preferably by twice or more and 6 times or less.

[0088]

The thickness of the polyester film is preferably 12 μm or more and 50 μm or less, more preferably 15 μm or more and 38 μm or less, and still more preferably 19 μm or more and 33 μm or less. When the thickness of the film is 12 μm or more, there is no risk of deformation due to heat during film production, processing steps, and forming, which is preferable. Whereas, the thickness of the film of 50 μm or less is preferable for saving the environmental load, because the amount of the film to be disposed after being used is not extremely large.

[0089]

The polyester film substrate may have a single layer or two or more layers. For example, the substrate film may be a polyester film including a surface layer A substantially free of particles having a particle size of 1.0 μm or more and a surface layer B containing particles. Preferably, the surface layer A is substantially free of inorganic particles having a particle size of 1.0 μm or more.

[0090]

In this aspect, particles having a particle size of less than 1.0 μm and 1 nm or more may be present in the surface layer A. The surface layer A is substantially free of particles having a particle size of 1.0 μm or more, for example, inorganic particles, and therefore the occurrence of defects due to the transfer of the particle shape in the substrate to the resin sheet can be reduced.

[0091]

In one aspect, the surface layer A does not contain particles having a particle size of less than 1.0 μm, and therefore the occurrence of defects due to the transfer of the particle shape in the substrate to the resin sheet can be more effectively suppressed.

[0092]

In one aspect, the polyester film substrate is preferably a laminated film including a surface layer A substantially free of inorganic particles in at least one surface. This makes it possible to more effectively suppress the occurrence of defects due to the transfer of the particle shape in the substrate to the resin sheet.

[0093]

For example, in a preferred aspect, the surface layer A substantially free of particles having a particle size of less than 1.0 μm is substantially free of particles having

a particle size of 1.0 μm or more.

[0094]

Here, in the present invention, the phrase "substantially free of particles" means, for example, in the case of particles of less than 1.0 μm, a content that is 50 ppm or less, preferably 10 ppm or less, and most preferably equal to or less than the detection limit when an inorganic element is quantified by fluorescent X-ray analysis. This is because, even if the particles are not positively added into the film, contamination components derived from foreign matters, and dirt attached to raw material resins, or lines or devices in film manufacturing steps may be peeled off and mixed into the film. The phrase "substantially free of particles having a particle size of 1.0 μm or more" means that particles having a particle size of 1.0 μm or more are not actively contained.

[0095]

A laminated polyester film having a multilayer configuration including two or more layers preferably includes a surface layer B that can contain inorganic particles and the like on the opposite surface of the surface layer A substantially free of inorganic particles.

[0096]

As the laminated configuration, when the layer on the side to which the release layer is applied is a layer A,

the layer on the opposite surface thereof is a layer B, and the core layer other than these is a layer C, the layer configuration in the thickness direction may be a laminated structure such as release layer/A/B or release layer/A/C/B. As a matter of course, the layer C may have a plurality of layer configurations. The surface layer B may contain no inorganic particles. In that case, a coat layer D containing at least inorganic particles and a binder is preferably provided on the surface layer B in order to impart slipperiness for winding the film into a roll.

[0097]

In the polyester film substrate of the present invention, the surface layer B forming the surface opposite from the surface to which the release layer is applied preferably contains inorganic particles, and especially, silica particles and/or calcium carbonate particles are preferably used, from the viewpoint of the slipperiness of the film and the ease of air release. As to the content of inorganic particles contained, the inorganic particles are preferably contained in the surface layer B in an amount of 5000 ppm or more and 15000 ppm or less in total.

[0098]

At this time, the average area surface roughness (Sa) of the film of the surface layer B is preferably in a range of 1 nm or more and 40 nm or less. More preferably, the

average area surface roughness is 5 nm or more and 35 nm or less. When the total content of the silica particles and/or the calcium carbonate particles is 5000 ppm or more, and the Sa is 1 nm or more, air can be uniformly released when the film is wound into a roll, and the film has a good winding appearance and good flatness, so that the film is suitable for the manufacture of an ultrathin ceramic green sheet. In addition, when the total content of the silica particles and/or the calcium carbonate particles is 15000 ppm or less and the Sa is 40 nm or less, the aggregation of the lubricant is less likely to occur, and coarse protrusions cannot be formed, so that the quality is stable during the manufacture of the ultrathin ceramic green sheet, which is preferable.

[0099]

As the particles contained in the layer B, inert inorganic particles other than silica and/or calcium carbonate particles and/or heat-resistant organic particles can be used, but silica particles and/or calcium carbonate particles are more preferably used from the viewpoint of transparency and cost. Other examples of the inorganic particles that can be used include alumina-silica composite oxide particles and hydroxyapatite particles. Examples of the heat-resistant organic particles include crosslinked polyacrylic particles, crosslinked polystyrene particles,

and benzoguanamine-based particles. When silica particles are used, porous colloidal silica is preferable, whereas when calcium carbonate particles are used, light calcium carbonate surface-treated with a polyacrylic acid-based polymeric compound is preferable from the viewpoint of preventing the lubricant from falling off.

[0100]

The average particle diameter of the inorganic particles to be added to the surface layer B is preferably 0.1 μm or more and 2.0 μm or less, and particularly preferably 0.5 μm or more and 1.0 μm or less. When the average particle diameter of the inorganic particles is 0.1 μm or more, the slipperiness of the release film is good, which is preferable. When the average particle diameter is 2.0 μm or less, there is no possibility of adversely affecting the smoothness of the surface of the release layer, and therefore there is no possibility of generating pinholes in the ceramic green sheet, which is preferable. The average particle diameter of the particles can be measured by a method in which particles in the cross section of a processed film are observed with a scanning electron microscope, 100 particles are observed, and the average value thereof is taken as the average particle diameter. The shape of the particles is not particularly limited as long as the shape of the particles satisfies the

object of the present invention, and spherical particles and non-spherical particles having an indefinite shape can be used. The particle diameter of the particles having an indefinite shape can be calculated as an equivalent circle diameter. The equivalent circle diameter is a value obtained by dividing the area of the observed particles by the circular constant (π), calculating the square root, and doubling the square root.

[0101]

From the viewpoint of reducing pinholes, it is preferable not to use a recycled raw material or the like for the surface layer A, which is a layer on which the release layer is to be provided, in order to prevent the contamination of inorganic particles such as a lubricant.

[0102]

The thickness ratio of the surface layer A, which is a layer on which the release layer is provided, is preferably 20% or more and 50% or less of the total thickness of all the layers of the substrate film. When the thickness ratio of the surface layer A is 20% or more, the film is hardly affected from the inside of the film by particles contained in the surface layer B or the like, and the average area surface roughness Sa easily satisfies the above range, which is preferable. When the thickness ratio of the surface layer A is 50% or less of the total

thickness of all the layers of the substrate film, the use ratio of a recycled raw material in the surface layer B can be increased, so that the environmental load is reduced, which is preferable.

[0103]

From the viewpoint of economic performance, for the layer other than the surface layer A (the surface layer B or the above-mentioned intermediate layer C), 50 to 90% by mass of film scraps or reused materials for PET bottles can be used. Even in this case, it is preferable that the type, the amount, and the particle size of the lubricant contained in the layer B, and the average area surface roughness (Sa) of the surface layer B satisfy the above ranges.

[0104]

In order to improve the adhesion of the release layer or the like to be applied later, or in order to prevent electric charge, a coat layer D may be provided on the surface of the surface layer A and/or the surface of the surface layer B, before the film is subjected to stretching or after the film is subjected to uniaxial stretching in the film forming process, or the film may be subjected to a corona treatment or the like.

[0105]

When the surface layer B is free of particles, it is

also preferable to impart slipperiness to the surface layer B with a coat layer D containing particles. Means for providing the coat layer D is not particularly limited, but it is preferable to provide the coat layer D by a so-called in-line coating method in which coating is performed during the formation of a polyester film. When a coat layer D that imparts slipperiness is provided on the surface of the polyester film on which the release layer is not laminated, the polyester film does not need to have the surface layers A and B, and may be a single-layer polyester film substantially free of inorganic particles.

[0106]

The average area surface roughness (Sa) of the surface layer B is preferably 40 nm or less, more preferably 35 nm or less, and still more preferably 30 nm or less. When slipperiness is imparted to the surface of the surface layer B or the single layer polyester film on which the release layer is not laminated with the coat layer D, the Sa of the surface is measured for the surface on which the coat layer D is laminated, and is preferably in the same range as the average area surface roughness (Sa) of the surface layer B.

[0107]

It is preferable that at least a binder resin and particles are contained in the coat layer D on the surface

of the polyester film on which the release layer is not laminated.

[0108]

(Binder resin of coat layer D)

The binder resin constituting the easy-to-slip coating layer is not particularly limited. Specific examples of the polymer include a polyester resin, an acrylic resin, an urethane resin, a polyvinyl-based resin (polyvinyl alcohol and the like), polyalkylene glycol, polyalkyleneimine, methylcellulose, hydroxycellulose, and starches. Among these, from the viewpoints of retention and adhesion of the particles, a polyester resin, an acrylic resin, and an urethane resin are preferably used. In consideration of the compatibility of the binder resin with the polyester film, the polyester resin is particularly preferable. The polyester of the binder is preferably a copolyester in order to achieve solubility and dispersibility in a solvent, and adhesion with a substrate film and other layer. The polyester resin may be modified with polyurethane. Other preferable examples of the binder resin constituting the easy-to-slip coating layer on the polyester substrate film include an urethane resin. Examples of the urethane resin include a polycarbonate polyurethane resin. Furthermore, the polyester resin and the polyurethane resin may be used in combination, and the

above-mentioned other binder resins may be used in combination.

[0109]

(Crosslinking agent of coat layer D)

In the present invention, in order to form a crosslinked structure in the easy-to-slip coating layer, the easy-to-slip coating layer may be formed so as to contain a crosslinking agent. The easy-to-slip coating layer contains the crosslinking agent, which makes it possible to further improve the adhesion under high temperature and high humidity. Specific examples of the crosslinking agent include urea-based, epoxy-based, melamine-based, isocyanate-based, oxazoline-based, and carbodiimide-based crosslinking agents, and aziridine. In order to promote a crosslinking reaction, a catalyst and the like may be appropriately used, if necessary.

[0110]

(Particles in coat layer D)

The easy-to-slip coating layer preferably contains lubricant particles in order to impart slipperiness to the surface of the easy-to-slip coating layer. The particles may be inorganic particles or organic particles, and are not particularly limited. Examples thereof include (1) inorganic particles made of silica, kaolinite, talc, light calcium carbonate, heavy calcium carbonate, zeolite,

alumina, barium sulfate, carbon black, zinc oxide, zinc sulfate, zinc carbonate, zirconium oxide, titanium dioxide, satin white, aluminum silicate, diatomaceous earth, calcium silicate, aluminum hydroxide, hydrous halloysite, calcium carbonate, magnesium carbonate, calcium phosphate, hydroxide magnesium, and the like, and (2) acrylic or methacrylic, vinyl chloride-based, vinyl acetate-based, nylon, styrene/acrylic, styrene/butadiene-based, polystyrene/acrylic, polystyrene/isoprene-based, polystyrene/isoprene-based, methyl methacrylate/butyl methacrylate-based, melamine-based, polycarbonate-based, urea-based, epoxy-based, urethane-based, phenol-based, diallyl phthalate-based, and polyester-based organic particles. Silica is particularly preferably used in order to impart appropriate slipperiness to the coating layer.

[0111]

The average particle size of particles is preferably 10 nm or more, more preferably 20 nm or more, and still more preferably 30 nm or more. It is preferable that the average particle size of particles is 10 nm or more since the particles are less likely to aggregate and slipperiness may be secured.

[0112]

The average particle size of the particles is preferably 1000 nm or less, more preferably 800 nm or less,

still more preferably 600 nm or less. It is preferable that the average particle size of the particles is 1000 nm or less since the transparency is maintained and the particles do not fall off.

[0113]

For example, the mixture of small particles having an average particle size of about 10 nm or more and 270 nm or less and large particles having an average particle size of about 300 nm or more and 1000 nm or less is also preferable in order to reduce an average length of a roughness curve element (RSm) to achieve both slipperiness and smoothness while keeping average area surface roughness (Sa) and a maximum protrusion height (Sp) to be described later small. Particularly preferably, small particles of 30 nm or more and 250 nm or less and large particles having an average particle size of 350 nm or more and 600 nm or less are used in combination. When small particles and large particles are mixed, the mass content rate of the small particles is preferably greater than the mass content rate of the large particles with respect to the entire solid content of the coating layer.

[0114]

[Formation of release layer]

In the present invention, the method for forming the release layer is not particularly limited, and the

following method is used. A coating solution in which a release compound is dissolved or dispersed is spread on one surface of the polyester film of the substrate by coating and the like. A solvent or the like is removed by drying, followed by curing.

[0115]

A drying temperature for solvent drying when the release layer of the present invention is applied on the substrate film by solution application is preferably 50°C or higher and 120°C or lower, and more preferably 60°C or higher and 100°C or lower. A heating time is preferably 30 seconds or less, and more preferably 20 seconds or less. Furthermore, after the solvent drying, the irradiation of active energy rays preferably advances the curing reaction. As the active energy rays used at this time, ultraviolet rays, electron beams, and X-rays and the like can be used, but ultraviolet rays are likely to be used, which are preferable. The amount of light of ultraviolet rays with which the composition is irradiated is preferably 30 mJ/cm^2 or more and 300 mJ/cm^2 or less, and more preferably 30 mJ/cm^2 or more and 200 mJ/cm^2 or less. By setting the amount of light to 30 mJ/cm^2 or more, the curing of the composition is sufficiently advanced, and by setting the amount of light to 300 mJ/cm^2 or less, the speed during processing can be improved, whereby the release film can be

economically prepared, which is preferable.

[0116]

In the present invention, the surface tension of the coating solution when the release layer is applied is not particularly limited, but it is preferably 30 mN/m or less. By setting the surface tension as described above, wettability after coating is improved, and the unevenness of the surface of the coating film after drying can be reduced.

[0117]

As the applying method of the coating solution, any known applying methods can be applied. For example, conventionally known methods such as a roll coating method (such as a gravure coating method or a reverse coating method), a bar coating method (such as a wire bar), a die coating method, a spray coating method, and an air knife coating method can be utilized.

[0118]

[Ceramic green sheet]

A release film for manufacturing a ceramic green sheet of the present invention is suitably used for manufacturing a ceramic green sheet. A method for manufacturing a ceramic green sheet of the present invention includes forming a ceramic green sheet using the release film described above, wherein the formed ceramic

green sheet has a thickness of 0.2 μm to 1.0 μm.

[0119]

The ceramic green sheet is not particularly limited as long as the ceramic green sheet is a sheet containing ceramic. In one aspect, the release film of the present invention is a release film for forming a ceramic green sheet containing an inorganic compound. Examples of the inorganic compound include metal particles, metal oxides, and minerals, and specific examples thereof include calcium carbonate, silica particles, aluminum particles, and barium titanate particles. Since the present invention includes the release layer having high smoothness, it is possible to suppress drawbacks that may be caused by the inorganic compounds, for example, problems such as breakage of the ceramic green sheet and difficulty in peeling the ceramic green sheet from the release layer even in an aspect in which these inorganic compounds are contained in the ceramic green sheet.

[0120]

Resin components forming the ceramic green sheet can be appropriately selected according to the application. In one aspect, the ceramic green sheet is a ceramic green sheet containing an inorganic compound. For example, the ceramic green sheet can contain barium titanate as the inorganic compound. As the resin components, for example,

a polyvinyl butyral-based resin can be contained.

[0121]

In one aspect, the ceramic green sheet has a thickness of 0.2 μm or more and 1.0 μm or less.

[0122]

For example, the present invention can provide a method for manufacturing a release film for manufacturing a ceramic green sheet containing such an inorganic compound. The method for manufacturing a release film of the present invention may include a step of forming a ceramic green sheet having a thickness of 0.2 μm or more and 1.0 μm or less.

[0123]

[Ceramic green sheet and ceramic capacitor]

In general, a laminated ceramic capacitor has a rectangular parallelopiped ceramic body. Inside the ceramic body, first internal electrodes and second internal electrodes are provided alternately along a thickness direction. The first internal electrodes are exposed to the first end surface of the ceramic body. First external electrodes are provided on the first end surface. The first internal electrodes are electrically connected to the first external electrodes at the first end surface. The second internal electrodes are exposed to the second end surface of the ceramic body. Second external electrodes

are provided on the second end surface. The second internal electrodes are electrically connected to the second external electrodes at the second end surface.

[0124]

In one aspect, the release film of the present invention is a release film, and is used for manufacturing such a laminated ceramic capacitor.

[0125]

For example, the method for manufacturing a ceramic green sheet in which the release film according to the present invention is used to form the ceramic green sheet can form the ceramic green sheet having a thickness of 0.2 μm or more and 1.0 μm or less.

[0126]

More specifically, for example, the ceramic green sheet is manufactured as follows. First, the release film of the present invention is used as a carrier film, and a ceramic slurry for constituting a ceramic body is applied and dried. An extremely thin ceramic green sheet having a thickness of 0.2 μm or more and 1.0 μm or less has been required. A conductive layer for constituting a first or second internal electrode is printed on the applied and dried ceramic green sheet. A ceramic green sheet, a ceramic green sheet on which a conductive layer for constituting a first internal electrode is printed, and a

ceramic green sheet on which a conductive layer for constituting a second internal electrode is printed are appropriately laminated and pressed to obtain a mother laminated body. The mother laminated body is divided into a plurality of raw ceramic bodies. The raw ceramic body is fired to obtain a ceramic body. Thereafter, the laminated ceramic capacitor can be completed by forming first and second external electrodes.

EXAMPLES

[0127]

The present invention will be more specifically described by reference to Examples and Comparative Examples. In the present invention, physical properties and the like were measured or evaluated by the following methods. Hereinafter, unless otherwise specified, “part” means “part by mass”, and “%” means “% by mass”.

[0128]

(Amount of functional groups in mixture of polysiloxane)

Heavy chloroform was added to and dissolved in a silicone mixture having the same mixing ratio as that of polysiloxanes A and B to be used to have a solid content of 10 mass%, and the resulting mixture liquid was placed in an NMR tube. The sample placed in the NMR tube was subjected to NMR measurement using a nuclear magnetic resonance

apparatus (NMR AVANCE NEO 600 manufactured by BRUKER), and the amount (mmol) of each functional group of an alkenyl group and a hydrosilyl group was quantified.

[0129]

From the above measurement results, the molar ratio of the alkenyl groups and the hydrosilyl groups was calculated using the following formula.

Molar ratio = Si-H/Si-A

(wherein Si-H represents the molar amount of the hydrosilyl groups, and Si-A represents the molar amount of the alkenyl groups.)

[0130]

(Weight average molecular weight)

A sample solution with a sample concentration adjusted to 0.2% was filtered through a 0.2 μm membrane filter, and subjected to gel permeation chromatography (GPC) analysis under the following conditions to determine the weight average molecular weight of a sample. The molecular weight was calculated in terms of standard polystyrene.

Apparatus: TOSOH HLC-8320GPC

Column: TSKgel SuperHM-H × 2 + TSKgel SuperH 2000 (TOSOH)

Solvent: Chloroform 100%

Flow rate: 0.6 ml/min

Concentration: 0.2%

Injection volume: 20 μL

Temperature: 40°C

Detector: RI

[0131]

(Thickness of release layer)

A release film was embedded in a resin, and ultrathinly sectioned using an ultramicrotome. Thereafter, the cross section of a release film was observed using a JEM 2100 transmission electron microscope manufactured by JEOL Ltd., and the film thickness of a release layer was measured from the observed TEM image. When the thickness was too thin to accurately evaluate by cross-section observation, the Si intensity was measured with an X-ray fluorescence apparatus (ZSX PRIMUSII manufactured by Rigaku Corporation), and the coating amount was calculated by a calibration curve method.

[0132]

(Average area surface roughness Sa and maximum protrusion height Sp of release layer)

The average area surface roughness and the maximum protrusion height were measured under the following conditions using a noncontact surface profilometer system (VertScan R550H-M100). For the average area surface roughness (Sa), the average value of five measurements was

employed. For the maximum protrusion height (Sp), seven measurements were performed, and the maximum value of five measurements excluding the maximum and minimum values was employed.

[0133]

(Measurement conditions)

- Measurement mode: WAVE mode
- Objective lens: 50 times
- 0.5×Tube lens
- Measurement area 187 μm×139 μm

(Analysis conditions)

- Surface correction: 4th order correction
- Interpolation processing: complete interpolation

[0134]

(Surface free energy of release layer)

A release film was fixed on a flat glass substrate, 1.9 μL of water was added dropwise onto the release film using a contact angle meter (DM-501 manufactured by Kyowa Interface Science Co., Ltd.), an angle formed by a droplet and a release layer was measured 60 seconds after the droplet stopped, and an average value of 5 measurements was taken as θ_1. Similarly, 0.9 μL of methylene iodide was added dropwise onto the release film, the angle formed by the droplet and the release layer was measured 30 seconds after the droplet stopped, and the average value of 5

measurements was taken as θ_2. Furthermore, 0.9 μL of ethylene glycol was added dropwise onto the release film, the angle formed by the droplet and the release layer was measured 30 seconds after the droplet stopped, and the average value of 5 measurements was taken as θ_3.

[0135]

From θ_1, θ_2, and θ_3 described above and $\gamma LVnd$, $\gamma LVnp$, $\gamma LVnh$, and γLn (with the proviso that n = 1, 2, or 3, and corresponds to water, methylene iodide, or ethylene glycol) of water, methylene iodide, and ethylene glycol described in Table 2, a dispersion component γSVd, a dipole component γSVp, and a hydrogen bond component γSVh of the surface free energy of the release layer were calculated by the following formula, and the total thereof was defined as the surface free energy γS of the release layer. The unit of the surface free energy and each component is "mJ/m^2".

[0136]

[Table 2]

	Dispersion component	Dipole component	Hydrogen bonding component	Total
	$\gamma LVnd$	$\gamma LVnp$	$\gamma LVnh$	γLn
Water	29.1	1.3	42.4	72.8
Methylene iodide	46.8	4.0	0.0	50.8
Ethylene glycol	30.1	0.0	17.6	47.7

[0137]

[Math 2]

$$\sqrt{\gamma_{SV}{}^{d}\gamma_{LV1}{}^{d}} + \sqrt{\gamma_{SV}{}^{p}\gamma_{LV1}{}^{p}} + \sqrt{\gamma_{SV}{}^{h}\gamma_{LV1}{}^{h}} = \frac{\gamma_{L1}(1+\cos\Theta_1)}{2}$$

$$\sqrt{\gamma_{SV}{}^{d}\gamma_{LV2}{}^{d}} + \sqrt{\gamma_{SV}{}^{p}\gamma_{LV2}{}^{p}} + \sqrt{\gamma_{SV}{}^{h}\gamma_{LV2}{}^{h}} = \frac{\gamma_{L2}(1+\cos\Theta_2)}{2}$$

$$\sqrt{\gamma_{SV}{}^{d}\gamma_{LV3}{}^{d}} + \sqrt{\gamma_{SV}{}^{p}\gamma_{LV3}{}^{p}} + \sqrt{\gamma_{SV}{}^{h}\gamma_{LV3}{}^{h}} = \frac{\gamma_{L3}(1+\cos\Theta_3)}{2}$$

[0138]

$\gamma SVd + \gamma SVp + \gamma SVh = \gamma S$

(Peeling force of ceramic green sheet)

A slurry composition I composed of materials shown below was stirred and mixed for 10 minutes, and dispersed for 10 minutes with zirconia beads having a diameter of 0.5 mm using a bead mill to obtain a primary dispersion. Thereafter, a slurry composition II composed of materials shown below was added to the primary dispersion at a ratio of (slurry composition I):(slurry composition II)=3.4:1.0, followed by secondarily dispersing for 10 minutes with zirconia beads having a diameter of 0.5 mm using a bead mill to obtain a ceramic slurry.

(Slurry Composition I)

Toluene	22.3 parts by mass
Ethanol	18.3 parts by mass

Barium titanate (average particle size: 100 nm)

57.5 parts by mass

HOMOGENOL L-18 (manufactured by Kao Corporation)

1.9 parts by mass

(Slurry composition II)

Toluene 39.6 parts by mass

Ethanol 39.6 parts by mass

Dioctyl phthalate 3.3 parts by mass

Polyvinyl butyral (S-LEC BM-S manufactured by SEKISUI CHEMICAL CO., LTD.) 16.3 parts by mass

1-Ethyl-3-methylimidazolium ethyl sulfate 0.5 parts by mass

Then, the slurry was coated on the release surface of the obtained release film sample using an applicator such that the thickness after drying was 1.0 μm, and dried at 60°C for 1 minute, to obtain a release film including a ceramic green sheet. The obtained release film including the ceramic green sheet was statically eliminated using a static eliminator (SJ-F020 manufactured by Keyence Corporation), and then peeled off at a peeling angle of 90 degrees, a peeling temperature of 25°C, and a peeling speed of 10 m/min using a peeling tester (VPA-3 manufactured by Kyowa Interface Science Co., Ltd., load of load cell: 0.1 N). As a direction of peeling, a double-sided adhesive tape (No. 535A manufactured by Nitto Denko Corporation) was attached on a SUS plate attached to the peeling tester, and

the release film was fixed thereon by bonding the ceramic green sheet side to a double-sided tape. The release film was peeled off by pulling the release film side. Among the obtained measured values, the average value of peeling forces at a peel distance of 20 mm or more and 70 mm or less was calculated, and the value was taken as the peeling force. The measurement was performed five times in total, and the average value of the peeling forces was adopted.

[0139]

(Evaluation of pinholes of ceramic green sheet)

A ceramic green sheet having a thickness of 1 μm was formed on the release surface of the release film in the same manner as in the evaluation of the peeling force of the ceramic green sheet. Subsequently, the release film was peeled off from the release film including the formed ceramic green sheet to obtain the ceramic green sheet. In a range of 25 cm^2 in the central region of the obtained ceramic green sheet in the film transverse direction, light was applied to a surface opposite from a surface to which a ceramic slurry was applied, and the occurrence status of pinholes viewed from the transmission of light was observed. The pinholes were visually determined according to the following criteria.

○: No occurrence of pinholes

×: Occurrence of one or more pinholes

[0140]

(Amount of Si transferred to PVB sheet)

Polyvinyl butyral (S-LEC BM-S manufactured by Sekisui Chemical Co., Ltd.) was coated on the release surface of the release film sample using an applicator such that the thickness of the dried resin was 1.0 μm, and dried at 60°C for 1 minute to obtain a release film with a PVB sheet. The release film with a PVB sheet was allowed to stand in an environment of 23°C and 65RH for 24 hours, then the PVB sheet was peeled off from the release film, and the surface of the PVB sheet in contact with the release film was measured for Si intensity (Kcps) by a fluorescent X-ray apparatus (ZSX PRIMUSII manufactured by Rigaku Corporation).

[0141]

(Backmigration of release layer to polyester substrate)

The release film sample was cut into six films of 5 cm × 5 cm, and the films were stacked in such a manner that the release surface and a surface opposite to the release surface were in contact with each other, and subjected to a pressure treatment for 10 minutes under a load of 30 MPa. Thereafter, the six release films were peeled off, and the surface opposite to the release surface was painted red with a red magic pen (MGD-T2 manufactured by Teranishi Chemical Industry Co., Ltd.) for the six films, and whether

or not the magic ink repelled was confirmed.

○: 0 cissing place in all six films

×: 1 or more cissing places in any of six films

[0142]

(Adhesion of release layer over time)

The release film sample was stored in an environment of 60°C and 90%RH for 3 days. Thereafter, the release layer was subjected to a Gakushin-type friction tester (manufactured by Yamaguchi Kagaku Sangyo Co., Ltd,) using pearl paper (Toyobo ester film P4255-35 manufactured by Toyobo Co., Ltd.) at a contact portion between a load head portion and the film through gauze (Hakujuji gauze manufactured by Hakujuji Co., Ltd.). The load of the head portion was set to 200 gf/25 mm^2 (5 mm × 5 mm) [0.0785 MPa]. The film was rubbed against the load head portion by reciprocating 10 times, and then the release surface was painted red with a red magic pen (MGD-T2 manufactured by Teranishi chemical industry co., ltd.) to confirm whether or not the magic ink repelled.

○: magic ink repels.

△: there is a site where magic ink does not repel.

×: magic ink does not repel.

[0143]

(Preparation of polyethylene terephthalate pellets (PET (I))

As an esterification reactor, a continuous esterification reactor including a three-stage complete mixing tank including a stirrer, a partial condenser, a raw material charging port, and a product outlet was used. The amount of TPA (terephthalic acid) was set to 2 tons/hour, and the amount of EG (ethylene glycol) was set to 2 mol per 1 mol of TPA. The amount of antimony trioxide was set such that the amount of Sb atoms with respect to produced PET was set to 160 ppm. These slurries were continuously supplied to a first reaction can of the esterification reactor, and reacted at normal pressure at 255°C for an average residence time of 4 hours. Next, the reaction product in the first esterification reaction can was continuously taken out of the system, and supplied to a second esterification reaction can. 8% by mass of EG distilled off from the first esterification reaction can with respect to produced PET was supplied into the second esterification reaction can. Furthermore, an EG solution containing magnesium acetate tetrahydrate set such that the amount of Mg atoms with respect to the produced PET was set to 65 ppm and an EG solution containing TMPA (trimethyl phosphate) set such that the amount of P atoms with respect to the produced PET was set to 40 ppm were added, and reacted at 260°C at normal pressure for an average residence time of 1 hour. Subsequently, the reaction

product of the second esterification reaction can was continuously taken out of the system, and fed to a third esterification reaction can. 0.2% by mass of porous colloidal silica having an average particle size of 0.9 μm and subjected to a dispersion treatment with the average number of treatments of 5 passes under pressure of 39 MPa (400 kg/cm^2) using a high pressure disperser (manufactured by Nippon Seiki Co., Ltd.), and 0.4% by mass of synthetic calcium carbonate having an average particle size of 0.6 μm and obtained by attaching 1% by mass of a polyacrylic acid ammonium salt per calcium carbonate were added in the forms of 10% EG slurries, and reacted at 260°C at normal pressure for an average residence time of 0.5 hours. The esterification reaction product produced in the third esterification reaction can was continuously fed to a three-stage continuous polycondensation reaction apparatus to perform polycondensation, and the polycondensation product was filtered with a filter prepared by sintering stainless steel fibers having a 95% cut diameter of 20 μm, and then subjected to ultrafiltration. Then, the filtered product was extruded into water, cooled, and then cut into a chip shape to obtain PET chips having an intrinsic viscosity of 0.60 dl/g (hereinafter abbreviated as PET (I)). The content of the lubricant in the PET chip was 0.6% by mass.

[0144]

(Preparation of polyethylene terephthalate pellets (PET (II))

Meanwhile, in the manufacture of the PET (I) chip, a PET chip having an intrinsic viscosity of 0.62 dl/g and containing no particles made of calcium carbonate and silica and the like was obtained (hereinafter abbreviated as PET (II)).

[0145]

(Manufacture of laminated film X1)

These PET chips were dried, then melted at 285°C, melted at 290°C by a separate melt extruder, subjected to two-stage filtration of a filter obtained by sintering stainless steel fibers having a 95% cut diameter of 15 μm and a filter obtained by sintering stainless steel particles having a 95% cut diameter of 15 μm, and merged in a feed block. The PET (I) and the PET (II) were laminated such that the PET (I) was a surface layer B (opposite side layer to release surface) and the PET (II) was a surface layer A (release surface side layer), extruded (cast) into a sheet shape at a speed of 45 m/min, and electrostatically adhered and cooled on a casting drum at 30°C by an electrostatic adhesion method, to obtain an un-stretched polyethylene terephthalate sheet having an intrinsic viscosity of 0.59 dl/g. The layer ratio was adjusted such

that PET (I)/PET (II) = 60% by mass/40% by mass was set in the calculation of the discharge amount of each extruder. Then, this un-stretched sheet was heated with an infrared heater, and then stretched by 3.5 times in a machine direction at a roll temperature of 80°C according to the speed difference between rolls. Thereafter, the sheet was guided to a tenter, and stretched by 4.2 times in a transverse direction at 140°C. Then, a heat treatment was performed at 210°C in a heat fixation zone. Thereafter, a 2.3% relaxation treatment was performed at 170°C in a transverse direction to obtain a biaxially stretched polyethylene terephthalate film X1 having a thickness of 31 μm. In the obtained film X1, Sa of the surface layer A was 1 nm, and Sa of the surface layer B was 28 nm.

[0146]

(Manufacture of laminated film X2)

As the laminated film X2, PET (II) was used for both the surface layer A side and the surface layer B side, and was laminated in the same manner as the laminated film X1. The laminated product was extruded (cast) in the form of a sheet at a speed of 45 m/min, and electrostatically adhered and cooled on a casting drum at 30°C by an electrostatic adhesion method to obtain an un-stretched polyethylene terephthalate sheet having an intrinsic viscosity of 0.59 dl/g. This un-stretched PET sheet was heated to 100°C with

a heated roll group and an infrared heater, and then stretched by 3.5 times in a machine direction with a roll group having a circumferential velocity difference to obtain a uniaxially stretched PET film. Subsequently, the easily slipping coating liquid was applied to one surface of a PET film with a bar coater, and then dried at 80°C for 15 seconds. The applied amount of the coating liquid after final stretching and drying was adjusted to 0.1 μm. Subsequently, using a tenter, the film was stretched by 4.0 times in a transverse direction at 150°C, and heated at 230°C for 0.5 seconds with the length of the film in the transverse direction fixed. The film was further subjected to relaxation treatment in the transverse direction by 3% at 230°C for 10 seconds to obtain an in-line coating polyester film having a thickness of 31 μm. In the obtained film X2, Sa of the surface layer A was 1 nm, and Sa of the surface layer B was 14 nm.

[0147]

(Easily slipping coating solution)

Water	45.82 parts by mass
Isopropyl alcohol	35.00 parts by mass
Acrylic polyol resin	10.36 parts by mass

(NeoCryl A-614 manufactured by DSM Coating Resins, Tg: 74°C, acid value: 55%, solid concentration: 32% by mass)

Oxazoline-based cross-linking agent D-1:

5.68 parts by weight

(Solid content concentration: 25% by mass)

Acrylic particle water dispersion

2.37 parts by mass

(trade name: MX200W, manufactured by Nippon Shokubai Co., Ltd., average particle size: 350 nm, solid content concentration: 10% by mass)

Acrylic particle water dispersion

0.47 parts by mass

(trade name: MX300W, manufactured by Nippon Shokubai Co., Ltd., average particle size: 450 nm, solid content concentration: 10% by mass)

Surfactant H-1 (fluorine-based, solid content concentration: 10% by mass): 0.30 parts by mass

[0148]

(Example 1)

A silicone mixture R1 containing a vinyl-modified silicone resin (weight average molecular weight: 466000, in Structural Formula (1), l = 3120, m = 46, n = 0) represented by Structural Formula (1) as polysiloxane A and a polymethylhydrogensiloxane (weight average molecular weight: 8400, in Structural Formula (2), o = 3, p = 65) represented by Structural Formula (2) as polysiloxane B was prepared so that a molar ratio (amount of hydrosilyl groups

/amount of alkenyl groups) was adjusted to 2.0, and the following coating liquid M1 for forming a release layer containing the silicone mixture R1, an adhesion imparting agent S1, and a catalyst P1 was prepared.

(Coating liquid M1 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R1	1.5 parts
Adhesion imparting agent S1	0.083 parts

(SD7200 (reaction product of vinyltriacetoxysilane and glycidoxypropyltrimethoxysilane, solid concentration: 90%) manufactured by Dow Toray Co., Ltd.)

Catalyst P1	0.1 parts

(SRX212 (1,1,3,3-tetramethyl-1,3-divinyldisiloxane platinum complex, solid concentration: 5%) manufactured by Dow Toray Co., Ltd.)

The coating liquid M1 for forming a release layer having the above composition was coated on a surface layer A of a laminated film X1 using reverse gravure so that an applied amount after drying was 0.020 μm. Thereafter, a processing speed was adjusted so that the laminated film X1 entered a first drying furnace after 0.5 seconds, and the laminated film X1 was continuously dried by heating at a first drying furnace temperature of 120°C and a second drying furnace temperature of 90°C. After the drying step,

the laminated film X1 was irradiated with ultraviolet rays with an integrated light amount of 100 mJ/cm^2 on a cooling roll using an ultraviolet irradiator (manufactured by Heraeus, H valve) to cure a release layer, thereby obtaining a release film for manufacturing a ceramic green sheet. The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0149]

(Example 2)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that a silicone mixture R2 containing a vinyl-modified silicone resin (weight average molecular weight: 495000, in Structural Formula (1), l = 2820, m = 60, n = 0) represented by Structural Formula (1) as polysiloxane A and a polymethylhydrogensiloxane (weight average molecular weight: 8400, in Structural Formula (2), o = 3, p = 65) represented by Structural Formula (2) as polysiloxane B was prepared so that a molar ratio (amount of hydrosilyl groups/amount of alkenyl groups) was adjusted to 1.0, and the following coating liquid M2 for forming a release layer containing the silicone mixture R2, an adhesion imparting

agent S1, and a catalyst P1 was prepared.

(Coating liquid M2 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R2	1.5 parts
Adhesion imparting agent S1	0.083 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0150]

(Example 3)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that a silicone mixture R3 containing a vinyl-modified silicone resin (weight average molecular weight: 520000, in Structural Formula (1), l = 3700, m = 40, n = 0) represented by Structural Formula (1) as polysiloxane A and a polymethylhydrogensiloxane (weight average molecular weight: 8400, in Structural Formula (2), o = 3, p = 65) represented by Structural Formula (2) as polysiloxane B was prepared so that a molar ratio (amount of hydrosilyl groups/amount of alkenyl groups) was adjusted to 3.0, and

the following coating liquid M3 for forming a release layer containing the silicone mixture R3, an adhesion imparting agent S1, and a catalyst P1 was prepared.

(Coating liquid M3 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R3	1.5 parts
Adhesion imparting agent S1	0.083 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0151]

(Example 4)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the coating liquid M1 for forming a release layer was coated so that an applied amount after drying was 0.050 μm. The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0152]

(Example 5)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the coating liquid M1 for forming a release layer was coated so that an applied amount after drying was 0.080 μm. The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0153]

(Example 6)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the following coating liquid M4 for forming a release layer containing a silicone mixture R1, an adhesion imparting agent S2, and a catalyst P1 was coated so that an applied amount after drying was 0.020 μm.

(Coating liquid M4 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R1	1.5 parts
Adhesion imparting agent S2 (KBM503 (3-methacryloxypropyltrimethoxysilane, solid	0.075 parts

concentration: 100%) manufactured by Shin-Etsu Chemical Co., Ltd.)

p-toluenesulfonic acid	0.008 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0154]

(Example 7)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the following coating liquid M5 for forming a release layer containing a silicone mixture R1, an adhesion imparting agent S3, and a catalyst P1 was coated so that an applied amount after drying was 0.020 μm.

(Coating liquid M5 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R1	1.5 parts
Adhesion imparting agent S3	0.075 parts

(KBM403 (3-glycidoxypropyltrimethoxysilane, solid concentration: 100%) manufactured by Shin-Etsu Chemical Co., Ltd.)

p-toluenesulfonic acid 0.008 parts

Catalyst P1 0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0155]

(Example 8)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the following coating liquid M6 for forming a release layer containing a silicone mixture R1, an adhesion imparting agent S4, and a catalyst P1 was coated so that an applied amount after drying was 0.020 μm.

(Coating liquid M6 for forming release layer)

Methyl ethyl ketone 64.3 parts

Toluene 34.0 parts

Silicone mixture R1 1.5 parts

Adhesion imparting agent S4 0.075 parts

(KBM1003 (vinyltrimethoxysilane, solid concentration: 100%) manufactured by Shin-Etsu Chemical Co., Ltd.)

p-toluenesulfonic acid 0.008 parts

Catalyst P1 0.1 parts

The outline of the coating liquid for forming a

release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0156]

(Example 9)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the following coating liquid M7 forming a release layer having a different content ratio of an adhesion imparting agent S1 was coated so that an applied amount after drying was 0.020 μm.

(Coating liquid M7 for forming release layer)

Methyl ethyl ketone	64.4 parts
Toluene	34.0 parts
Silicone mixture R1	1.5 parts
Adhesion imparting agent S1	0.042 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0157]

(Example 10)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the following coating liquid M8 forming a release layer having a different content ratio of an adhesion imparting agent S1 was coated so that an applied amount after drying was 0.020 μm.

(Coating liquid M8 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R1	1.5 parts
Adhesion imparting agent S1	0.125 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0158]

(Example 11)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the following coating liquid M9 forming a release layer having a different content ratio of an adhesion imparting agent S1 was coated so that an applied amount after drying was 0.020 μm.

(Coating liquid M9 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R1	1.5 parts
Adhesion imparting agent S1	0.008 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0159]

(Example 12)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the following coating liquid M10 forming a release layer having a different content ratio of an adhesion imparting agent S1 was coated so that an applied amount after drying was 0.020 μm.

(Coating liquid M10 for forming release layer)

Methyl ethyl ketone	64.1 parts
Toluene	34.0 parts
Silicone mixture R1	1.5 parts
Adhesion imparting agent S1	0.250 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0160]

(Example 13)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the coating liquid M1 for forming a release layer was coated on the laminated film X2. The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0161]

(Example 14)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that a silicone mixture R4 containing a vinyl-modified silicone resin (weight average molecular weight: 18000, in Structural Formula (1), l = 110, m = 3, n = 1) represented by Structural Formula (1) as polysiloxane A and a polymethylhydrogensiloxane (weight average molecular weight: 8400, in Structural Formula (2), o = 3, p = 65)

represented by Structural Formula (2) as polysiloxane B was prepared so that a molar ratio (amount of hydrosilyl groups/amount of alkenyl groups) was adjusted to 1.6, and the following coating liquid M11 for forming a release layer containing the silicone mixture R4, an adhesion imparting agent S1, and a catalyst P1 was prepared.

(Coating liquid M11 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R4	1.5 parts
Adhesion imparting agent S1	0.083 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0162]

(Example 15)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that a silicone mixture R5 containing a vinyl-modified silicone resin (weight average molecular weight: 500000, in Structural Formula (1), l = 3460, m = 25, n = 4) represented by Structural Formula (1) as polysiloxane A and

a polymethylhydrogensiloxane (weight average molecular weight: 8400, in Structural Formula (2), o = 3, p = 65) represented by Structural Formula (2) as polysiloxane B was prepared so that a molar ratio (amount of hydrosilyl groups/amount of alkenyl groups) was adjusted to 3.5, and the following coating liquid M12 for forming a release layer containing the silicone mixture R5, an adhesion imparting agent S1, and a catalyst P1 was prepared.

(Coating liquid M12 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R5	1.5 parts
Adhesion imparting agent S1	0.083 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0163]

(Comparative Example 1)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that a silicone mixture R6 containing a vinyl-modified silicone resin (weight average molecular weight:

480000, in Structural Formula (1), l = 3220, m = 13, n = 7) represented by Structural Formula (1) as polysiloxane A and a polymethylhydrogensiloxane (weight average molecular weight: 8400, in Structural Formula (2), o = 3, p = 65) represented by Structural Formula (2) as polysiloxane B was prepared so that a molar ratio (amount of hydrosilyl groups/amount of alkenyl groups) was adjusted to 4.0, and the following coating liquid M13 for forming a release layer containing the silicone mixture R6, an adhesion imparting agent S1, and a catalyst P1 was prepared.

(Coating liquid M13 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R6	1.5 parts
Adhesion imparting agent S1	0.083 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0164]

(Comparative Example 2)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1

except that a silicone mixture R7 containing a vinyl-modified silicone resin (weight average molecular weight: 462000, in Structural Formula (1), l = 2820, m = 60, n = 0) represented by Structural Formula (1) as polysiloxane A and a polymethylhydrogensiloxane (weight average molecular weight: 8400, in Structural Formula (2), o = 3, p = 65) represented by Structural Formula (2) as polysiloxane B was prepared so that a molar ratio (amount of hydrosilyl groups/amount of alkenyl groups) was adjusted to 0.8, and the following coating liquid M14 for forming a release layer containing the silicone mixture R7, an adhesion imparting agent S1, and a catalyst P1 was prepared.

(Coating liquid M14 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R7	1.5 parts
Adhesion imparting agent S1	0.083 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0165]

(Comparative example 3)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1 except that the following coating liquid M15 for forming a release layer containing a silicone mixture R1, an adhesion imparting agent S5, and a catalyst P1 was coated so that an applied amount after drying was 0.020 μm.

(Coating liquid M15 for forming release layer)

Methyl ethyl ketone	64.3 parts
Toluene	34.0 parts
Silicone mixture R1	1.5 parts
Adhesion imparting agent S5 (KBM503 (N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, solid concentration: 100%) manufactured by Shin-Etsu Chemical Co., Ltd.)	0.075 parts
p-toluenesulfonic acid	0.008 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0166]

(Comparative Example 4)

A release film for manufacturing a ceramic green sheet was obtained in the same manner as in Example 1

except that the following coating liquid M16 for forming a release layer containing a silicone mixture R1 and a catalyst P1 and not containing an adhesion imparting agent was coated so that an applied amount after drying was 0.020 μm.

(Coating liquid M16 for forming release layer)

Methyl ethyl ketone	64.4 parts
Toluene	34.0 parts
Silicone mixture R1	1.5 parts
Catalyst P1	0.1 parts

The outline of the coating liquid for forming a release layer and the laminated film used at that time is shown in Table 3. The results of evaluating various physical properties of the obtained release film are shown in Table 4.

[0167]

[Table 3]

	Coating liquid for forming release layer						Laminated film
		Silicone mixture			Adhesion imparting agent		
	Type	Type	Weight average molecular weight	Molar ratio (amount of hydrosilyl groups/ amount of alkenyl groups)	Type	Ratio to silicone mixture (% by mass)	
Example 1	M1	R1	466000	2.0	S1	5.0	X1
Example 2	M2	R2	495000	1.0	S1	5.0	X1
Example 3	M3	R3	520000	3.0	S1	5.0	X1
Example 4	M1	R1	466000	2.0	S1	5.0	X1
Example 5	M1	R1	466000	2.0	S1	5.0	X1
Example 6	M4	R1	466000	2.0	S2	5.0	X1
Example 7	M5	R1	466000	2.0	S3	5.0	X1
Example 8	M6	R1	466000	2.0	S4	5.0	X1
Example 9	M7	R1	466000	2.0	S1	2.5	X1
Example 10	M8	R1	466000	2.0	S1	7.5	X1
Example 11	M9	R1	466000	2.0	S1	0.5	X1
Example 12	M10	R1	466000	2.0	S1	15	X1
Example 13	M1	R1	466000	2.0	S1	5.0	X2
Example 14	M11	R4	18000	1.6	S1	5.0	X1
Example 15	M12	R5	500000	3.5	S1	5.0	X1
Comparative Example 1	M13	R6	480000	4.0	S1	5.0	X1
Comparative Example 2	M14	R7	462000	0.8	S1	5.0	X1
Comparative Example 3	M15	R1	466000	2.0	S5	5.0	X1
Comparative Example 4	M16	R1	466000	2.0	-	0.0	X1

[0168]

[Table 4]

	Physical properties of release layer					Surface free energy of release layer					Ceramic green sheet		PVB
	Thickness (μm)	Average area surface roughness Sa (nm)	Maximum protrusion height Sp (nm)	Backmigration	Adhesion over time	γSVd (mJ/m2)	γSVp (mJ/m2)	γSVh (mJ/m2)	γS (mJ/m2)	γSVh/γS X100	Peeling force (mN/mm)	Evaluation of pinholes	Amount of Si transferred (Kcps)
Example 1	0.020	1.5	29.2	○	○	16.4	2.2	0.3	18.8	1.6	0.82	○	0.003
Example 2	0.020	2.0	30.5	○	○	12.9	2.7	0.8	16.4	4.8	0.56	○	0.011
Example 3	0.020	1.8	45.2	○	○	9.7	5.9	1.0	16.7	6.3	0.90	○	0.031
Example 4	0.050	1.9	26.8	○	○	15.5	1.0	0.3	16.8	1.9	0.50	○	0.014
Example 5	0.080	1.6	29.5	○	○	16.2	0.3	0.2	16.7	1.5	0.94	○	0.018
Example 6	0.020	1.8	48	○	○	13.8	2.2	0.6	16.7	3.6	0.85	○	0.016
Example 7	0.020	1.7	43.9	○	○	14.0	1.9	0.6	16.5	3.5	0.85	○	0.007
Example 8	0.020	1.6	40.2	○	○	17.1	0.1	0.5	17.8	3.0	0.90	○	0.006
Example 9	0.020	1.6	35.3	○	○	11.9	5.7	0.8	18.4	4.2	0.76	○	0.003
Example 10	0.020	1.6	41.8	○	○	11.8	5.6	0.8	18.2	4.6	0.73	○	0.001
Example 11	0.020	1.8	35.5	○	△	16.2	2.4	0.3	18.9	1.6	0.88	○	0.112
Example 12	0.020	1.4	47.2	○	○	12.1	3.8	0.8	16.2	4.9	1.15	○	0.084
Example 13	0.020	0.8	16.0	○	○	16.4	2.1	0.3	18.8	1.6	0.82	○	0.003
Example 14	0.020	1.8	30.3	○	△	15.4	3.4	0.6	19.4	3.0	0.88	○	0.110
Example 15	0.020	0.5	43	○	○	9.0	7.3	1.1	17.4	6.3	1.00	○	0.020
Comparative Example 1	0.020	1.7	32.2	○	○	8.7	8.6	1.3	18.6	6.9	1.32	○	0.055
Comparative Example 2	0.020	1.8	31.3	×	○	12.0	0.7	0.1	12.8	0.8	0.29	○	0.425
Comparative Example 3	0.020	1.9	166	×	○	14.8	1.6	1.2	17.6	6.7	0.88	○	0.071
Comparative Example 4	0.020	1.8	31.3	○	×	11.9	5.7	0.8	18.4	4.2	1.66	○	0.132

[0169]

As shown in the results of Table 4, since in Examples 1 to 15, the release layer was a layer obtained by curing the curable composition containing the polysiloxane A, the polysiloxane B, and the adhesion imparting agent C, and the formulas (a) and (b) were satisfied, a release film having excellent releasability and hardly causing the transfer/falling off of the release layer or poor adhesion was obtained.

[0170]

In Example 11, it was found that since the content ratio of the adhesion imparting agent was too small, the effect of improving the adhesion over time was reduced, and thus a preferred lower limit value was present in the content ratio of the adhesion imparting agent. In Example 12, it was found that since the content ratio of the adhesion imparting agent was too large, the peeling force was slightly increased, and a preferred upper limit value was present in the content ratio of the adhesion imparting agent. In Example 14, it was found that since the weight average molecular weight of the polysiloxane A was too small, the amount of silicone transferred to PVB was slightly increased, and a preferred lower limit value was present in the weight average molecular weight of the polysiloxane A. In Example 15, it was found that since the

molar ratio (amount of hydrosilyl groups/amount of alkenyl groups) was slightly increased, the ceramic peeling force was slightly increased, and a preferred upper limit was present in the molar ratio.

[0171]

Meanwhile, in Comparative Example 1 in which the molar ratio (amount of hydrosilyl groups/amount of alkenyl groups) was increased and thus exceeded the upper limit value of the formula (a), the peeling force was increased. In Comparative Example 2 in which the molar ratio (amount of hydrosilyl groups/amount of alkenyl groups) was decreased and thus was less than the lower limit value of the formula (a), the result of backmigration was poor, and the release layer was transferred to the surface of the substrate opposite to the release layer, so that there was a concern that the ceramic green sheet processing step was significantly contaminated, and the amount of Si transferred to the PVB sheet was also increased. As a result of using an undesirable adhesion imparting agent, in Comparative Example 3 exceeding the upper limit value of the formula (a), the result of backmigration is poor as a result of inhibiting curing by the adhesion imparting agent, and thus there is an extremely high concern that the ceramic green sheet processing step is contaminated. In Comparative Example 4 in which the adhesion imparting agent

was not used, the peeling force was increased, the adhesion over time was decreased, and the amount of Si transferred to the PVB sheet was also slightly increased.

INDUSTRIAL APPLICABILITY

[0172]

According to the present invention, by providing a release film capable of forming a ceramic green sheet having few defects even in an ultrathin product having a thickness of 1 μm or less by enhancing the smoothness and peelability of a release layer, the ceramic green sheet can be manufactured without the risk of causing defects.