

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, and more particularly to a release film for manufacturing a super-thin ceramic green sheet, which can suppress occurrence of step defects such as plane defects and peeling defects during manufacture of the super-thin ceramic green sheet, and reduce the charge amount of the release film to reduce adhesion of foreign matters to the release film, thereby suppressing mixing of foreign matters into the ceramic green sheet.

BACKGROUND ART

[0002]

Conventionally, a release film including a polyester film as a substrate and a release layer laminated on the polyester film has been used for forming a ceramic green sheet for a laminated ceramic capacitor and a ceramic substrate and the like. 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 onto 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. When a ceramic green sheet is formed on a release layer surface of a polyester film, minute projections on the release layer surface affect the formed ceramic green sheet. These are disadvantageously apt to cause defects such as cissing and pinholes. Therefore, various techniques for achieving a release layer surface having excellent flatness have been developed (for example, Patent Document 1).

[0003]

However, in recent years, the thickness of the ceramic green sheet has further been reduced, and a ceramic green sheet having a thickness of 1.0 μm or less, more specifically, 0.2 μm to 1.0 μm has been required. Therefore, extremely few unevenness present on the surface of the release layer is also transferred to the formed

ceramic green sheet. This causes thickness unevenness, which may lead to defects.

[0004]

Therefore, in recent years, various techniques for achieving smoothing of the release layer have been developed. For example, there is a technique in which a smoothing layer is provided between a release layer and a substrate to fill unevenness generated by particles contained in the substrate with the smoothing layer, thereby to improve the smoothness of the surface of the release layer (for example, Patent Document 2). It has been proposed to form a surface of a substrate on which a release layer is provided as a layer substantially containing no particles to improve the smoothness of the surface of the release layer (for example, Patent Document 3).

[0005]

However, the techniques of Patent Documents 2 and 3 have a problem that the release film is apt to be charged by the smooth release layer. More specifically, when the film is wound into a roll, a contact area between the release layer and the surface opposite to the release layer (back surface) increases, whereby the release layer and the surface opposite to the release layer (back surface) tend to be rubbed with each other, and more easily charged due

to fastening of the film, and vibration during transportation, and the like. When the release film is charged, extremely minute environmental foreign matters during the step and film scraps generated during slitting are apt to adhere to the release film due to static electricity. These may be mixed into the ceramic green sheet, leading to defects.

[0006]

Examples of the method for suppressing the charge of the release film include a method in which an anti-static agent is contained in a release layer, and a method in which an anti-static layer is provided on a surface opposite to a release layer or an intermediate layer between the release layer and a substrate film (for example, Patent Documents 4 and 5). However, when the anti-static agent is contained in the release layer as in Patent Document 4, the anti-static agent having poor compatibility with a release component may aggregate to form coarse protrusions. Also, the anti-static agent may adversely affect surface characteristics and curability to cause insufficient peelability of the super-thin ceramic green sheet. When the anti-static layer is provided on the surface opposite to the release layer or the intermediate layer between the release layer and the substrate film as in Patent Document 5, the number of processing steps

increases, and the anti-static agent is generally expensive, resulting in an increase in cost. This has a large economic problem.

PRIOR ART DOCUMENT

PATENT DOCUMENTS

[0007]

Patent Document 1: JP-A-2000-117899

Patent Document 2: JP-A-2009-208236

Patent Document 3: JP-A-2015-033811

Patent Document 4: JP-A-2014-189007

Patent Document 5: International Publication No.

2016/133092

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008]

The present invention has been made in view of the problems of the conventional techniques. That is, an object of the present invention is to provide a release film for manufacturing a ceramic green sheet, which can form a ceramic green sheet having a low and uniform peel force, and providing a low charge amount of the release film and few defects even in a super-thin product having a thickness of 1 μm or less, while maintaining high

smoothness of a release layer surface of the release film.

MEANS FOR SOLVING THE PROBLEMS

[0009]

As a result of intensive studies to solve the above problems, the present inventors have found that a release layer obtained by curing a composition containing a specific release agent and a melamine-based compound is provided on a surface layer A of a polyester film directly or with other layer interposed between the release layer and the surface layer A, which makes it possible to provide a release film for manufacturing a ceramic green sheet, which has excellent smoothness and peelability of the ceramic green sheet, and a small charge amount.

[0010]

That is, the present invention has the following configurations.

1. A release film for manufacturing a ceramic green sheet, the release film including: a polyester film substrate including a surface layer A forming one surface of the substrate and a surface layer B forming other surface; and a release layer laminated on the surface layer A directly or with other layer interposed between the release layer and the surface layer A, wherein a charge amount of the release layer is ± 5 kV or less when the release layer and

the surface layer B are held for 48 hours under an atmosphere of 50°C and a pressure of 10 kPa in a state where the release layer and the surface layer B are brought into contact with each other, and then peeled off from each other.

2. The release film for manufacturing a ceramic green sheet according to the above 1, wherein a coefficient of static friction μ_s when the release layer and the surface layer B are overlapped with each other is less than 0.30.

3. The release film for manufacturing a ceramic green sheet according to the above 1 or 2, wherein an anti-static layer is not provided on surfaces of the surface layer A and the surface layer B, and the surface layer A and the surface layer B contain no anti-static agent.

4. The release film for manufacturing a ceramic green sheet according to any one of the above 1 to 3, wherein the release layer is formed by curing a composition containing at least a release agent and a melamine-based compound, the composition for forming the release layer contains no anti-static agent, and a weight average polymerization degree of the melamine-based compound is 1.7 or less, and a content of the melamine-based compound in the release layer is 80% by mass or more with respect to a solid content of the composition for forming the release layer.

5. The release film for manufacturing a ceramic green

sheet according to any one of the above 1 to 4, wherein the release agent contained in the composition for forming the release layer is polyorganosiloxane containing carboxyl group.

6. The release film for manufacturing a ceramic green sheet according to any one of the above 1 to 5, wherein the surface layer A contains substantially no inorganic particles.

7. The release film for manufacturing a ceramic green sheet according to any one of the above 1 to 6, wherein the surface layer B contains particles, at least a part of the particles are silica particles and/or calcium carbonate particles, and a total content of the particles with respect to a mass of the surface layer B is 5000 to 15000 ppm.

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

9. A method for manufacturing a ceramic capacitor, wherein the method for manufacturing a ceramic green sheet according to the above 8 is employed.

EFFECT OF THE INVENTION

[0011]

The release film for manufacturing a super-thin ceramic green sheet of the present invention has a small charge amount, includes a release layer having a smooth surface, and has excellent peelability of the ceramic green sheet, whereby mixing of foreign matters into the ceramic green sheet and occurrence of defects can be suppressed, and the super-thin ceramic green sheet of 0.2 to 1.0 μm can be efficiently manufactured.

MODE FOR CARRYING OUT THE INVENTION

[0012]

Hereinafter, the present invention will be described in detail.

[0013]

In a release film for manufacturing a ceramic green sheet of the present invention, it is preferable that a release layer is laminated on a surface layer A of a polyester film substrate directly or with other layer interposed between the release layer and the surface layer A, and an anti-static layer is not provided on the surface layer A and a surface layer B opposite to the surface layer A. The release layer is preferably formed by curing a composition containing at least a melamine-based compound and polyorganosiloxane without containing an anti-static

agent.

[0014]

The release film for manufacturing a ceramic green sheet of the present invention preferably includes a release layer that is less likely to be charged. More specifically, charge that increases with time when a film is wound and stored in a roll form after release layer processing in a release film manufacturing step may have a problem. For example, when the charge amount of the roll-shaped film is large, in a slitting step and a ceramic green sheet forming step, extremely minute environmental foreign matters during the steps and film scraps occurring during slitting are apt to adhere to the film. These foreign matters adhering to the film may be mixed in the ceramic green sheet, leading to defects, whereby the release film preferably includes a release layer that is less likely to be charged.

[0015]

An example of evaluating the difficulty in charge is the following method. The difficulty in charge can be confirmed by evaluating the charge amount of the release layer after the release layer and the surface layer B are held for a certain period of time under a load in a state where the release layer and the surface layer B are brought into contact with each other. In this evaluation method,

the charge amount that increases with time when the film is stored in a roll form can be evaluated in a model manner. The evaluation method will be described in detail later.

[0016]

The charge amount of the release layer measured by the evaluation method to be described later is preferably ± 5 kV or less, for example, ± 3.4 or less, and more preferably ± 3 kV or less. The absolute value is preferably smaller. When the charge amount of the release layer is set to ± 5 kV or less, an increase in the charge amount over time when the film is stored in a roll form is small, whereby foreign matters can be less likely to adhere to the film, which are preferable. The charge amount of the release layer is preferably smaller, but may be 0.1 kV or more or 0.3 kV or more.

[0017]

In the present invention, the anti-static agent means a substance used for the purpose of imparting conductivity, such as a conductive filler, a metal layer, or a metal oxide layer, in addition to an ion-conductive polymer compound and a π -electron conjugated polymer compound and the like. Examples of the ion-conductive polymer compound include an ammonium group-containing compound, a polyether compound, a sulfonic acid compound, and a betaine compound. Examples of the π -electron conjugated polymer compound

include polyacetylene, polyphenylene, polyaniline, polypyrrole, polyisothianaphthene, and polythiophene. Examples of the conductive filler include fillers and fibers made of metals such as gold, silver, copper, aluminum, nickel, titanium, iron, zinc, and tin and alloys thereof, metal oxide fillers (excluding those such as silica and titania, exclusively used for purposes other than conductivity such as slipperiness), metal-coated synthetic fibers, and conductive carbon fibers such as carbon nanotubes. In the present invention, the anti-static layer means a layer that contains the anti-static agent as described above to exhibit an anti-static effect.

[0018]

(Polyester film)

Polyester constituting the polyester film substrate used in the present invention is not particularly limited, and a film formed from polyester usually used generally as a release film substrate can be used. However, the polyester is preferably crystalline linear saturated polyester composed of an aromatic dibasic acid component and a diol component. For example, the polyester is more suitably polyethylene terephthalate, polyethylene-2,6-naphthalate, polybutylene terephthalate, polytrimethylene terephthalate, or a copolymer containing constituent components of these resins

as main components. Above all, a polyester film formed from polyethylene terephthalate is particularly suitable. In the polyethylene terephthalate, the content of the repeating unit of ethylene terephthalate is preferably 90 mol% or more, and more preferably 95 mol% or more. Small amounts of other dicarboxylic acid component and diol component may be copolymerized with the polyethylene terephthalate. From the viewpoint of cost, the polyethylene terephthalate is preferably manufactured only from terephthalic acid and ethylene glycol. Known additives such as an antioxidant, a light stabilizer, an ultraviolet absorber, and a crystallization agent may be added as long as the effects of the film of the present invention are not impaired. The polyester film is preferably a biaxially oriented polyester film for reasons such as a high bidirectional elastic modulus.

[0019]

The intrinsic viscosity of the polyester film is preferably 0.50 to 0.70 dl/g, and more preferably 0.52 to 0.62 dl/g. When the intrinsic viscosity is 0.50 dl/g or more, no breakage often occurs in a stretching step, which is preferable. Conversely, when the intrinsic viscosity is 0.70 dl/g or less, the cuttability of the film when being cut to a predetermined product width is good, and dimensional defects do not occur, which are preferable. It

is preferable that raw material pellets are sufficiently dried in vacuum.

[0020]

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 uniaxially or biaxially stretching the un-stretched film. The biaxially stretched film can be obtained by a method for sequentially biaxially stretching a longitudinally or transversely uniaxially stretched film in a transverse or machine direction, or a method for simultaneously biaxially stretching an un-stretched film in machine and transverse directions.

[0021]

In the present invention, a stretching temperature when the polyester film is stretched is preferably equal to or higher than the secondary transition point (T_g) of the polyester. The film is preferably stretched 1 to 8 times, particularly 2 to 6 times in each of the machine and transverse directions.

[0022]

The polyester film preferably has a thickness of 12 to 50 μm , more preferably 15 to 38 μm , and still more preferably 19 μm to 33 μm . When the thickness of the film is 12 μm or more, the film may not be deformed by heat during the production of the film, the processing step of the release layer, and the forming of the ceramic green sheet and the like, which is preferable. Meanwhile, when the thickness of the film is 50 μm or less, the amount of the film to be discarded after use is not extremely increased, which is preferable in order to reduce an environmental load.

[0023]

The polyester film substrate may be a single layer, but is preferably a multilayer including two or more layers. An aspect in which a release layer is laminated on a surface layer A forming one surface of the polyester film substrate, and a surface layer B forms the other surface will be described below. It is preferable that the surface layer A substantially contains no inorganic particles. Meanwhile, the surface layer B preferably contains particles and the like. As a laminated structure of the release film, a layer onto which the release layer is applied is the surface layer A; a layer opposite to the surface layer A is the surface layer B; and an intermediate layer other than these is a layer C. Examples of a layer

structure in a thickness direction include a laminated structure such as release layer/A/B, or release layer/A/C/B. Of course, the layer C may have a plurality of layer structures.

[0024]

The surface layer B may be a layer formed of polyester as a main constituent resin together with the surface layer A by a so-called co-extrusion method, but may be provided as a coating layer on a surface opposite to the surface layer A of the polyester film. When the surface layer B is the coating layer described above, the surface layer B preferably contains a binder resin and particles. In this case, the surface layer B is also referred to as an easy-to-slip coating layer.

[0025]

It is preferable that, in the polyester film substrate of the present invention, the surface layer A forming the surface on which the release layer is applied contains substantially no inorganic particles. At this time, the average area surface roughness (S_a) of the surface layer A is preferably 7 nm or less. When S_a is 7 nm or less, pinholes and the like are less likely to occur when super-thin ceramic green sheets to be laminated are formed, which are preferable. The average area surface roughness (S_a) of the surface layer A can be said to be

preferably smaller, but the average area surface roughness may be 0.1 nm or more. Here, it is preferable that, when an anchor coat layer and the like to be described below is provided on the surface layer A, the coat layer preferably contains substantially no inorganic particles. The average area surface roughness (S_a) after the coat layer is laminated is preferably in the above range. In the present invention, "contain substantially no inorganic particles" means that the content of an inorganic element quantified by fluorescent X-ray analysis is 50 ppm or less, preferably 10 ppm or less, and most preferably equal to or less than the detection limit. This is because, even if the inorganic 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.

[0026]

In the polyester film substrate of the present invention, the surface layer B forming the surface opposite to the surface on which the release layer is applied preferably contains particles from the viewpoints of the slipperiness of the film and the ease of air release. In particular, it is preferable to use silica particles and/or calcium carbonate particles. The content of the particles

to be contained is preferably 5000 to 15000 ppm in total of the particles in the surface layer B. At this time, the average area surface roughness (Sa) of the film of the surface layer B is preferably in a range of 1 to 40 nm. More preferably, the average area surface roughness (Sa) is in a range of 5 to 35 nm. When the total content of silica particles and/or calcium carbonate particles is 5000 ppm or more, and the Sa is 1 nm or more, air can be uniformly released in the case where the film is wound into a roll, and the film has a good winding appearance and good flatness. Therefore, the film is suitable for manufacturing the super-thin ceramic green sheet. When the total content of silica particles and/or calcium carbonate particles is 15000 ppm or less, and the Sa is 40 nm or less, the aggregation of a lubricant is less likely to occur, and coarse projections cannot be formed, whereby the quality of the super-thin ceramic green sheet to be manufactured is stable, which is preferable.

[0027]

As the particles contained in the surface layer B, inactive inorganic particles and/or heat-resistant organic particles other than silica and/or calcium carbonate, and the like can be used. From the viewpoints of transparency and cost, it is more preferable to use silica particles and/or calcium carbonate particles, but other examples of

inorganic particles which 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 the silica particles are used, porous colloidal silica is preferable. When the calcium carbonate particles are used, light calcium carbonate surface-treated with a polyacrylic acid-based polymer compound is preferable from the viewpoint of preventing the lubricant from falling off.

[0028]

The average particle size of the particles 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 size of the particles is 0.1 μm or more, the slipperiness of the release film is good, which is preferable. The average particle diameter of 2.0 μm or less is free from the possibility of causing pinholes to occur in the ceramic green sheet due to coarse particles on the release layer surface, which is preferable.

[0029]

The surface layer B may contain two or more types of particles made of different materials. The surface layer B

may contain the same type of particles having different average particle diameters.

[0030]

The easy-to-slip coating layer described above is preferably provided as the surface layer B on the surface opposite to the surface layer A by in-line coating during the formation of the polyester film. Even when the easy-to-slip coating layer is provided, the average area surface roughness (S_a) of the surface layer B by the easy-to-slip coating layer is preferably in a range of 1 to 40 nm for the same reason as described above.

[0031]

The film thickness of the surface layer B by the easy-to-slip coating layer is preferably 2 μm or less, more preferably 1 μm or less, still more preferably 0.8 μm or less, and particularly preferably 0.5 μm or less. If the film thickness of the coating layer is 2 μm or less, there is no fear of blocking, which is preferable.

[0032]

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, a 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 a urethane resin are preferably used. In consideration of the hardness of the easy-to-slip coating layer, an acrylic resin is particularly preferable. Other preferable examples of the binder resin constituting the easy-to-slip coating layer on the polyester substrate film include a polyester resin and a urethane resin. The polyester resin is preferably a copolymerized polyester. The polyester resin may be modified with polyurethane. Examples of the urethane resin include a polycarbonate polyurethane resin. Furthermore, the acrylic resin, the polyester resin, and the polyurethane resin may be used in combination, and the above-mentioned other binder resins may be used in combination.

[0033]

In the present invention, in order to form a crosslinked structure in the easy-to-slip coating layer forming the surface layer B, 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 increase the hardness of the easy-to-slip coating layer. Specific examples of the crosslinking agent include urea-based, epoxy-based, melamine-based, isocyanate-based, oxazoline-based, and

carbodiimide-based crosslinking agents. In particular, oxazoline-based and carbodiimide-based crosslinking agents are particularly preferable because the crosslinking density can be improved. In order to promote a crosslinking reaction, a catalyst and the like can be appropriately used as needed.

[0034]

The easy-to-slip coating layer forming the surface layer B 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 barium sulfate 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.

[0035]

From the viewpoint of reducing the pinholes, it is preferable that a reused material or the like is not used in the surface layer A as a layer on which the release layer is provided, in order to prevent particles such as a lubricant from being mixed.

[0036]

The thickness ratio of the surface layer A as the layer on which the release layer is provided is preferably 20% or more and 50% or less of the total thickness of the substrate film. When the thickness ratio is 20% or more, the surface layer A is less likely to be affected by the particles contained in the surface layer B and the like from the inside of the film, and the average area surface roughness S_a easily satisfies the above-mentioned range, which is preferable. When the thickness ratio is 50% or less of the total thickness of the substrate film, the use ratio of the reused material in the surface layer B and the above-mentioned intermediate layer C in coextrusion can be increased, to reduce the environmental load, which is

preferable.

[0037]

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, amount, and particle size of the lubricant contained in the surface layer B and the average area surface roughness (S_a) satisfy the above ranges.

[0038]

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

[0039]

However, it is preferable that no anti-static layer is provided on the surface layer A and the surface layer B, and it is preferable that the surface layer A and the surface layer B contain no anti-static agent. It is preferable that when the intermediate layer C is provided, the intermediate layer C also contains no anti-static agent. A configuration not including an anti-static layer

or an anti-static agent makes it possible to provide a release film having a low peel force at low cost.

[0040]

(Structure of release layer)

The release layer in the present invention contains no anti-static agent, and is preferably formed by curing a composition containing at least a melamine-based compound and polyorganosiloxane.

[0041]

It is preferable that the release layer in the present invention has a high crosslinking density and a high elastic modulus in order to suppress the deformation of the release layer occurring during peeling and to provide a low and uniform peel force. Here, the elastic modulus of the release layer refers to an elastic modulus thereof in a compression direction. The release layer has a high crosslinking density and a high elastic modulus, whereby an increase in the charge amount over time when the film is stored in a roll form is suppressed, which is preferable. When the elastic modulus of the release layer is increased, the slipperiness of the release layer with the surface layer B brought into contact with the release layer during the storage of the roll is improved (slippery). When the release layer is slippery, a pressure applied in a direction perpendicular to the film surface is

likely to escape in a horizontal direction, whereby the adhesion force of the release layer with the surface layer B when the film is stored in a roll form can be reduced, to allow charge to be suppressed, which is preferable.

[0042]

The crosslinking density of the release layer has been found to be importantly increased in order to suppress the charge amount. The crosslinking density of the release layer is increased, whereby electrons easily transfer in the melamine resin present in the release layer, and the release layer is less likely to be charged, which is preferable. In order to increase the crosslinking density of the release layer, it is preferable to increase the reactivity of the melamine-based compound. The highly reactive melamine-based compound will be described in detail later.

[0043]

The melamine-based compound used in the release layer in the present invention is not particularly limited, and general melamine-based compounds can be used, but a preferable melamine-based compound is obtained by condensation of melamine and formaldehyde, and has one or more of triazine rings and methylol groups and/or alkoxymethyl groups respectively in one molecule. Specifically, an etherified compound obtained by subjecting

a methylolmelamine derivative obtained by condensation of melamine and formaldehyde, and methyl alcohol, ethyl alcohol, isopropyl alcohol, or butyl alcohol or the like as a lower alcohol, and the like to a dehydration condensation reaction is preferable. Examples of the methylolated melamine derivative include monomethylol melamine, dimethylol melamine, trimethylol melamine, tetramethylol melamine, pentamethylol melamine, and hexamethylol melamine. One kind may be used, or two kinds or more may be used.

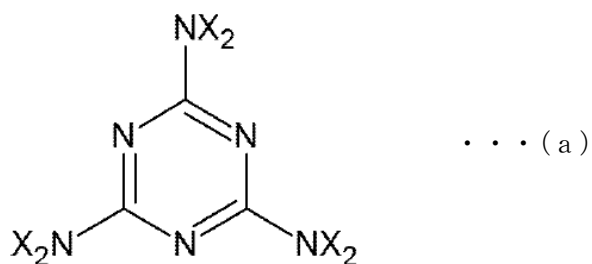
[0044]

In order to increase the reactivity of the melamine-based compound and increase the elastic modulus of the release layer, it is preferable to use hexamethylol melamine and hexaalkoxymethyl melamine which have more crosslinking points in one molecule, but it is more preferable to use hexaalkoxymethyl melamine having more excellent reactivity, and it is particularly preferable to use hexamethoxymethyl melamine. At this time, hexamethylolmelamine is a compound in which X is a methylol group ($-\text{CH}_2\text{-OH}$) in the following formula (a). Hexaalkoxymethylmelamine is obtained by subjecting a methylol melamine derivative to a dehydration condensation reaction using an alcohol, and is a compound in which X is $-\text{CH}_2\text{-OR}$ (R is an alkyl group having 1 to 4 carbon atoms).

Hexamethoxymethylmelamine is a compound in which X is (-CH₂-OMe) .

[0045]

[Formula 1]



[0046]

Respective X in the above (a) may be the same as or different from each other. The above respective R may be the same as or different from each other. X may be (-H) .

[0047]

The melamine-based compound used in the present invention is preferably not a single compound but a mixture of a plurality of compounds. From the structure of the main component compound in the melamine-based compound, the melamine-based compound can be roughly classified into a full ether-type (X = -CH₂-OR, R: an alkyl group having 1 to 4 carbon atoms), a methylol-type (X = -CH₂-OH), and an imino-type (X = -H). From the viewpoint of reactivity, it is preferable to use a full ether-type or a methylol-type,

and more preferable to use a full ether-type. Among the full ether-type, it is most preferable to use hexamethoxymethylmelamine (CAS No. 3089-11-0) in which R is a methyl group. As the melamine-based compound having a higher content of hexamethoxymethylmelamine is used, a release layer having high reactivity and a high elastic modulus can be provided.

[0048]

The melamine-based compound used for the release layer in the present invention preferably has a weight average molecular weight of 250 or more and 1000 or less. The weight average molecular weight is more preferably 300 or more and 900 or less, and still more preferably 400 or more and 800 or less. When the weight average molecular weight is 1000 or less, a crosslinking reaction is likely to proceed, so that a film having a higher crosslinking density can be formed, whereby a release layer having light peeling and a low charge amount is obtained, which is preferable. When the weight average molecular weight is 250 or more, the crosslinking density is not excessively increased, whereby curl is not deteriorated, which is preferable. 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.

[0049]

The fact that the weight average molecular weight of the melamine-based compound is 250 to 1000 means that the melamine-based compound used in the present invention contains a large amount of mononuclear body. The mononuclear body has more crosslinking points than that of a multinuclear body which is obtained by condensation of two or more melamine derivatives to have more excellent reactivity, whereby the mononuclear body can provide a release layer having a higher crosslinking density and more excellent peelability. The content of the mononuclear body is preferably higher, and it is most preferable to use a melamine-based compound made only of the mononuclear body.

[0050]

The weight average molecular weight can also be represented by a weight average polymerization degree. The weight average polymerization degree of the melamine-based compound to be used is preferably 1.7 or less, more preferably 1.5 or less, and still more preferably 1.3 or less. The melamine-based compound having a smaller weight average polymerization degree can be more suitably used. When the weight average polymerization degree is 1.7 or less, the content of the mononuclear body contained in the melamine-based compound increases, whereby the release layer having excellent reactivity and peelability, and

being less likely to be charged can be provided, which is preferable. The weight average polymerization degree in the present specification is a value calculated based on a weight average molecular weight obtained in terms of standard polystyrene by gel permeation chromatography.

[0051]

In the synthesis process of the melamine-based compound, a compound containing an imino group ($-\text{NH}_2-$) or a multinuclear body may be mixed. Even when these melamine derivatives are mixed, the melamine-based compound has excellent reactivity if the weight average molecular weight (that is, the weight average polymerization degree) of the melamine-based compound is within the above range, and can be suitably used.

[0052]

In the release layer of the present invention, the melamine-based compound is preferably contained in an amount of 80% by mass or more and 99.9% or less, more preferably 90% by mass or more and 99.9% or less, and still more preferably 95% by mass or more and 99.9% or less, with respect to the solid content of the composition for forming the release layer. When the melamine-based compound is contained in an amount of 80% by mass or more, the release layer can have a high crosslinking density provided by the self-crosslinking of the melamine-based compound, whereby

the release layer has a high elastic modulus, which is preferable. At this time, the solid content of the composition for forming a release layer may be substantially regarded as a total value of the solid contents of the melamine-based compound and the release agent since a solvent and an acid catalyst are considerably evaporated in the drying process.

[0053]

An acid catalyst is preferably added to the release layer in the present invention in order to promote the crosslinking reaction of the melamine-based compound, and the acid catalyst is preferably added to the composition for forming a release layer, followed by applying and curing. As the acid catalyst to be used, a sulfonic acid-based catalyst is preferably used.

[0054]

As the sulfonic acid-based catalyst, for example, p-toluenesulfonic acid, xylenesulfonic acid, cumenesulfonic acid, dodecylbenzenesulfonic acid, dinonylnaphthalenesulfonic acid, and trifluoromethanesulfonic acid and the like can be suitably used, but p-toluenesulfonic acid can be particularly suitably used from the viewpoint of reactivity.

[0055]

As the sulfonic acid-based catalyst used in the

present invention, commercially available sulfonic acid-based catalysts may also be used. Examples of the commercially available product include Dryer (registered trademark) 900 (p-toluenesulfonic acid, manufactured by Hitachi Chemical Co., Ltd.), NACURE (registered trademark) DNNDISA series (dinonylnaphthalenedisulfonic acid, manufactured by Kusumoto Chemicals, Ltd.), DNNSA series (dinonylnaphthalene (mono) sulfonic acid, manufactured by Kusumoto Chemicals, Ltd.), DDBSA series (dodecylbenzenesulfonic acid, manufactured by Kusumoto Chemicals, Ltd.), and p-TSA series (p-toluenesulfonic acid, manufactured by Kusumoto Chemicals, Ltd.).

[0056]

The sulfonic acid-based catalyst has higher acidity and more excellent reactivity than those of other acid catalysts such as a carboxylic acid-based catalyst, whereby the release layer can be processed at a lower temperature. Therefore, deterioration in the flatness of the film due to heat during processing and deterioration in winding appearance can be suppressed, which is preferable.

[0057]

The addition amount of the acid catalyst is preferably 0.1 to 10% by mass with respect to the melamine-based compound contained in the release layer. The addition amount is more preferably 0.5 to 8% by mass. The

addition amount is still more preferably 0.5 to 5% by mass. When the addition amount is 0.1% by mass or more, the curing reaction is likely to proceed, which is preferable. Meanwhile, when the addition amount is 10% by mass or less, the acid catalyst is less likely to transfer to or adversely affect a ceramic green sheet to be formed, which is preferable.

[0058]

As the release agent (an additive for improving the releasability of the release layer) used in the release layer in the present invention, general release agents can be used without particular limitation, but polyorganosiloxane having a functional group capable of reacting with a melamine-based compound such as a carboxyl group, a hydroxyl group, an amino group, or a thiol group is preferably used. Among them, polyorganosiloxane having a hydroxyl group or a carboxyl group is more preferably used, and polyorganosiloxane containing a carboxyl group is most preferably used from the viewpoints of peelability and prevention of charge. Among the polyorganosiloxane structure, those having a polydimethylsiloxane structure (abbreviated as PDMS) can be suitably used.

[0059]

When the polyorganosiloxane as the release agent contains a carboxyl group, the release agent does not

exhibit a strong interaction with the melamine-based compound in the drying step, and is likely to be oriented to the surface of the release layer, whereby good releasability is obtained. Therefore, the polyorganosiloxane containing a carboxyl group is used, whereby the releasability can be satisfied even when the addition amount of the release agent is small, which is preferable. When the release agent is likely to be oriented to the surface of the release layer, the slipperiness of the surface of the release layer is improved, whereby the release layer is less likely to be charged, which is preferable.

[0060]

The carboxyl group may be introduced into one terminal, both terminals, or a side chain of polydimethylsiloxane. The carboxyl group may be introduced into one position or each of a plurality of positions.

[0061]

The carboxyl group-modified polyorganosiloxane may have a carboxyl group directly bonded to a silicon atom of the polyorganosiloxane, or may have a carboxyl group bonded to the polyorganosiloxane via an alkyl group or an aryl group. However, polyorganosiloxane to which a carboxyl group is bonded via an organic group having a repeating structure such as polyether, polyester, or polyurethane is

not so preferable.

[0062]

A functional group to be introduced into the polyorganosiloxane as the release agent may have other functional group than a carboxyl group in one molecule, but only a carboxyl group is preferable. When the functional group other than a carboxyl group is contained, an intermolecular interaction with the melamine-based compound increases more than necessary, whereby the polyorganosiloxane may be less likely to be oriented to the surface of the release layer, which is not preferable.

[0063]

The polyorganosiloxane modified with a hydroxyl group or the like, which exhibits a strong interaction with a melamine-based compound, rapidly reacts with the melamine-based compound in the drying step, whereby the polyorganosiloxane may be less likely to be oriented to the surface of the release layer, and the releasability may be less likely to be exhibited. Therefore, it is necessary to increase the addition amount thereof in order to provide sufficient releasability, but in this case, the elastic modulus of the release layer may decrease to increase the peel force. When the addition amount of the polyorganosiloxane is increased, the coatability while ceramic green sheet is formed may be deteriorated, which is

not preferable.

[0064]

The polyorganosiloxane containing a carboxyl group used in the present invention preferably has a weight average molecular weight of 40,000 or less. More preferably, the weight average molecular weight is 30,000 or less. When the weight average molecular weight is 40,000 or less, the polyorganosiloxane containing a carboxyl group is likely to be segregated to the surface of the release layer, which is preferable from the viewpoints of peelability and a charge amount.

[0065]

As described above, the polyorganosiloxane containing a carboxyl group is more preferably polydimethylsiloxane containing a carboxyl group. As the polydimethylsiloxane containing a carboxyl group, X22-3701E (side chain carboxyl-modified polydimethylsiloxane, manufactured by Shin-Etsu Chemical Co., Ltd.), X22-3710 (one-terminal carboxyl-modified polydimethylsiloxane, manufactured by Shin-Etsu Chemical Co., Ltd.), X22-162C (both-terminals carboxyl-modified polydimethylsiloxane, manufactured by Shin-Etsu Chemical Co., Ltd.), BY16-750 (both-terminals carboxyl-modified polydimethylsiloxane, manufactured by Dow Corning Toray Co., Ltd.), BY16-880 (side chain carboxyl-modified polydimethylsiloxane, manufactured by Dow Corning

Toray Co., Ltd.), and Magnasoft 800L (both-terminals carboxyl-modified polydimethylsiloxane, manufactured by Momentive Performance Materials Inc.), and the like can be used.

[0066]

The polydimethylsiloxane containing a carboxyl group in the present invention may be an acrylic resin in which polydimethylsiloxane is introduced as a side chain into an acrylic main chain containing a carboxyl group. As the acrylic resin in which polydimethylsiloxane is introduced as a side chain into an acrylic main chain containing a carboxyl group, SYMAC (registered trademark) US-350, US-352, US-380 (manufactured by Toagosei Co., Ltd.) and the like can be used. The acrylic resin may be an acrylic resin in which polydimethylsiloxane is introduced as a side chain into an acrylic main chain containing a carboxyl group and a hydroxyl group in one molecule. As the acrylic resin in which polydimethylsiloxane is introduced as a side chain into an acrylic main chain containing a carboxyl group and a hydroxyl group in one molecule, SYMAC (registered trademark) US-450, US-480 (manufactured by Toagosei Co., Ltd.) and the like can be used.

[0067]

The release layer of the present invention preferably contains the release agent in an amount of 0.05% by mass or

more and 5% by mass or less with respect to the solid content of the composition for forming the release layer. The amount is more preferably 0.1% by mass or more and 3% by mass or less, and still more preferably 0.1% by mass or more and 1% by mass or less. When the amount is 0.05% by mass or more, not only the peelability is improved, but also the release layer is slippery, and is less likely to be charged, which is preferable. Meanwhile, when the amount is 5% by mass or less, the elastic modulus of the entire release layer does not excessively decrease, which is preferable. The amount is also preferably 5% by mass or less from the viewpoint that the coatability while the ceramic green sheet is formed may not be deteriorated. At this time, the solid content of the composition for forming a release layer may be substantially regarded as a total value of the solid contents of the melamine-based compound and the release agent since a solvent and an acid catalyst are considerably evaporated in the drying process.

[0068]

The release layer of the present invention can contain particles having a particle size of 1 μm or less, but it is preferable that the release layer contains no component forming protrusions such as particles from the viewpoint of the occurrence of the pinholes.

[0069]

Other additives and the like may be added to the release layer in the present invention as long as the effect of the present invention is not impaired, but it is preferable that the release layer contains no anti-static agent. The fact that the release layer contains no anti-static agent causes no possibility that compatibility with the release agent and the melamine-based compound is deteriorated, and aggregates occur to impair the smoothness of the release layer, which is preferable. The release layer can be more economically formed, which is preferable.

[0070]

(Other characteristics)

In the present invention, the thickness of the release layer may be set according to the purpose of use, and is not particularly limited. The thickness of the release coating layer after curing is preferably 0.01 to 1.0 μm , more preferably 0.05 to 0.8 μm , still more preferably 0.1 to 0.6 μm , and yet still more preferably 0.1 to 0.4 μm . When the thickness of the release layer is 0.01 μm or more, peeling performance is obtained, which is preferable. When the thickness is 1.0 μm or less, a curing time can be shortened, and the flatness of the release film can be maintained, whereby the thickness unevenness of the ceramic green sheet can be suppressed, which is preferable. As the thickness of the release layer is smaller, the

release layer is less likely to be charged, which is preferable.

[0071]

The release layer surface of the release film of the present invention 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 (P) 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 (P) may be 45 nm or less.

If the 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 the average area surface roughness (Sa) is preferably smaller, but the average area surface roughness may be 0.1 nm or more, or 0.3 nm or more. It can be said that the maximum protrusion height (P) is also preferably smaller, but the maximum protrusion height may be 1 nm or more, or 3 nm or more.

[0072]

As the release film of the present invention, a

substrate film in which the surface layer A is highly flattened is preferably used. Even if the thickness of the release layer is less than 0.5 μm , and further less than 0.2 μm , the surface of the release layer can be made smooth. Therefore, even the release layer using the highly reactive melamine-based compound can suppress the occurrence of curls. The amounts of a solvent and resin to be used can be reduced, whereby the environmentally-friendly release film for forming a super-thin ceramic green sheet can be produced at low cost.

[0073]

In the release film of the present invention, a peel force when the ceramic green sheet is peeled off is preferably 0.5 mN/mm or more and 2.0 mN/mm or less. More preferably, the peel force is 0.5 mN/mm or more and 1.5 mN/mm or less. If the peel force is 0.5 mN/mm or more, the peel force is not too light. This is free from the possibility of causing the ceramic green sheet to float during transportation, which is preferable. The peel force of 2.0 mN/mm or less is free from the possibility of causing the ceramic green sheet to be damaged during peeling, which is preferable. For example, the release film of the present invention can favorably peel off even an extremely thin ceramic green sheet having a required thickness of 0.2 to 1.0 μm .

[0074]

In the release film of the present invention, a coefficient of static friction when the release layer and the surface layer B are overlapped with each other is preferably less than 0.30, for example, 0.25 or less, and more preferably less than 0.25. When the coefficient of static friction is less than 0.30, the adhesion force between the release layer and the surface layer B is reduced, whereby charge caused by winding tightness occurring when the film is stored in a roll form, and vibration during transportation, and the like can be suppressed, which is preferable. As the coefficient of static friction is smaller, the charge can be suppressed, which is preferable, but the coefficient of static friction is preferably 0.01 or more, and more preferably 0.03 or more, from the viewpoint of windability.

[0075]

The curl of the release film of the present invention after heating at 80°C for 5 minutes without applying tension is preferably 3 mm or less, and more preferably 1 mm or less. Of course, it is also preferable that the release film does not curl at all. The curl of 3 mm or less can provide less curl when the ceramic green sheet is formed and an electrode is printed, to improve the precision of printing, which is preferable.

[0076]

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 resin is dissolved or dispersed is spread on one surface of a polyester film of a substrate by applying and the like. A solvent or the like is removed by drying, followed by heat drying or heat curing. At this time, a drying temperature during solvent drying and thermosetting is preferably 100°C or higher and 180°C or lower, more preferably 100°C or higher and 160°C or lower, and most preferably 100°C or higher and 140°C or lower. A heating time is preferably 30 seconds or less, and more preferably 20 seconds or less. When the temperature is 180°C or lower, the flatness of the film is maintained to be less likely to cause the thickness unevenness of the ceramic green sheet, which is preferable. When the temperature is 140°C or lower, the film can be processed without impairing the flatness of the film, to further reduce the possibility of causing the thickness unevenness of the ceramic green sheet, which is particularly preferable. When the temperature is lower than 100°C, the curing reaction of melamine does not sufficiently proceed, whereby the elastic modulus of the release layer decreases, which is not preferable.

[0077]

In the present invention, the coating solution when the release coating layer is applied is not particularly limited, but it is preferable to add a solvent having a boiling point of 90°C or higher. The addition of a solvent having a boiling point of 90°C or higher makes it possible to prevent bumping during drying, to level the coating film, and to improve the smoothness of the surface of the coating film after drying. The addition amount thereof is preferably about 10 to 80% by mass with respect to the whole coating solution.

[0078]

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.

[0079]

(Ceramic green sheet and ceramic capacitor)

In general, a multilayer ceramic capacitor includes a rectangular parallelepiped ceramic body. In the ceramic body, first internal electrodes and second internal electrodes are alternately provided along a thickness

direction. The first internal electrode is exposed in a first end face of the ceramic body. A first external electrode is provided on the first end face. The first internal electrode is electrically connected to the first external electrode in the first end face. The second internal electrode is exposed in a second end face of the ceramic body. A second external electrode is provided on the second end face. The second internal electrode is electrically connected to the second external electrode in the second end face.

[0080]

The release film for manufacturing a ceramic green sheet of the present invention is used for manufacturing such a multilayer ceramic capacitor. For example, the release film for manufacturing a 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 to 1.0 μm 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, the ceramic green sheet printed with the conductive layer for constituting the first internal electrode, and the ceramic green sheet printed with the

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

EXAMPLES

[0081]

Hereinafter, the present invention will be described in more detail with reference to Examples, but the present invention is not limited to the following Examples. Characteristic values used in the present invention were evaluated using the following methods.

[0082]

(Surface roughness)

The surface characteristics are represented by values measured under the following conditions using a non-contact surface shape measurement system (VertScan R550H-M100). For average area surface roughness (S_a), the average value of five measurements was employed. For a maximum protrusion height (P), seven measurements were performed, and the maximum value of five measurements excluding the maximum and minimum values was used.

(Measurement conditions)

Measurement mode: WAVE mode

Objective lens: 10x

0.5×Tube lens

Measurement area 936 μm × 702 μm

(Analysis conditions)

Surface correction: 4th order correction

Interpolation processing: Complete interpolation

[0083]

(Evaluation of coatability of ceramic slurry)

A slurry composition I containing the following materials was stirred and mixed for 10 minutes. The slurry composition I was dispersed for 10 minutes using a bead mill with 0.5 mm zirconia beads to obtain a primary dispersion. Thereafter, a slurry composition II containing the following materials 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 using a bead mill with 0.5 mm zirconia beads to obtain a ceramic slurry.

(Slurry composition I)

Toluene: 22.3 parts by mass

Ethanol: 18.3 parts by mass

Barium titanate (average particle diameter: 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

Diethyl 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. The coatability was then evaluated
according to the following criteria.

Good: Cissing or the like was not found, and coating could
be provided on the entire surface.

Poor: Sheet defects such as cissing were observed.

[0084]

(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 coatability of the
ceramic slurry. Next, the release film was peeled off from
the release film including the formed ceramic green sheet

to obtain the ceramic green sheet. In the central region of the obtained ceramic green sheet in the film transverse direction, light was applied from the opposite surface of the coating surface of the ceramic slurry in a range of 25 cm², and the occurrence status of pinholes viewed from the transmission of light was observed. The pinholes were visually determined according to the following criteria.

Good: No occurrence of pinholes

Average: Almost no pinholes

Poor: Occurrence of a large number of pinholes

[0085]

(Evaluation of peelability of ceramic green sheet)

A slurry composition I containing the following materials was stirred and mixed for 10 minutes. The slurry composition I was dispersed for 10 minutes using a bead mill with 0.5 mm zirconia beads to obtain a primary dispersion. Thereafter, a slurry composition II containing the following materials 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 using a bead mill with 0.5 mm zirconia beads to obtain a ceramic slurry.

(Slurry composition I)

Toluene: 22.3 parts by mass

Ethanol: 18.3 parts by mass

Barium titanate (average particle diameter: 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

[0086]

Then, the slurry was applied 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 form a ceramic green sheet on the release film. 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 the double-sided tape. The release film was peeled off by pulling the release film side. Among the obtained measured values, the average value of peel forces in a peeling distance of 20 mm to 70 mm was calculated, and the value was taken as a peeling force. A total of five measurements was carried out, and the average value of the peel forces was employed for evaluation. Determination was made based on the following criteria from the obtained numerical values of the peel forces.

Very good: 0.5 mN/mm or more and 1.5 mN/mm or less

Good: more than 1.5 mN/mm and 2.0 mN/mm or less

Poor: less than 0.5 mN/mm or more than 2.0 mN/mm

[0087]

(Evaluation of curl of release film)

The release film sample was cut into a size of 10 cm × 10 cm, and heat-treated in a hot-air oven at 80°C for 5 minutes without tension being applied to the release film. Thereafter, the release film sample was taken out of the oven, and cooled to room temperature. The release film sample was then placed on a glass plate with the release surface facing upward. A height of a portion floating from

the glass plate at each of four corners was measured. The average value of floating amounts at the four corners measured at this time was taken as a curl amount. The curl property was evaluated according to the following criteria. Very good: Curl was 1 mm or less, and almost no curl was found.

Good: Curl was more than 1 mm and 3 mm or less, and slight curls were found.

Poor: Curl was more than 3 mm, and curls were found.

[0088]

(Method for measuring weight average polymerization degree)

Analysis conditions

A sample (16 mg) was weighed, and dissolved in 8 ml of chloroform. The resulting solution was filtered through a 0.2 μm -membrane filter. The resulting sample solution was subjected to GPC analysis under the following conditions.

Apparatus: TOSOH HLC-8320GPC

Column: K-G+K-802 (elimination limit molecular weight: 5×10^3) + K-801 (elimination limit molecular weight: 1.5×10^3) (Shodex)

Solvent: Chloroform 100%

Flow rate: 1.0 ml/min

Concentration: 0.2%

Injection volume: 50 μL

Temperature: 40°C

Detector: RI

[0089]

A weight average molecular weight was calculated in terms of polystyrene, and a weight average polymerization degree was calculated based on the calculated value. As the polystyrene, PStQuick C (TOSOH) in PStQuick series was used. Among polystyrenes added to PStQuick C (TOSOH), polystyrenes Mw 2110000, 427000, and 37900, which were largely beyond the elimination limit molecular weight of the column, were excluded from the formation of a calibration curve.

[0090]

(Charge amount)

Two evaluation samples obtained by cutting the release film into 10 cm × 10 cm were prepared. The two evaluation samples were statically eliminated using a static eliminator (SJ-F020, manufactured by Keyence Corporation). The voltage was confirmed to be 0 kV, and the release layer and the surface layer B were then brought into contact with each other with the release layer facing upward. The two samples brought into contact with each other were sandwiched between drug wrappers. The two samples were held at 50°C for 48 hours in a state where a load of 10.2 Kg (pressure: 10 kPa) was applied thereto from

above. After 48 hours, the temperature was returned to room temperature (25°C), and the two evaluation samples that had been brought into contact with each other were then peeled off from each other. The charge amount of the release layer that had been brought into contact with the surface layer B was measured using a digital electrostatic potential measuring device (KSD-1000, manufactured by KASUGA ELECTRIC WORKS LTD.). The charge amount measured at this time was evaluated according to the following criteria.

Very good: The absolute value of the charge amount was less than 3 kV.

Good: The absolute value of the charge amount was 3 kV or more and 5 kV or less.

Poor: The absolute value of the charge amount was more than 5 kV.

[0091]

(Coefficient of static friction)

A film was cut into an area of 8 cm × 5 cm from a release film roll to prepare a sample film. This was fixed onto a bottom surface of a metal rectangular parallelepiped having a weight of 4.4 kg and a bottom surface size of 6 cm × 5 cm so that a surface layer B was exposed. At this time, the 5-cm-transverse direction of the sample film was made consistent with the 5-cm-transverse direction of the

metal rectangular parallelepiped. A side in the long direction of the sample film was folded, and the sample film was then fixed onto a side surface of the metal rectangular parallelepiped using a pressure-sensitive adhesive tape.

[0092]

Then, the sample film was cut into an area of 20 cm × 10 cm from the same release film roll. End portions in the long direction were fixed using a pressure-sensitive adhesive tape onto a flat metal plate so that the release layer surface was exposed. The metal rectangular parallelepiped onto which the sample film adhered was put onto this different sample film so as to bring a measuring surface of the sample into contact with the different sample. A coefficient of static friction was measured at a pulling speed of 100 mm/minute under conditions of a temperature of 23°C and a humidity of 65% RH. The measurement was performed three times, and the average value was employed as the coefficient of static friction (μ_s). The measurement was performed using a Tensilon universal tester RTG-1210 manufactured by A & D Company, Limited.

[0093]

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

As an esterification reactor, a continuous esterification reactor was used, which included a three-stage complete mixing tank including a stirrer, a partial condenser, a raw material charging port, and a product outlet. 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. EG (8% by mass) 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. Then, the reaction product of

the second esterification reaction can was continuously taken out of the system, and supplied to a third esterification reaction can. Porous colloidal silica (0.2% by mass) 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 a pressure of 39 MPa (400 kg/cm^2) using a high pressure disperser (manufactured by Nippon Seiki Co., Ltd.), and synthetic calcium carbonate (0.4% by mass) 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 as 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 supplied to a three-stage continuous polycondensation reaction apparatus to perform polycondensation. The polycondensation product was filtered with a filter obtained 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 a PET chip 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.

[0094]

(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)).

[0095]

(Manufacture of laminated film X1)

These PET chips were dried, then melted at 285°C, melted at 290°C by a separate melt extruder, and 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.

[0096]

(Manufacture of laminated film X2)

As a laminated film X2, E5101 (Toyobo Ester (registered trademark) film, manufactured by Toyobo Co., Ltd.) having a thickness of 25 µm was used. In E5101, particles are contained in a surface layer A and a surface layer B. Sa of the surface layer A of the laminated film X2 was 24 nm, and Sa of the surface layer B was 24 nm.

[0097]

(Manufacture of laminated film X3)

As a film raw material polymer, a PET resin pellet (PET II) having an intrinsic viscosity (solvent:

phenol/tetrachloroethane = 60/40) of 0.62 dl/g and substantially containing no inorganic particles was dried at 135°C for 6 hours under reduced pressure of 133 Pa. Thereafter, the PET resin pellet was supplied to an extruder, and melt-extruded into a sheet shape at about 280°C. The melt-extruded product was rapidly quenched, adhered, and solidified on a rotating cooling metal roll maintained at a surface temperature of 20°C to obtain an un-stretched PET sheet.

[0098]

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.

[0099]

Then, an easily slipping coating solution having the following composition was applied on one surface of a PET film with a bar coater, and then dried at 80°C for 15 seconds. The applying amount after final stretching and drying was adjusted to 0.1 μm . Subsequently, with a tenter, the film was stretched by 4.0 times in a transverse direction at 150°C. The film was heated at 230°C for 0.5 seconds in a state where the length in the transverse direction was fixed. The film was further subjected to a

loosening treatment by 3% in the transverse direction at 230°C for 10 seconds to obtain a laminated film X3 having a thickness of 31 μm . In the laminated film X3, a surface layer A contains substantially no inorganic particles, and an easy-to-slip coating layer is formed on a surface opposite to the surface layer A. The easy-to-slip coating layer is a surface layer B. Sa of the surface layer A was 1 nm, and Sa of the surface layer B was 2 nm.

[0100]

(Composition of easily slipping coating solution)

Water: 41.86 parts by mass

Isopropyl alcohol: 35.00 parts by mass

Acrylic polyol resin (solid content concentration: 20% by mass): 16.57 parts by mass

Oxazoline-based crosslinking agent (solid content concentration: 25% by mass): 5.68 parts by mass

Colloidal silica: 0.59 parts by mass (Trade name: MP2040, manufactured by Nissan Chemical Industries, Ltd., average particle diameter: 200 nm, solid content concentration: 40% by mass)

Fluorine-based surfactant (solid content concentration: 10% by mass): 0.30 parts by mass

[0101]

(Manufacture of acrylic polyol resin)

Methyl methacrylate (MMA) (77 parts by mass),

hydroxyethyl methacrylate (HEMA) (100 parts by mass), methacrylic acid (MAA) (33 parts by mass), and isopropyl alcohol (IPA) (490 parts by mass) were charged into a four-neck flask equipped with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube, and the temperature in the flask was raised to 80°C during stirring. The stirring was carried out for 3 hours while the temperature in the flask was maintained at 80°C, and 2,2-azobis-2-methyl-N-2-hydroxyethylpropionamide (0.5 parts by mass) was then added into the flask. The atmosphere in the flask was substituted by nitrogen while the temperature in the flask was raised to 120°C, and the mixture was then stirred at 120°C for 2 hours.

Then, a pressure reducing operation of 1.5 kPa was performed at 120°C to remove unreacted raw materials and solvent, thereby obtaining an acrylic polyol. The inside of the flask was returned to atmospheric pressure, and cooled to room temperature. An IPA aqueous solution (water content: 50% by mass) (840 parts by mass) was added and mixed. Thereafter, triethylamine was added using a dropping funnel during stirring, and the acrylic polyol was neutralized until the pH of the solution was in a range of 5.5 to 7.5, to obtain an acrylic polyol having a solid content concentration of 20% by mass.

[0102]

(Manufacture of oxazoline-based crosslinking agent)

Isopropyl alcohol (460.6 parts) was charged into a flask equipped with a stirrer, a reflux condenser, a nitrogen introducing pipe, and a thermometer, and heated to 80°C while gently flowing nitrogen gas thereinto. A monomer mixture prepared beforehand and containing methyl methacrylate (126 parts), 2-isopropenyl-2-oxazoline (210 parts), and methoxy polyethylene glycol acrylate (84 parts), and an initiator solution prepared beforehand and containing 2,2'-azobis(2-methylbutyronitrile) (21 parts) ("ABN-E", manufactured by Japan Finechem Inc.) that was a polymerization initiator, and isopropyl alcohol (189 parts), were dropped from dropping funnels, respectively, over 2 hours to cause reaction. After the end of dropping, the reaction was continuously carried out for 5 hours. The flow of nitrogen gas was continued during the reaction, and the temperature in the flask was kept at $80 \pm 1^{\circ}\text{C}$. Thereafter, the reaction solution was cooled to obtain a resin having a solid content concentration of 25% and having an oxazoline group. The oxazoline group amount of the obtained resin having an oxazoline group was 4.3 mmol/g, and the number-average molecular weight thereof measured by gel permeation chromatography (GPC) was 20000.

[0103]

(Example 1)

A release layer forming product having the following composition (described in an amount converted as a solid content, and the same applies hereinafter) was mixed with a mixed solvent of methyl ethyl ketone, toluene, and isopropyl alcohol to prepare an applying solution. The applying solution was coated on a surface layer A of a laminated film X1 using a reverse gravure so that a film thickness of a release layer after being dried was 0.5 μm , and then dried at 130°C for 15 seconds to obtain a release film for manufacturing a super-thin ceramic green sheet. For the obtained release film, the charge amount of the release layer, slipperiness, surface roughness, ceramic sheet peelability, ceramic sheet coatability, curl, and pinholes were evaluated, so that good evaluation results were obtained.

Melamine-based compound: 99.7 parts by mass (Full ether-type methylated melamine, manufactured by SANWA CHEMICAL CO., LTD., trade name: NIKALAC MW-30M, weight average polymerization degree: 1.3, main component: hexamethoxymethylmelamine)

Release agent: 0.3 parts by mass (One-terminal carboxyl-modified PDMS, manufactured by Shin-Etsu Chemical Co., Ltd., trade name: X22-3710, alkyl group intervening between dimethylsiloxane and carboxyl group)

p-Toluenesulfonic acid: 2.0 parts by mass

[0104]

(Examples 2 and 3)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that the contents of a melamine-based compound and one-terminal carboxyl-modified PDMS were changed to amounts shown in Table 1.

[0105]

(Example 4)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a release agent was changed to both-terminals carboxyl-modified PDMS (trade name: X22-162C, manufactured by Shin-Etsu Chemical Co., Ltd., alkyl group intervening between dimethylsiloxane and carboxyl group).

[0106]

(Example 5)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that the content of a melamine-based compound was changed to 99.9 parts by mass; and a release agent was changed to 0.1 parts by mass of both-terminals carboxyl-modified PDMS (trade name: X22-162C, manufactured by Shin-Etsu Chemical Co., Ltd., alkyl group intervening between dimethylsiloxane and carboxyl group).

[0107]

(Example 6)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a release agent was changed to side-chain carboxyl-modified PDMS (trade name: X22-3701E, manufactured by Shin-Etsu Chemical Co., Ltd., alkyl group intervening between dimethylsiloxane and carboxyl group).

[0108]

(Example 7)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a release agent was changed to COOH-modified copolymerized acrylic silicone (trade name: SYMAC US-352, manufactured by Toagosei Co., Ltd.).

[0109]

(Example 8)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a melamine-based compound was changed to full ether-type methylated melamine (trade name: NIKALAC MW-30, manufactured by Sanwa Chemical Co., Ltd., weight-average polymerization degree: 1.5, main component: hexamethoxymethylmelamine).

[0110]

(Example 9)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a melamine-based compound was changed to full ether-type methylated melamine (trade name: NIKALAC MW-390, manufactured by Sanwa Chemical Co., Ltd., weight-average polymerization degree: 1.0, main component: hexamethoxymethylmelamine).

[0111]

(Example 10)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a melamine-based compound (MW-30M) of Example 1 was changed to full ether-type methylated melamine (weight average polymerization degree: 1.1, main component: hexamethoxymethylmelamine) obtained by recrystallizing the melamine-based compound in isopropanol.

[0112]

(Examples 11 and 12)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a film thickness of a release layer was changed to a film thickness shown in Table 1.

[0113]

(Example 13)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that coating was performed on a surface layer A of a laminated film X2.

[0114]

(Example 14)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that coating was performed on a surface layer A of a laminated film X3.

[0115]

(Example 15)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 under conditions shown in Table 1B except that one-terminal hydroxyl group-modified PDMS was used as a release agent. The obtained release film had a charge amount of 3.5 kV, a coefficient of static friction of 0.28, and a floating amount of 0.7, and had good ceramic sheet coatability. The obtained release film exhibited the same degree of peel force as that of the release film obtained in Example 7, and had almost no pinholes.

[0116]

(Example 16)

A release film for manufacturing a super-thin ceramic

green sheet was obtained in the same manner as in Example 1 under conditions shown in Table 1B except that one-terminal amino group-modified PDMS was used as a release agent.

Under the conditions shown in Table 1B, a release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1. The obtained release film had a charge amount of 3.9 kV, a coefficient of static friction of 0.26, and a floating amount of 0.7, and had good ceramic sheet coatability. The obtained release film exhibited the same degree of peel force as that of the release film obtained in Example 7, and had almost no pinholes.

[0117]

(Comparative Example 1)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a melamine-based compound was changed to 99.5 parts by mass of an imino-type melamine resin (trade name: NIKALAC MX-730, manufactured by Sanwa Chemical Co., Ltd., weight-average polymerization degree: 2.4); a release agent was changed to 0.5 parts by mass of polyether-modified hydroxyl group-containing PDMS (trade name: BYK-377, manufactured by BYK Japan KK); and coating was performed so that a film thickness was 1.0 μm .

[0118]

(Comparative Example 2)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a melamine-based compound was changed to an imino-type melamine resin (trade name: NIKALAC MX-730, manufactured by Sanwa Chemical Co., Ltd., weight-average polymerization degree: 2.4).

[0119]

(Comparative Example 3)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that the contents of a melamine-based compound and one-terminal carboxyl-modified PDMS were changed to amounts shown in Table 1.

[0120]

(Comparative Example 4)

A release film for manufacturing a super-thin ceramic green sheet was obtained in the same manner as in Example 1 except that a melamine-based compound was changed to a methylol-type melamine resin (trade name: NIKALAC MS-11, manufactured by Sanwa Chemical Co., Ltd., weight-average polymerization degree: 1.8).

[0121]

(Comparative Example 5)

A release film for manufacturing a super-thin ceramic

green sheet was obtained in the same manner as in Example 1 except that a melamine-based compound was changed to an imino methylol-type melamine resin (trade name: NIKALAC MS-001, manufactured by Sanwa Chemical Co., Ltd., weight average polymerization degree: 5.7).

[0122]

[Table 1A]

	Substrate Film			Release Layer										
	Surface Roughness Sa (nm)		Thickness (μm)	Melamine-based Compound			Release Agent		Catalyst		Thickness of Release Layer (μm)	Surface Shape (nm)		
	Surface Layer A	Surface Layer B		Type	Weight Average Polymerization Degree	Rate in Release Layer (parts by mass)	Type	Rate in Release Layer (parts by mass)	Type	Rate to Melamine Resin (parts by mass)		Roughness Sa	Height P	
Example 1	X1	31	1	28	Full Ether-type	1.3	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	28
Example 2	X1	31	1	28	Full Ether-type	1.3	99.5	One-terminal Carboxyl Group-modified PDMS	0.5	p-Toluenesulfonic Acid	2	0.5	1	28
Example 3	X1	31	1	28	Full Ether-type	1.3	99	One-terminal Carboxyl Group-modified PDMS	1	p-Toluenesulfonic Acid	2	0.5	1	27
Example 4	X1	31	1	28	Full Ether-type	1.3	99.7	Both-terminals Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	25
Example 5	X1	31	1	28	Full Ether-type	1.3	99.9	Both-terminals Carboxyl Group-modified PDMS	0.1	p-Toluenesulfonic Acid	2	0.5	1	25
Example 6	X1	31	1	28	Full Ether-type	1.3	99.7	Side-chain Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	29
Example 7	X1	31	1	28	Full Ether-type	1.3	99.7	Carboxyl Group-containing Acrylic Silicone	0.3	p-Toluenesulfonic Acid	2	0.5	1	31
Reference Example 8	X1	31	1	28	Full Ether-type	1.5	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	27
Example 9	X1	31	1	28	Full Ether-type	1	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	27
Example 10	X1	31	1	28	Full Ether-type	1.1	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-toluenesulfonic Acid	2	0.5	1	27
Example 11	X1	31	1	28	Full Ether-type	1.3	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	P-Toluenesulfonic Acid	2	0.2	1	28

PDMS: Polydimethylsiloxane

[0123]

[Table 1B]

	Substrate Film				Release Layer										Surface Shape	
	Type	Thickness (μm)		Surface Roughness Sa (nm)		Melamine-based Compound				Release Agent		Catalyst		Thickness of Release Layer (μm)	Surface Shape (nm)	
		Thickness (μm)	Surface Layer A	Surface Layer B	Type	Weight Average Polymerization Degree	Rate in Release Layer (parts by mass)	Type	Rate in Release Layer (parts by mass)	Type	Rate to Melamine Resin (parts by mass)	Type	Rate to Melamine Resin (parts by mass)		Roughness Sa	Height P
Example 12	X1	31	1	28	Full Ether-type	1.3	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	1	1	1	1	25
Example 13	X2	25	24	24	Full Ether-type	1.3	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	4	49		
Example 14	X3	31	1	2	Full Ether-type	1.3	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	26		
Example 15	X1	31	1	28	Full Ether-type	1.3	99.7	One-terminal Hydroxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	28		
Example 16	X1	31	1	28	Full Ether-type	1.3	99.7	One-terminal Amino Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	30		
Comparative Example 1	X1	31	1	28	Imino-type	2.4	99.5	Polyether-modified Hydroxyl Group-containing PDMS	0.5	p-Toluenesulfonic Acid	2	1	1	29		
Comparative Example 2	X1	31	1	28	Imino-type	2.4	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	25		
Comparative Example 3	X1	31	1	28	Full Ether-type	1.3	99.97	One-terminal Carboxyl Group-modified PDMS	0.03	p-Toluenesulfonic Acid	2	0.5	1	28		
Comparative Example 4	X1	31	1	28	Methylol-type	1.8	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	29		
Comparative Example 5	X1	31	1	28	Imino Methylol-type	5.7	99.7	One-terminal Carboxyl Group-modified PDMS	0.3	p-Toluenesulfonic Acid	2	0.5	1	32		

PDMS: Polydimethylsiloxane

[0124]

[Table 1C]

	Physical Properties								
	Charge		Slipperiness	Peel Force of Ceramic Sheet		Curl		Coatability	Pinhole
	Charge Amount (kV)	Evaluation	Coefficient of Static Friction (-)	(mN/mm)	Evaluation	Floating Amount (mm)	Evaluation		
Example 1	2.4	Very good	0.26	1.1	Very good	0.7	Very good	Good	Good
Example 2	1.1	Very good	0.19	0.8	Very good	0.7	Very good	Good	Good
Example 3	0.8	Very good	0.15	0.7	Very good	0.7	Very good	Good	Good
Example 4	2.3	Very good	0.16	0.9	Very good	0.7	Very good	Good	Good
Example 5	2.8	Very good	0.28	1.4	Very good	0.7	Very good	Good	Good
Example 6	0.5	Very good	0.17	0.9	Very good	0.7	Very good	Good	Good
Example 7	3.9	Good	0.18	1.9	Good	0.7	Very good	Good	Average
Reference Example 8	3.2	Good	0.24	0.9	Very good	0.5	Very good	Good	Good
Example 9	3.3	Good	0.25	1	Very good	1.5	Good	Good	Good
Example 10	2.3	Very good	0.24	1	Very good	0.9	Very good	Good	Good
Example 11	1.2	Very good	0.29	1.6	Good	0.3	Very good	Good	Good
Example 12	4.5	Good	0.19	0.6	Very good	2.1	Good	Good	Good
Example 13	1.2	Very good	0.22	1.1	Very good	0.7	Very good	Good	Average
Example 14	3.2	Good	0.29	1.1	Very good	0.7	Very good	Good	Good
Comparative Example 1	9.2	Poor	0.19	1.6	Good	0.4	Very good	Good	Average
Comparative Example 2	5.1	Poor	0.31	Unmeasurable Heavy Peeling	Poor	0.2	Very good	Good	Poor
Comparative Example 3	7.5	Poor	0.37	2.8	Poor	0.7	Very good	Good	Poor
Comparative Example 4	5.2	Poor	0.24	1.4	Very good	0.4	Very good	Good	Good
Comparative Example 5	5.3	Poor	0.22	2.6	Poor	0.2	Very good	Good	Poor

[0125]

The release films obtained in Comparative Examples all had a charge amount outside the range defined by the present invention. Therefore, extremely minute environmental foreign matters during the step tended to adhere to the release film.

INDUSTRIAL APPLICABILITY

[0126]

According to the present invention, the surface of a release layer is highly smooth, and not only a ceramic green sheet can be peeled off with a low and uniform force, but also the release layer is less likely to be charged, whereby foreign matters are less likely to adhere to a film, and a super-thin ceramic green sheet having a thickness of 1 μm or less can be manufactured without practically causing defects due to foreign matters.

CLAIMS

1. A release film for manufacturing a ceramic green sheet, the release film comprising:

5 a polyester film substrate including a surface layer A forming one surface of the substrate and a surface layer B forming other surface; and

a release layer directly laminated on the surface layer A,

10 wherein

a charge amount of the release layer is ± 5 kV or less when the release layer and the surface layer B are held for 48 hours under an atmosphere of 50°C and a pressure of 10 kPa in a state where the release layer and the surface layer B are brought into contact with each other, and then peeled off from each other,

an anti-static layer is not provided on surfaces of the surface layer A and the surface layer B, and the surface layer A and the surface layer B contain no anti-static agent,

20 the release layer is formed by curing a composition for forming the release layer,

the composition for forming the release layer contains polyorganosiloxane containing a carboxyl group as a release agent,

a content of a release agent is 0.05% by mass or more
5 and 5% by mass or less in the release layer,

the composition for forming the release layer contains a melamine-based compound, and

a weight average polymerization degree of the melamine-based compound is more than 1.0 and 1.7 or less.
10

2. The release film for manufacturing a ceramic green sheet according to claim 1, wherein a coefficient of static friction μ_s when the release layer and the surface layer B are overlapped with each other is less than 0.30.

15 3. The release film for manufacturing a ceramic green sheet according to claim 1 or 2, wherein the ceramic green sheet has a thickness of 0.2 μm to 1.0 μm .

20 4. The release film for manufacturing a ceramic green sheet according to any one of claims 1 to 3, wherein

the composition for forming the release layer contains no anti-static agent, and

a content of the melamine-based compound in the release layer is 80% by mass or more with respect to a solid content of the composition for forming the release layer.

5

5. The release film for manufacturing a ceramic green sheet according to any one of claims 1 to 4, wherein a weight average molecular weight of the melamine-based compound is of 400 or more and 1000 or less.

10

6. The release film for manufacturing a ceramic green sheet according to any one of claims 1 to 5, wherein the surface layer A contains substantially no inorganic particles.

15

7. The release film for manufacturing a ceramic green sheet according to any one of claims 1 to 6, wherein

the surface layer B contains particles,

at least a part of the particles are silica particles

20 and/or calcium carbonate particles, and

a total content of the particles with respect to a mass of the surface layer B is 5000 to 15000 ppm.

8. The release film for manufacturing a ceramic green sheet according to any one of claims 1 to 7, wherein a thickness of the release layer is less than 1.0 μm .

5 9. A method for manufacturing a ceramic green sheet,
the method comprising using the release film for
manufacturing a ceramic green sheet according to any one of
claims 1 to 8 and forming the ceramic green sheet, wherein
the formed ceramic green sheet has a thickness of 0.2 μm to
10 1.0 μm .

10. A method for manufacturing a ceramic capacitor,
wherein the method for manufacturing a ceramic green sheet
according to claim 9 is employed.