

DESCRIPTION

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

TECHNICAL FIELD

[0001]

The present invention relates to a release film for production of a super-thin ceramic green sheet, and more specifically, a release film for production of a super-thin ceramic green sheet, which can produce the super-thin ceramic green sheet which suppresses the occurrence of process defects due to pinholes and thickness irregularity or peeling defects during the production of the super-thin 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 multilayer ceramic capacitor (hereinafter, referred to as MLCC) 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 multilayer ceramic capacitor and an increase in the

capacity thereof. The ceramic green sheet is formed by applying a slurry containing a ceramic component such as barium titanate and a binder resin on a release film and drying the slurry. On the formed ceramic green sheet, an electrode is printed, and the ceramic green sheet is peeled off from the release film. Another ceramic green sheet is then laminated on the ceramic green sheet, followed by pressing, cutting, firing, and applying an external electrode, to produce a multilayer ceramic capacitor. Hitherto, when a ceramic green sheet is formed on a release layer surface of a polyester film, minute protrusions 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, the release layer surface is required to have high smoothness. As the thickness of the ceramic green sheet is reduced, the strength of the ceramic green sheet

decreases, whereby it is preferable that the release layer surface is smoothed and a peeling force when the ceramic green sheet is peeled off from the release film is low and uniform. It is preferable to reduce a load applied to the ceramic green sheet when the ceramic green sheet is peeled off from the release film as much as possible so as not to damage the ceramic green sheet.

[0004]

As the method for smoothing the release layer surface and suppressing the load on the ceramic green sheet during peeling from the release layer side, there has been studied a measure for increasing the crosslinking density of the release layer using an active energy ray curing component in the release layer of the release film, thereby increasing the elastic modulus thereof. This suppresses the elastic deformation of the release layer when the ceramic green sheet is peeled off to reduce the peeling force (for example, Patent Documents 2 and 3). However, this method causes too high smoothness, so that surface peeling occurs. This causes a heavy peeling force, so that cracks may occur in the green sheet. Furthermore, if a smooth surface of a super-thin ceramic green sheet comes into contact with a smooth roll or a rubber roll for controlling the tension of applying equipment to process the super-thin ceramic green sheet, sliding property

between the roll and the smooth surface is insufficient, which causes unstable tension control. This disadvantageously causes deteriorated smoothness of the coated surface of the green sheet.

[0005]

Therefore, a release film having an excellent balance between smoothness and uniform peelability has been reported. The release film is composed of a polyester film having appropriate large protrusions which become a trigger at the start of peeling (peeling start point) (for example, Patent Document 4). However, in the case of fillers kneaded into PET, coarse protrusions due to the aggregation of the fillers cannot be completely eliminated. The coarse protrusions disadvantageously cause defect factors in products. In particular, in a super-thin ceramic green sheet, an inorganic filler used as a ceramic material has a particle size of about 60 nm to 800 nm (Patent Documents 5 and 6), so that the use of a film as described in Patent Document 4 disadvantageously causes local holes to occur in a peeled surface.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0006]

Patent Document 1: JP-A-2000-117899

Patent Document 2: International Publication No.
2013/145864

Patent Document 3: International Publication No.
2013/145865

Patent Document 4: International Publication No.
2014/203702

Patent Document 5: JP-A-2016-127120

Patent Document 6: JP-A-2017-081805

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

Therefore, as a result of intensive studies, the present inventors found that the above-mentioned heavy peeling, deterioration in processing suitability, and occurrence of defect factors can be simultaneously suppressed by forming surface unevenness due to low protrusions on a release layer surface. An object of the present invention is to provide a release film for forming of a ceramic green sheet, which has excellent light peelability and is less likely to cause damage such as cracks in a half cut test for a super-thin ceramic green sheet to be formed.

MEANS FOR SOLVING THE PROBLEMS

[0008]

That is, the present invention has the following configurations.

1. A release film for production of a ceramic green sheet, the release film including: a polyester film; and a release layer laminated on at least one surface of the polyester film directly or with another layer interposed therebetween, wherein: the release layer is formed by curing a coating film containing at least an energy ray-curable compound (I), a polyester resin or a polyester urethane resin (II), and a release component (III); and the energy ray-curable compound (I) has a hydroxyl value of 45 mgKOH/g or less.

2. The release film for production of a ceramic green sheet according to the above 1, wherein the release layer has a phase-separated structure containing the energy ray-curable compound (I) as a sea component and the polyester resin or the polyester urethane resin (II) as an island component, and has surface unevenness.

3. The release film for production of a ceramic green sheet according to the above 1 or 2, wherein the release layer does not substantially contain inorganic particles.

4. The release film for production of a ceramic green sheet according to any one of the above 1 to 3, wherein the energy ray-curable compound (I) is a (meth) acrylic acid

ester having 3 or more acryloyl groups in one molecule.

5. The release film for production of a ceramic green sheet according to any one of the above 1 to 4, wherein the release layer has a thickness of 0.2 to 3.5 μm .

6. The release film for production of a ceramic green sheet according to any one of the above 1 to 5, wherein the release layer has average area surface roughness (S_a) of 5 to 40 nm.

7. The release film for production of a ceramic green sheet according to any one of the above 1 to 6, wherein the release film has a release layer surface having a maximum protrusion height (R_p) of 60 nm or less.

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

EFFECT OF THE INVENTION

[0009]

A release film for production of a ceramic green sheet of the present invention has a peeling force which is not much heavier than that of a conventional release film for production of a ceramic green sheet, has excellent

processability, and has no large protrusions in a release layer, whereby the release film for production of a ceramic green sheet can be provided, which is less likely to cause damage such as cracks in a half cut test for a formed super-thin ceramic green sheet having a thickness of 1 μm or less.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

Fig. 1 is an electron micrograph of the surface of a release layer of a product of the present invention (Example 1).

Fig. 2 is an electron micrograph of the surface of a release layer of a product of the present invention (Example 2).

Fig. 3 is an electron micrograph of the surface of a release layer of a product of the present invention (Example 3).

Fig. 4 is an electron micrograph of the surface of a release layer of a product of the present invention (Example 4).

Fig. 5 is an electron micrograph of the surface of a release layer of a comparative control product (Comparative Example 1).

Fig. 6 is an electron micrograph of the surface of a

release layer of a comparative control product (Comparative Example 2).

MODE FOR CARRYING OUT THE INVENTION

[0011]

Hereinafter, the present invention will be described in detail.

[0012]

(Polyester film)

Polyester constituting a polyester film used as a substrate in a release film of 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 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 produced 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-stretched polyester film for reasons such as a high bidirectional elastic modulus.

[0013]

The intrinsic viscosity of the polyethylene terephthalate 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, breakage is less likely to occur 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 materials are sufficiently dried in vacuum.

[0014]

The method for producing 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 longitudinal direction, or a method for simultaneously biaxially stretching an un-stretched film in longitudinal and transverse directions.

[0015]

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 by 1 to 8 times, particularly 2 to 6 times in each of the longitudinal and transverse directions.

[0016]

The polyester film preferably has a thickness of 12 to 50 μm , more preferably 12 to 38 μm , and still more preferably 15 to 31 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, which is preferable. Meanwhile, if the thickness of the film is 50 μm or less, the amount of the film to be discarded after use is not extremely large, which is preferable in reducing an environmental load. Furthermore, the amount of a material per area of the release film to be used is small, which is also preferable from the economic viewpoint.

[0017]

The polyester film substrate may be a single layer or a multilayer of two or more layers, but the polyester film substrate is preferably a laminated polyester film including a surface layer A which does not substantially contain inorganic particles on at least one surface. A laminated polyester film having a multilayer structure of two or more layers preferably includes a surface layer B capable of containing particles and the like on a surface opposite to the surface layer A which does not substantially contain inorganic particles. As a laminated structure, 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 a core layer other than these is a core layer C. Examples of a layer structure in a thickness direction include a laminated structure such as

release layer/surface layer A/surface layer B or release layer/surface layer A/core layer C/surface layer B. Of course, the core layer C may have a plurality of layer structures. The surface layer B may not contain particles. In that case, a coat layer (D) containing particles and a binder is preferably provided on the surface layer B in order to impart slipperiness for winding the film into a roll.

[0018]

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 does not substantially contain inorganic particles. At this time, the average area surface roughness (S_a) of the surface layer A is preferably 7 nm or less. When the S_a is 7 nm or less, pinholes and the like are less likely to occur when a super-thin ceramic green sheet to be laminated is formed even if the release layer has a film thickness of 2.0 μm or less, and a smaller film thickness of 0.5 μm or less, which is 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, when an anchor coat layer and the like to be described below are provided on the surface layer A, it is preferable that the coat layer does not

substantially contain inorganic particles. The average area surface roughness (Sa) after the coat layer is laminated is preferably within the above range. In the present invention, "does not substantially contain inorganic particles" is defined by the fact that the content of an inorganic element is 50 ppm or less when the inorganic element is quantified by fluorescent X-ray analysis. The content of the inorganic element is 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 producing processes may be peeled off, and mixed into the film.

[0019]

When the polyester film substrate of the present invention is a laminated film, the surface layer B forming the surface opposite to the surface layer A 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 that the surface layer B contains 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 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 of the surface layer B 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 producing 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 protrusions cannot be formed, whereby defects such as pinholes do not occur in the ceramic green sheet even when the super-thin ceramic green sheet is formed and then wound, which is preferable.

[0020]

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

[0021]

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 size of 2.0 μm or less is free from the possibility of causing pinholes to occur due to coarse particles on the release layer surface, which is preferable. A method for measuring the average particle size of the particles can be performed as follows. The particles in the cross section of the processed film are observed with a scanning electron microscope, and the 100

particles are observed. The average value of the particle sizes of the particles is determined as the average particle size. The shapes of the particles are not particularly limited as long as they satisfy the object of the present invention, and spherical particles and non-spherical particles having an indefinite shape can be used. The average particle size of the particles having an indefinite shape can be calculated as an equivalent circle diameter. The equivalent circle diameter is a value obtained by dividing the area of the observed particle by the circular constant (π), calculating the square root, and doubling the value of the square root.

[0022]

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 sizes.

[0023]

It is also preferable that, when the surface layer B does not contain particles, slipperiness is imparted to the surface layer B by a coat layer containing particles. Means for providing the coat layer is not particularly limited, and the coat layer is preferably provided by a so-called in-line coating method in which the coat layer is applied during the formation of the polyester film. When a

coat layer imparting slipperiness is provided on the surface of the polyester film on which the release layer is not laminated, the polyester film may not include the surface layers A and B, and may be composed of a single-layer polyester film which does not substantially contain inorganic particles.

[0024]

The average area surface roughness (Sa) of the surface layer B is preferably 40 nm or less, more preferably 35 nm or less, and still more preferably 30 nm or less. When slipperiness is imparted to the surface layer B or the surface of the single-layer polyester film on which the release layer is not laminated by the coat layer (D), it is preferable that the Sa of the surface is measured on the surface on which the coat layer is laminated, and is equivalent to the average area surface roughness (Sa) of the surface layer B.

[0025]

(Coat layer D)

It is preferable that at least a binder resin and particles are contained in the coat layer D on the surface of the polyester film on which the release layer is not laminated.

[0026]

(Binder resin of coat layer D)

The binder resin constituting the easy-to-slip coating layer is not particularly limited. Specific examples of the polymer include a polyester resin, an acrylic resin, 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 compatibility of the binder resin with the polyester film, the polyester resin is particularly preferable. The polyester of the binder is preferably a copolyester in order to achieve solubility and dispersibility in a solvent, and adhesiveness with a substrate film and other layer. The polyester resin may be modified with polyurethane. Other preferable examples of the binder resin constituting the easy-to-slip coating layer on the polyester substrate film include a urethane resin. Examples of the urethane resin include a polycarbonate polyurethane resin. Furthermore, the polyester resin and the polyurethane resin may be used in combination, and the above-mentioned other binder resins may be used in combination.

[0027]

(Crosslinking agent of coat layer D)

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

[0028]

(Particles in coat layer D)

The easy-to-slip coating layer preferably contains lubricant particles in order to impart slipperiness to the surface of the easy-to-slip coating layer. The particles may be inorganic particles or organic particles, and are not particularly limited. Examples thereof include (1) inorganic particles such as 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 (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.

[0029]

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

[0030]

The average particle size of the particles is preferably 1000 nm or less, more preferably 800 nm or less, and still more preferably 600 nm or less. If the average particle size of the particles is 1000 nm or less, the transparency is maintained, and the particles do not fall off, which is preferable.

[0031]

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

[0032]

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.

[0033]

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 can be increased, to reduce the environmental load, which is preferable.

[0034]

From the viewpoint of economic performance, for the layer other than the surface layer A (the surface layer B or the above-mentioned core 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.

[0035]

In order to improve the adhesion of the release layer or the like to be applied later, or in order to prevent charging, 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 on a film after uniaxial stretching in the film forming process, or the film may be subjected to a corona treatment or the like. When a coat layer is also provided, the (Sa) of each layer is substituted by the measurement value of the surface of the coat layer. It is preferable that, when these coat layers are provided on the surface of the surface layer A, the coat layers do not contain particles.

[0036]

(Release layer)

The release layer in the present invention is preferably formed by curing a coating film containing at least an energy ray-curable compound (I), a polyester resin or a polyester urethane resin (II), and a release component (III). The energy ray-curable compound (I) and the polyester resin or polyester urethane resin (II) are phase-separated from each other, to form a sea-island structure, whereby unevenness having an appropriate height due to low protrusions can be easily formed, which causes no coarse protrusions. Therefore, no pinholes and the like occur in the formed green sheet. Since the flat surface portion is reduced by the appropriate unevenness, stress during cutting is likely to be released during the half cut test of the green sheet, whereby point peeling (small peeling which naturally occurs in the end part) occurs in the cut

end part. This makes it possible to suppress damage such as cracks and deformation of the end part, and become a trigger for peeling in a peeling step as the next step to provide smooth peeling.

[0037]

(Energy ray-curable compound (I))

The energy ray-curable compound (I) used in the present invention preferably has a hydroxyl value of 45 mgKOH/g or less. When the hydroxyl value is 45 mgKOH/g or less, the compatibility with the polyester resin or the polyester urethane resin (II) is reduced, whereby surface unevenness due to an appropriate sea-island structure is easily formed in the release layer, which is preferable. More preferably, the hydroxyl value is 35 mgKOH/g or less. The hydroxyl value of the energy ray-curable compound (I) is preferably small, but it may be 1 mgKOH/g or more, or 3 mgKOH/g or more.

[0038]

A method for setting the hydroxyl value of the energy ray-curable compound (I) to 45 mgKOH/g or less is a method using an energy ray-curable compound having a hydroxyl value of 45 mgKOH/g or less, or a method mixing two or more energy ray-curable compounds to adjust a hydroxyl value to 45 mgKOH/g or less, but it is not particularly limited.

[0039]

An energy ray-curable compound having 3 or more reactive groups in one molecule can be used. The energy ray-curable compound has 3 or more reactive groups in one molecule, whereby a release layer having a high elastic modulus can be obtained. This can suppress the deformation of the release layer when the green sheet is peeled off to suppress heavy peeling, which is preferable. The solvent resistance of the release layer can be improved, whereby the erosion and the like of the release layer due to the solvent when the slurry is applied can also be prevented, which is preferable. The energy ray-curable compound having 3 or more reactive groups in one molecule is not particularly limited as to whether it reacts directly by energy rays or indirectly with active species generated. The content of the energy ray-curable compound (I) in the solid content of the release layer-forming coating solution is preferably 60 to 98% by mass, and more preferably 75 to 97% by mass. By adding 60% by mass or more of the energy ray-curable compound (I), the degree of crosslinking can be maintained to provide a high elastic modulus.

[0040]

Examples of the reactive group of the energy ray-curable compound (I) include a (meth)acryloyl group, an alkenyl group, an acrylamide group, a maleimide group, an epoxy group, and a cyclohexene oxide group. Among these,

the energy ray-curable compound having a (meth)acryloyl group, which has excellent processability, is preferable.

[0041]

The energy ray-curable compound having a (meth)acryloyl group can be used without being limited to a monomer, an oligomer, and a polymer. The energy ray-curable compound having a (meth)acryloyl group preferably contains at least a compound having 3 or more reactive groups in one molecule, but 2 or more compounds such as a compound having 1 or 2 reactive groups in its molecule can also be used in a mixture. Curling and the like can be suppressed by mixing the compounds having a small number of reactive groups.

[0042]

Examples of the energy ray-curable monomer having 3 or more (meth)acryloyl groups in its molecule include polyfunctional (meth)acrylates such as isocyanuric acid triacrylate, glycerin tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, dipentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, and dipentaerythritol hexa(meth)acrylate, and ethylene oxide-modified products, propylene oxide-modified products, and caprolactone-

modified products thereof.

[0043]

Examples of the energy ray-curable monomer having 1 or 2 reactive groups in its molecule include monomers such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, isopropyl(meth)acrylate, butyl(meth)acrylate, isobutyl(meth)acrylate, t-butyl(meth)acrylate, pentyl(meth)acrylate, cyclopentyl(meth)acrylate, hexyl(meth)acrylate, cyclohexyl(meth)acrylate, octyl(meth)acrylate, isooctyl(meth)acrylate, nonyl(meth)acrylate, lauryl(meth)acrylate, stearyl(meth)acrylate, behenyl(meth)acrylate, isobornyl(meth)acrylate, cyclic trimethylolpropane formal(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxybutyl(meth)acrylate, hydroxypropyl(meth)acrylate, (meth)acrylic acid, dicyclopentenylloxyethyl(meth)acrylate, dicyclopentanylmethyl(meth)acrylate, benzyl(meth)acrylate, phenoxyethyl(meth)acrylate, tetrahydrofurfuryl(meth)acrylate, methoxypolyethyleneglycol(meth)acrylate, pentamethylpiperidinyl(meth)acrylate, tetramethylpiperidinyl(meth)acrylate, 1,4-butanediol di(meth)acrylate, polyethyleneglycol di(meth)acrylate, nonanediol di(meth)acrylate, bisphenol A di(meth)acrylate,

neopentylglycol di(meth)acrylate, and cyclohexanediol di(meth)acrylate, and ethylene oxide-modified products, propylene oxide-modified products, and caprolactone-modified products thereof.

[0044]

Examples of the energy ray-curable oligomer having 3 or more (meth)acryloyl groups in its molecule include urethane acrylate, polyester acrylate, polyether acrylate, epoxy acrylate, and silicone-modified acrylate, and commercially available products can be generally used. Examples thereof include Beam Set (registered trademark) Series manufactured by Arakawa Chemical Co., Ltd., NK Oligo Series manufactured by Shin Nakamura Chemical Co., Ltd., EBECRYL Series manufactured by Daicel-Allnex Ltd., Biscoat Series manufactured by Osaka Organic Chemical Industry Ltd., Urethane Acrylate Series manufactured by Kyoisha Chemical Co., Ltd., and Unidic Series manufactured by DIC Corporation.

[0045]

Examples of the energy ray-curable polymer having 3 or more (meth)acryloyl groups in its molecule include a graft polymer in which a (meth)acryloyl group is grafted to a polymer and a block polymer in which a polyfunctional acrylic monomer is added to a polymer terminal. As the above-mentioned polymers, an acrylic resin, an epoxy resin,

a polyester resin, and polyorganosiloxane and the like can be used without particular limitation.

[0046]

(Polyester resin or polyester urethane resin (II))

The polyester resin or polyester urethane resin (II) used in the present invention may be a single polyester resin or polyester urethane resin, or two or more polyester resins and/or polyester urethane resins may be simultaneously used. The content of the polyester resin or polyester urethane resin (II) in the solid content of the release layer-forming coating solution is preferably 1 to 40% by mass, and more preferably 1 to 10% by mass. When the content of the resin (II) is 1% by mass or more, sufficient surface unevenness can be formed, and when the content of the resin (II) is 40% by mass or less, the degree of crosslinking of the release layer by the energy ray-curable compound (I) is high, and the temperature dependency of the release layer during peeling is low, which is preferable.

[0047]

The polyester resin or the polyester urethane resin is not particularly limited, and commercially available products can be used. Examples thereof include Vylon (registered trademark) Series manufactured by Toyobo Co., Ltd., and Nichigo-Polyester (registered trademark) Series

manufactured by Nippon Synthetic Chemical Industry Co.,
Ltd.

[0048]

(Release component (III))

The release component (III) used in the present invention is not particularly limited as long as it is a material capable of exhibiting releasing property between the release component (III) and the green sheet, such as polyorganosiloxane, a fluorine compound, a long-chain alkyl compound, or waxes. These materials preferably have a functional group capable of reacting with and binding to the energy ray-curable compound (I) having a (meth)acryloyl group or the like. It is also possible to use a mixture of two or more materials. The content of the release component (III) in the solid content of the release layer-forming coating solution is preferably 0.05 to 10% by mass, and more preferably 0.1 to 5% by mass. The addition of the release component (III) in an amount of 0.05% by mass or more can provide a reduced peeling force, and the addition of the release component (III) in an amount of 10% by mass or less provides suppressed transfer of the release component to the ceramic green sheet or the like, which is preferable.

[0049]

As polyorganosiloxane, in addition to

polydimethylsiloxane, polydiethylsiloxane, and polyphenylsiloxane and the like, a partially organically modified siloxane-based compound, a block polymer having polyorganosiloxane, and a polymer grafted with polyorganosiloxane, and the like can also be used. As commercially available products, for example, BYK (registered trademark) Series manufactured by BYK Japan KK, and Modiper (registered trademark) Series manufactured by NOF CORPORATION can be used.

[0050]

The fluorine compound is not particularly limited, and commercially available products can be used. Examples thereof include MegaFac (registered trademark) Series manufactured by DIC Corporation.

[0051]

Examples of the long-chain alkyl compound include an acrylic polymer obtained by copolymerizing long-chain alkyl acrylate, a graft polymer obtained by grafting long-chain alkyl, and a block polymer obtained by adding long-chain alkyl to a terminal. The long-chain alkyl compound is not particularly limited, and commercially available compounds can be used. Examples thereof include Tesfine (registered trademark) Series manufactured by Hitachi Chemical Co., Ltd., and Pyroyl (registered trademark) manufactured by Lion Specialty Chemicals Co., Ltd.

[0052]

Examples of the energy rays include infrared rays, visible rays, ultraviolet rays, electromagnetic rays such as X-rays, electron rays, ion beams, neutron rays, and particle rays such as α rays. Among these, it is preferable to use ultraviolet rays providing excellent production cost.

[0053]

The atmosphere for the irradiation of the energy rays may be general air or a nitrogen gas atmosphere. In the nitrogen gas atmosphere, a radical reaction can be smoothly advanced by decreasing an oxygen concentration, to improve the elastic modulus of the release layer, but the irradiation of the energy rays in air is preferable from the economical viewpoint as long as the irradiation of the energy rays in air causes no practical problems.

[0054]

(Photopolymerization initiator)

When a radical polymerization-based compound is used for the release layer of the present invention, it is preferable to add a photopolymerization initiator. Specific examples of the photopolymerization initiator include benzophenone, acetophenone, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ether, benzoin benzoic acid, methyl

benzoin benzoate, benzoin dimethyl ketal, 2,4-diethylthioxanthone, 1-hydroxycyclohexyl phenyl ketone, benzyl diphenyl sulfide, tetramethyl thiuram monosulfide, azobisisobutyronitrile, benzyl, dibenzyl, diacetyl, β -chloranthraquinone, (2,4,6-trimethylbenzyldiphenyl)phosphine oxide, and 2-benzothiazole-N,N-diethyldithiocarbamate. In particular, preferred are 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]-phenyl}-2-methylpropane-1-one, 1-hydroxy-cyclohexyl-phenylketone, 2-hydroxy-2-methyl-1-phenyl-propane-1-one, and 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one which are said to have excellent surface curability. Among these, particularly preferred are 2-hydroxy-2-methyl-1-phenyl-propane-1-one and 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-one. These may be used alone or in combination of two or more.

[0055]

The amount of the photopolymerization initiator added is not particularly limited, but for example, it is preferable to add about 0.1 to 20% by mass of the photopolymerization initiator as the solid content in the release layer-forming coating solution.

[0056]

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.

[0057]

Additives such as an adhesion improver and an anti-static agent may be added to the release layer of the present invention as long as the effect of the present invention is not impaired. In order to improve the adhesion to the substrate, it is also preferable that the surface of the polyester film is subjected to a pretreatment such as anchor coating, a corona treatment, a plasma treatment, or an atmospheric pressure plasma treatment before providing the release layer.

[0058]

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 layer after curing is preferably 0.2 to 3.5 μm , and more preferably 0.5 to 3.0 μm . When the thickness of the release layer is 0.2 μm or more, the curability of the energy ray-curable copolymer is good to provide an improved elastic modulus of the release layer, whereby good peelability can be obtained, which is preferable. When the thickness of the release layer is 3.5 μm or less, curling is less likely to occur even when the release film is thin,

so that no traveling performance defects occur in the process of forming and drying the ceramic green sheet, which is preferable.

[0059]

In the release film of the present invention, it is preferable that the release layer surface has appropriate unevenness. Therefore, the average area surface roughness (Sa) of the release layer surface is preferably 5 to 40 nm. It is more preferable that the Sa is satisfied and the maximum protrusion height (Rp) of the release layer surface is 60 nm or less. The average area surface roughness (Sa) is preferably 5 to 20 nm, and simultaneously, the maximum protrusion height (Rp) is more preferably 50 nm or less. The average area surface roughness (Sa) is particularly preferably 8.1 to 18 nm, and most preferably 8.5 to 17 nm. When the average area surface roughness (Sa) is 5 nm or more, zipping is reduced when the ceramic green sheet is peeled off, whereby even the super-thin green sheet can be easily peeled off without being damaged. When the average area surface roughness (Sa) is 40 nm or less, the average area surface roughness (Sa) is sufficiently smaller than the particle size of the ceramic, and does not affect the surface shape of the green sheet. When the Sa is satisfied and the maximum protrusion height (Rp) of the release layer surface is 60 nm or less, pinhole defects occur with less

probability, which is preferable. The maximum protrusion height (R_p) is preferably small, but in order to adjust the average area surface roughness (S_a) to 5 nm or more, the maximum protrusion height (R_p) may also be 5 nm or more, or 10 nm or more. In order to adjust the average area surface roughness (S_a) and the maximum protrusion height (R_p) of the release layer as described above, various factors are involved. However, mainly, the surface layer A of the polyester film or the single-layer polyester film does not substantially contain inorganic particles, so that the followings are said to be related: the roughness of the surface on which the release layer is laminated is small; and the release layer contains the energy ray-curable compound (I) having 3 or more reactive groups in one molecule and serving as a sea component, and the resin (II) incompatible with the energy ray-curable compound (I) and serving as an island component, and is obtained by curing. The method for adjusting the average area surface roughness (S_a) and the maximum protrusion height (R_p) of the release layer to the appropriate range as described above is not particularly limited. However, mainly, the method can be preferably achieved by adjusting the combination of materials of the energy ray-curable compound (I) and the resin (II) and the content ratios thereof.

[0060]

In the present invention, the method for forming the release layer is not particularly limited, and the following method is used. A coating solution in which a release compound is dissolved or dispersed is spread on one surface of the polyester film of the substrate by coating and the like. A solvent or the like is removed by drying, followed by curing.

[0061]

A drying temperature for solvent drying when the release layer of the present invention is applied on the substrate film by solution application is preferably 50°C or higher and 120°C or lower, and more preferably 60°C or higher and 100°C or lower. A heating time is preferably 30 seconds or less, and more preferably 20 seconds or less. Furthermore, after the solvent drying, the irradiation of active energy rays preferably advances the curing reaction. As the energy rays used at this time, ultraviolet rays, electron beams, and X-rays and the like can be used, but ultraviolet rays are likely to be used, which are preferable. The amount of light of ultraviolet rays with which the composition is irradiated is preferably 30 to 300 mJ/cm², and more preferably 30 to 200 mJ/cm².

By setting the amount of light to 30 mJ/cm² or more, the curing of the composition is sufficiently advanced, and by setting the amount of light to 300 mJ/cm² or less, the

speed during processing can be improved, whereby the release film can be economically prepared, which is preferable.

[0062]

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

[0063]

As the coating method of the coating solution, any known coating 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.

EXAMPLES

[0064]

Hereinafter, the present invention will be described in 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. Hereinafter, a weight average molecular weight may be simply described as Mw.

[0065]

(1) (Thickness of substrate film)

Using Millitron (electronic microindicator), four 5 cm square samples were cut from any four locations on a film to be measured. 5 points per sample (total: 20 points) were measured, and the average value thereof was taken as a thickness.

[0066]

(2) Thickness of release layer

The thickness of the release layer was measured using an optical interference type film thickness meter (F20 manufactured by Filmetrics Co., Ltd.). (the refractive index of the release layer was calculated as 1.52)

[0067]

(3) Average area surface roughness (Sa), maximum protrusion height (Rp)

Area surface roughness (Sa) and a maximum protrusion height (Rp) are represented by values measured under the following conditions using a non-contact surface shape measurement system (VertScan R550H-M100 manufactured by Ryoka Systems Inc.). For the average area surface

roughness (Sa), the average value of five measurements was employed. For the maximum protrusion height (Rp), 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: 50 times
- 0.5 × Tube lens

(Analysis conditions)

- Surface correction: 4th correction
- Interpolation processing: Full interpolation

[0068]

(4) Surface unevenness due to phase-separated structure

Using an electron microscope (VE-8800 manufactured by KEYENCE CORPORATION), the surface of the release layer was observed at 5000 times, and the degree of the surface unevenness due to the phase-separated structure was evaluated.

Good: the unevenness structure due to phase separation can be confirmed

Poor: no unevenness structure due to phase separation cannot be observed

[0069]

(5) Half cut evaluation of ceramic green sheet

Compositions containing the following materials were stirred and mixed, and the mixture was dispersed for 60 minutes using a bead mill with 0.5 mm zirconia beads as a dispersion medium to prepare a ceramic slurry.

Toluene: 76.3 parts by mass

Ethanol: 76.3 parts by mass

Barium titanate (HPBT-1 manufactured by Fuji Titanium Industry Co., Ltd.): 35.0 parts by mass

Polyvinyl butyral: 3.5 parts by mass
(S-LEC (registered trademark) BM-S manufactured by Sekisui Chemical Co., Ltd.)

DOP (Dioctyl phthalate): 1.8 parts by mass

Next, the ceramic slurry was applied to the release surface of the release film sample using an applicator so that the dried ceramic green sheet had a size of 1.0 μm , and dried at 90°C for 2 minutes.

Using a rotary die cutter (R.D.C(FB)-A4 manufactured by Tsukatani Hamono Mfg. Co., Ltd.), the obtained release film with the ceramic green sheet was half cut so that a square of 16 mm $\times$ 32 mm and a depth of 3 μm were set with a double-edged blade of 50° from the surface side of the ceramic green sheet. Regarding a portion where the green sheet was peeled off by the half cut, a distance between a position where the peeling is reached and an end part where the film was half cut was measured with a laser microscope,

and determined according to the following criteria. Five measurements were performed, and the average value thereof was employed.

Good: no defects such as cracks in the end part, and a sufficient peeled part (indication: a distance in which peeling is reached is 4 mm or more from the end part)

Average: no defects such as cracks in the end part, and a slight peeled part (indication: a distance in which peeling is reached is 1 mm or more and less than 4 mm from the end part)

Poor: defects such as cracks in the end part, or no peeled part (indication: a distance in which peeling is reached is less than 1 mm from the end part)

[0070]

(6) Measurement of hydroxyl value

The hydroxyl value of the energy ray-curable compound (I) was measured by the following method. About 1 g of a sample was precisely weighed in a stoppered erlenmeyer flask, and 100 ml of a toluene/ethanol (volume ratio: toluene/ethanol = 2/1) mixed liquid was added thereto, followed by dissolving. Furthermore, 5 ml of an acetylating agent (a solution having a volume of 100 ml and obtained by dissolving 25 g of acetic anhydride in pyridine) was exactly added to the solution, followed by stirring for about 1 hour. Thereto, a phenolphthalein

reagent was added as an indicator, which was then kept for 30 seconds. Then, the solution was titrated with a 0.5 N alcoholic potassium hydroxide solution until the solution exhibited a faint red-pink color.

The hydroxyl value was calculated by the following formula. The hydroxyl value was taken as the numerical value of the dry state of the resin (unit: mgKOH/g).

$$\text{Hydroxyl value (mgKOH/g)} = \left[\frac{(b - a) \times F \times 28.05}{S} \right] / (\text{concentration of nonvolatile matter}/100)$$

S: Collection amount of sample (g)

a: Amount of consumption of 0.5 N alcoholic potassium hydroxide solution (ml)

b: Amount of consumption of 0.5 N alcoholic potassium hydroxide solution in blank experiment (ml)

F: Titer of 0.5 N alcoholic potassium hydroxide solution

[0071]

(Preparation of polyethylene terephthalate pellets (PET (1))

As an esterification reactor, a continuous esterification reactor including a three-stage complete mixing tank including a stirrer, a partial condenser, a raw material charging port, and a product outlet was used. The amount of terephthalic acid (TPA) was set to 2 tons/hour, and the amount of ethylene glycol (EG) 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 esterification reaction can of the esterification reactor, and reacted at normal pressure at 255°C for an average residence time of 4 hours. Next, the reaction product in the first esterification reaction can was continuously taken out of the system, and supplied to a second esterification reaction can. 8% by mass of EG distilled off from the first esterification reaction can with respect to produced PET was supplied into the second esterification reaction can. Furthermore, an EG solution containing magnesium acetate tetrahydrate set such that the amount of Mg atoms with respect to the produced PET was set to 65 ppm and an EG solution containing trimethyl phosphate (TMPA) 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. 0.2% by mass of porous colloidal silica having an average particle size of 0.9 μm and subjected to a dispersion treatment with the average number of treatments of 5 passes under pressure of 39 MPa (400 kg/cm²) using a

high pressure disperser (manufactured by Nippon Seiki Co., Ltd.), and 0.4% by mass of synthetic calcium carbonate having an average particle size of 0.6 μm and obtained by attaching 1% by mass of a polyacrylic acid ammonium salt per calcium carbonate were added 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 be 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 (1)). The content of the lubricant in the PET chip was 0.6% by mass.

[0072]

(Preparation of polyethylene terephthalate pellets (PET (2)))

Meanwhile, in the production of the PET chip, a PET chip having an intrinsic viscosity of 0.62 dl/g and being free of a particle made of calcium carbonate, silica or the like was obtained (hereinafter abbreviated as PET (2)).

[0073]

(Production of laminated film X1)

These PET chips were dried, then melted at 285°C, melted at 290°C by separate melt extruders, 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 (1) and the PET (2) were laminated such that the PET (1) was a surface layer B (opposite side layer to release surface) and the PET (2) 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 (1)/(2) = 60%/40% 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 longitudinal 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 2 nm, and Sa of the surface layer B was 29 nm.

[0074]

(Example 1)

A coating solution 1 having the following composition was applied on a surface layer A of a laminated film X1 using reverse gravure such that the thickness of a release layer after drying was set to 2.5 µm, dried at 90°C for 30 seconds, and then irradiated with ultraviolet rays of 200 mJ/cm² using a high pressure mercury lamp, to obtain a release film for production of a super-thin ceramic green sheet. The obtained release film was evaluated for the thickness of the release layer, average area surface roughness Sa, a maximum protrusion height Rp, surface unevenness due to a phase-separated structure, and a trigger for peeling of a ceramic green sheet during half cutting.

(Coating solution 1)

Compound (I): Dipentaerythritol hexaacrylate:

100.00 parts by mass

(NK ester manufactured by Shin-Nakamura Chemical Co., Ltd.

(registered trademark) A-DPH, hydroxyl value: 10 mgKOH/g, hexafunctional acrylate, solid content concentration: 100%)

Resin (II): Polyester resin: 9.45 parts by mass
(Vylon (registered trademark) RV280 manufactured by Toyobo Co., Ltd., solid content concentration: 100% by mass)

Release agent (III): 1.26 parts by mass
(Modified polydimethylsiloxane having acryloyl group, BYK-UV3505 manufactured by BYK Japan KK, solid content concentration: 40% by mass)

Photopolymerization initiator: 5.25 parts by mass

(OMNIRAD (registered trademark) 907 manufactured by IGM Japan GK, solid content concentration: 100% by mass)

Diluting solvent (MEK/toluene = 1/1): 431.30 parts by mass

[0075]

(Example 2)

The following coating solution 2 was used, in which the hydroxyl value of the compound (I) was set to be higher than that in Example 1. A release film was obtained in the same manner as in Example 1 except that the coating solution 2 was used. The obtained release film was evaluated for the thickness of a release layer, average area surface roughness S_a , a maximum protrusion height R_p , surface unevenness due to a phase-separated structure, and

a trigger for peeling of a ceramic green sheet during half cutting.

(Coating solution 2)

Compound (I): Dipentaerythritol hexaacrylate:

100.00 parts by mass

(Aronix (registered trademark) M-402 manufactured by Toagosei Co., Ltd., hydroxyl value: 30 mgKOH/g, hexafunctional acrylate, solid content concentration: 100%)

Resin (II): Polyester resin: 9.45 parts by mass

(Vylon (registered trademark) RV280 manufactured by Toyobo Co., Ltd., solid content concentration: 100% by mass)

Release agent (III): 1.26 parts by mass

(Modified polydimethylsiloxane having acryloyl group, BYK-UV3505 manufactured by BYK Japan KK, solid content concentration: 40% by mass)

Photopolymerization initiator: 5.25 parts by

mass

(OMNIRAD (registered trademark) 907 manufactured by IGM Japan GK, solid content concentration: 100% by mass)

Diluting solvent (MEK/toluene = 1/1): 431.30

parts by mass

[0076]

(Example 3)

In comparison with Example 1, the resin (II) was changed to a polyester urethane resin (Vylon (registered

trademark) UR1400 manufactured by Toyobo Co., Ltd., solid content concentration: 30% by mass), and the following coating solution 3 was used. The solid content concentration of the coating solution 3 was set to be less than that of the coating solution 1 of Example 1. The coating solution 3 was applied such that the thickness of a release layer after drying was set to 1.3 μm . A release film was obtained in the same manner as in Example 1 except that the coating solution 3 was used and the coating solution 3 was applied such that the thickness of the release layer after drying was set to 1.3 μm . The obtained release film was evaluated for the thickness of a release layer, average area surface roughness S_a , a maximum protrusion height R_p , surface unevenness due to a phase-separated structure, and a trigger for peeling of a ceramic green sheet during half cutting.

(Coating solution 3)

Compound (I): Dipentaerythritol hexaacrylate:

100.00 parts by mass

(NK ester manufactured by Shin-Nakamura Chemical Co., Ltd.

(registered trademark) A-DPH, hydroxyl value: 10 mgKOH/g, hexafunctional acrylate, solid content concentration: 100%)

Resin (II) Polyester urethane resin: 52.60 parts
by mass

(Vylon (registered trademark) UR1400 manufactured by Toyobo

Co., Ltd., solid content concentration: 30% by mass)

Release agent (III): 1.33 parts by mass

(Modified polydimethylsiloxane having acryloyl group, BYK-UV3505 manufactured by BYK Japan KK, solid content concentration: 40% by mass)

Photopolymerization initiator: 5.56 parts by mass

(OMNIRAD (registered trademark) 907 manufactured by IGM Japan GK, solid content concentration: 100% by mass)

Diluting solvent (MEK/toluene = 1/1): 998.32 parts by mass

[0077]

(Example 4)

The following coating solution 4 was used, in which the hydroxyl value of the compound (I) was set to be higher than that in Example 3. A release film was obtained in the same manner as in Example 1 except that the coating solution 4 was used. The obtained release film was evaluated for the thickness of a release layer, average area surface roughness Sa, a maximum protrusion height Rp, surface unevenness due to a phase-separated structure, and a trigger for peeling of a ceramic green sheet during half cutting.

(Coating solution 4)

Compound (I): Dipentaerythritol hexaacrylate:

100.00 parts by mass

(Aronix (registered trademark) M-402 manufactured by Toagosei Co., Ltd., hydroxyl value: 30 mgKOH/g, hexafunctional acrylate, solid content concentration: 100%)

Resin (II) Polyester urethane resin: 52.60 parts by mass

(Vylon (registered trademark) UR1400 manufactured by Toyobo Co., Ltd., solid content concentration: 30% by mass)

Release agent (III): 1.33 parts by mass
(Modified polydimethylsiloxane having acryloyl group, BYK-UV3505 manufactured by BYK Japan KK, solid content concentration: 40% by mass)

Photopolymerization initiator: 5.56 parts by mass

(OMNIRAD (registered trademark) 907 manufactured by IGM Japan GK, solid content concentration: 100% by mass)

Diluting solvent (MEK/toluene = 1/1): 998.32 parts by mass

[0078]

(Example 5)

The following coating solution 5 was used, in which the type of the release agent (III) was changed. A release film was obtained in the same manner as in Example 2 except that the coating solution 5 was used. The obtained release film was evaluated for the thickness of a release layer,

average area surface roughness Sa, a maximum protrusion height Rp, surface unevenness due to a phase-separated structure, and a trigger for peeling of a ceramic green sheet during half cutting.

(Coating solution 5)

Compound (I): Dipentaerythritol hexaacrylate:

100.00 parts by mass (Aronix (registered trademark) M-402 manufactured by Toagosei Co., Ltd., hydroxyl value: 30 mgKOH/g, hexafunctional acrylate, solid content concentration: 100%)

Resin (II): Polyester resin: 9.45 parts by mass (Vylon (registered trademark) RV280 manufactured by Toyobo Co., Ltd., solid content concentration: 100% by mass)

Release agent (III): 0.50 parts by mass (Polyether-modified siloxane, TSF4446 manufactured by Momentive performance materials inc., solid content concentration: 100% by mass)

Photopolymerization initiator: 5.25 parts by mass

(OMNIRAD (registered trademark) 907 manufactured by IGM Japan GK, solid content concentration: 100% by mass)

Diluting solvent (MEK/toluene = 1/1): 432.06 parts by mass

[0079]

(Example 6)

The following coating solution 6 was used, in which the type of the release agent (III) was changed. A release film was obtained in the same manner as in Example 1 except that the coating solution 6 was used. The obtained release film was evaluated for the thickness of a release layer, average area surface roughness Sa, a maximum protrusion height Rp, surface unevenness due to a phase-separated structure, and a trigger for peeling of a ceramic green sheet during half cutting.

(Coating solution 6)

Compound (I): Dipentaerythritol hexaacrylate:

100.00 parts by mass

(NK ester manufactured by Shin-Nakamura Chemical Co., Ltd. (registered trademark) A-DPH, hydroxyl value: 10 mgKOH/g, hexafunctional acrylate, solid content concentration: 100%)

Resin (II): Polyester resin: 9.45 parts by mass

(Vylon (registered trademark) RV280 manufactured by Toyobo Co., Ltd., solid content concentration: 100% by mass)

Release agent (III): 1.26 parts by mass

(Fluorine-based additive having acryloyl group, Megafac (registered trademark) RS-75 manufactured by DIC Corporation, solid content concentration: 40% by mass)

Photopolymerization initiator: 5.25 parts by mass

(OMNIRAD (registered trademark) 907 manufactured by IGM

Japan GK, solid content concentration: 100% by mass)

Diluting solvent (MEK/toluene = 1/1): 431.30

parts by mass

[0080]

(Comparative Example 1)

The following coating solution 7 was used, in which the hydroxyl value of the compound (I) was set to be higher than that in Example 2. A release film was obtained in the same manner as in Example 1 except that the coating solution 7 was used. The obtained release film was evaluated for the thickness of a release layer, average area surface roughness Sa, a maximum protrusion height Rp, surface unevenness due to a phase-separated structure, and a trigger for peeling of a ceramic green sheet during half cutting.

(Coating solution 7)

Compound (I): Dipentaerythritol hexaacrylate:

100.00 parts by mass

(NK ester manufactured by Shin-Nakamura Chemical Co., Ltd. (registered trademark) A-9550, hydroxyl value: 50 mgKOH/g, hexafunctional acrylate, solid content concentration: 100%)

Resin (II): Polyester resin: 9.45 parts by mass

(Vylon (registered trademark) RV280 manufactured by Toyobo Co., Ltd., solid content concentration: 100% by mass)

Release agent (III): 1.26 parts by mass

(Modified polydimethylsiloxane having acryloyl group, BYK-UV3505 manufactured by BYK Japan KK, solid content concentration: 40% by mass)

Photopolymerization initiator: 5.25 parts by mass

(OMNIRAD (registered trademark) 907 manufactured by IGM Japan GK, solid content concentration: 100% by mass)

Diluting solvent (MEK/toluene = 1/1): 431.30 parts by mass

[0081]

(Comparative Example 2)

The following coating solution 8 was used, in which the hydroxyl value of the compound (I) was set to be higher than that in Example 4. A release film was obtained in the same manner as in Example 1 except that the coating solution 8 was used. The obtained release film was evaluated for the thickness of a release layer, average area surface roughness Sa, a maximum protrusion height Rp, surface unevenness due to a phase-separated structure, and a trigger for peeling of a ceramic green sheet during half cutting.

(Coating solution 8)

Compound (I): Dipentaerythritol hexaacrylate:

100.00 parts by mass

(NK ester manufactured by Shin-Nakamura Chemical Co., Ltd.

(registered trademark) A-9550, hydroxyl value: 50 mgKOH/g, hexafunctional acrylate, solid content concentration: 100%)

Resin (II) Polyester urethane resin: 52.60 parts
by mass

(Vylon (registered trademark) UR1400 manufactured by Toyobo Co., Ltd., solid content concentration: 30% by mass)

Release agent (III): 1.33 parts by mass
(Modified polydimethylsiloxane having acryloyl group, BYK-UV3505 manufactured by BYK Japan KK, solid content concentration: 40% by mass)

Photopolymerization initiator: 5.56 parts by
mass

(OMNIRAD (registered trademark) 907 manufactured by IGM Japan GK, solid content concentration: 100% by mass)

Diluting solvent (MEK/toluene = 1/1): 998.32
parts by mass

[0082]

Figs. 1 to 6 show electron micrographs of the surfaces of the release layers of Examples 1 to 4 and Comparative Examples 1 and 2 used for evaluating the state of the surface unevenness of the release layer due to the phase-separated structure.

[0083]

[Table 1]

TYPE OF ENERGY RAY-CURABLE COMPOUND (I)	HYDROXYL VALUE [mgKOH/g]	NUMBER OF ACRYLOYL GROUPS
A-DPH (SHIN NAKAMURA CHEMICAL CO., LTD.)	10	6
M-402 (TOAGOSEI CO., LTD.)	30	6
A-9550 (SHIN NAKAMURA CHEMICAL CO., LTD.)	50	6

[0084]

[Table 2]

	POLYESTER FILM			COMPOSITION OF RELEASE LAYER											
	TYPE	THICKNESS (μm)	SURFACE ROUGHNESS OF SURFACE LAYER A Sa (nm)	RESIN (I)			RESIN (II)			RELEASE COMPONENT (III)			PHOTOPOLYMERIZATION INITIATOR		
				PRODUCT NAME	NUMBER OF PARTS OF COATING SOLUTION TO BE BLENDED (PARTS BY MASS)	BLENDING RATIO OF SOLID CONTENT (% BY MASS)	PRODUCT NAME	NUMBER OF PARTS OF COATING SOLUTION TO BE BLENDED (PARTS BY MASS)	BLENDING RATIO OF SOLID CONTENT (% BY MASS)	PRODUCT NAME	NUMBER OF PARTS OF COATING SOLUTION TO BE BLENDED (PARTS BY MASS)	BLENDING RATIO OF SOLID CONTENT (% BY MASS)	PRODUCT NAME	COATING SOLUTION BLENDING NUMBER OF PARTS (PARTS BY MASS)	SOLID CONTENT BLENDING RATIO (% BY MASS)
EXAMPLE 1	X1	31	2	A-DPH	100	86.8	VYLON RV280	9.45	8.2	BYK-UV3505	1.26	0.4	OMNIRAD 907	5.25	4.6
EXAMPLE 2	X1	31	2	M-402	100	86.8	VYLON RV280	9.45	8.2	BYK-UV3505	1.26	0.4	OMNIRAD 907	5.25	4.6
EXAMPLE 3	X1	31	2	A-DPH	100	82.1	VYLON UR1400	52.6	12.9	BYK-UV3505	1.33	0.4	OMNIRAD 907	5.56	4.6
EXAMPLE 4	X1	31	2	M-402	100	82.1	VYLON UR1400	52.6	12.9	BYK-UV3505	1.33	0.4	OMNIRAD 907	5.56	4.6
EXAMPLE 5	X1	31	2	M-402	100	86.8	VYLON RV280	9.45	8.2	TSF4446	0.50	0.4	OMNIRAD 907	5.25	4.6
EXAMPLE 6	X1	31	2	A-DPH	100	86.8	VYLON RV280	9.45	8.2	MegaFac RS-75	1.26	0.4	OMNIRAD 907	5.25	4.6
COMPARATIVE EXAMPLE 1	X1	31	2	A-9550	100	86.8	VYLON RV280	9.45	8.206	BYK-UV3505	1.26	0.4	OMNIRAD 907	5.25	4.6
COMPARATIVE EXAMPLE 2	X1	31	2	A-9550	100	82.1	VYLON UR1400	52.6	12.9	BYK-UV3505	1.33	0.4	OMNIRAD 907	5.56	4.6

· VYLON RV280, AMORPHOUS POLYESTER RESIN MANUFACTURED BY TOYOBO CO., LTD.,

SOLID CONTENT: 100% BY MASS

· VYLON UR1400, POLYESTER URETHANE RESIN MANUFACTURED BY TOYOBO CO., LTD.,

SOLID CONTENT: 30% BY WEIGHT

[Table 2] (continued)

	EVALUATION RESULTS					
	RELEASE LAYER				HALF CUT EVALUATION OF CERAMIC GREEN SHEET	
	FILM THICKNESS (μm)	CONFIRMATION OF SURFACE UNEVENNESS WITH MICROSCOPE	SURFACE ROUGHNESS S_a (nm)	MAXIMUM PROTRUSION HEIGHT R_p (nm)	DETERMINATION	DISTANCE IN WHICH PEELING IS REACHED (mm)
EXAMPLE 1	2.5	GOOD	14.8	48.5	GOOD	5.6
EXAMPLE 2	2.5	GOOD	10.6	38.0	GOOD	5.8
EXAMPLE 3	1.3	GOOD	11.0	63.8	GOOD	6.5
EXAMPLE 4	1.3	GOOD	8.1	42.9	GOOD	4.7
EXAMPLE 5	2.5	GOOD	10.0	36.1	GOOD	5.2
EXAMPLE 6	2.5	GOOD	13.4	46.7	GOOD	5.8
COMPARA TIVE EXAMPLE 1	2.5	POOR	1.3	25.2	POOR	0.6
COMPARA TIVE EXAMPLE 2	1.3	POOR	2.5	13.9	POOR	0.8

Industrial Applicability

[0085]

A release film for production of a ceramic green sheet of the present invention has a peeling force which is not much heavier than that of a conventional release film for production of a ceramic green sheet, has excellent processability, and has no large protrusions in a release layer, whereby the release film for production of a ceramic green sheet can be provided, which can reduce defects such as pinholes in a formed super-thin ceramic green sheet having a thickness of 1 μm or less.

CLAIMS

1. A release film for production of a ceramic green sheet,

the release film comprising:

a polyester film; and

a release layer laminated on at least one surface of the polyester film directly or with another layer interposed therebetween,

wherein:

the release layer is formed by curing a coating film containing at least an energy ray-curable compound (I), a polyester resin or a polyester urethane resin (II), and a release component (III); and

the energy ray-curable compound (I) has a hydroxyl value of 45 mgKOH/g or less.

2. The release film for production of a ceramic green sheet according to claim 1, wherein the release layer has a phase-separated structure containing the energy ray-curable compound (I) as a sea component and the polyester resin or the polyester urethane resin (II) as an island component, and has surface unevenness.

3. The release film for production of a ceramic

green sheet according to claim 1 or 2, wherein the release layer does not substantially contain inorganic particles.

4. The release film for production of a ceramic green sheet according to any one of claims 1 to 3, wherein the energy ray-curable compound (I) is a (meth) acrylic acid ester having 3 or more acryloyl groups in one molecule.

5. The release film for production of a ceramic green sheet according to any one of claims 1 to 4, wherein the release layer has a thickness of 0.2 to 3.5 μm .

6. The release film for production of a ceramic green sheet according to any one of claims 1 to 5, wherein the release layer has average area surface roughness (S_a) of 5 to 40 nm.

7. The release film for production of a ceramic green sheet according to any one of claims 1 to 6, wherein the release film has a release layer surface having a maximum protrusion height (R_p) of 60 nm or less.

8. A method for producing a ceramic green sheet, the method comprising forming the ceramic green sheet using

the release film for production of a ceramic green sheet according to any one of claims 1 to 7, wherein the formed ceramic green sheet has a thickness of 0.2 μm to 1.0 μm .