

DESCRIPTION

TITLE OF THE INVENTION: RELEASE FILM

TECHNICAL FIELD

[0001]

The present invention relates to a release film. More specifically, the present invention relates to a release film that can be prepared at low production cost, and have both good wettability of a slurry or a resin-dissolved solution and an appropriate sheet peeling force even when the sheet to be formed on a release layer is further thinned. For example, the release film is particularly preferably used for the production application of a ceramic green sheet that is an intermediate product in the producing step of a ceramic multilayer capacitor.

BACKGROUND ART

[0002]

A release film is a member used for uniformly forming and peeling off a sheet to be peeled off without causing damage. Examples of the sheet include a ceramic green sheet, a sheet containing other particles and a resin, or a resin sheet.

[0003]

The release film is produced by mainly using off-line

coating in which a solvent-based release formulation is coated on a substrate film obtained in a film forming step in a separate step (see, for example, Patent Document 1). However, in such a conventional technique, a film forming step and a release layer processing step of a film substrate are separately performed, which causes a cost increase.

[0004]

Therefore, techniques for preparing a release film by coating a water-based release formulation according to in-line coating during the film forming step are disclosed (see, for example, Patent Documents 2 and 3). However, in the conventional techniques, a main resin of the water-based release formulation is a silicone resin, which causes too low surface free energy. When the sheet is further thinned, poor wettability of a slurry or a resin-dissolved solution disadvantageously causes pinholes to occur.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0005]

Patent Document 1: JP-A-2010-155459

Patent Document 2: JP-A-2010-017932

Patent Document 3: JP-A-2013-208810

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006]

The present invention has been made in view of the problems of the conventional techniques. That is, it is an object of the present invention to provide a release film that can be prepared at low production cost, and have both good wettability of a slurry and a resin-dissolved solution for a sheet and an appropriate sheet peeling force even when the sheet to be formed on a release layer is further thinned.

MEANS FOR SOLVING THE PROBLEMS

[0007]

As a result of intensive studies to achieve the above object, the present inventors have completed the present invention. That is, the present invention has the following configurations.

1. A release film including: a polyester film; and a release layer, wherein: the release film includes the release layer provided on at least one surface of the polyester film directly or with other layer therebetween; and the release layer is obtained by curing a composition containing an acrylic resin having a long-chain alkyl group and at least one cross-linking agent selected from an

oxazoline-based cross-linking agent or a carbodiimide-based cross-linking agent.

2. The release film according to the above 1, wherein: the acrylic resin contains a long-chain alkyl group-containing acrylate monomer; and a copolymerization ratio of the long-chain alkyl group-containing acrylate monomer in the acrylic resin is 5 mol% or more and 60 mol% or less.

3. The release film according to the above 1 or 2, wherein: the cross-linking agent is the oxazoline-based cross-linking agent; and the oxazoline-based cross-linking agent contains 3.0 to 9.0 mmol/g of an oxazoline group.

4. The release film according to any one of the above 1 to 3, wherein the acrylic resin having the long-chain alkyl group has an acid value of 40 mgKOH/g or more and 400 mgKOH/g or less.

5. The release film according to any one of the above 1 to 4, wherein the release layer has a thickness of 0.001 μm or more and 2 μm or less.

6. The release film according to the above 1 to 5, wherein the release film is a release film for production of a ceramic green sheet.

7. A method for production of a release film comprising a polyester film and a release layer,

Wherein the release film includes the release layer

provided on at least one surface of the polyester film directly or with other layer therebetween;

the release layer is obtained by curing a composition containing an acrylic resin having a long-chain alkyl group and at least one cross-linking agent selected from an oxazoline-based cross-linking agent or a carbodiimide-based cross-linking agent; and

the method includes:

coating a release coating solution on a film being an un-stretched film or a uniaxially stretched film;

then stretching the film in at least a uniaxial direction in which the film is un-stretched; and

heat-treating the film.

8. The method for production of a release film according to the above 7, wherein the method is a method for production of a release film for production of a ceramic green sheet.

9. A method for production of a ceramic green sheet, wherein the ceramic green sheet is formed by using the release film for production of a ceramic green sheet according to the above 6 or the method for production of a release film for production of a ceramic green sheet according to the above 8.

10. The method for production of a ceramic green sheet according to the above 9, wherein the ceramic green

sheet to be produced has a thickness of 0.2 μm or more and 2.0 μm or less.

11. A method for production of a ceramic capacitor, wherein the method for production of a ceramic green sheet according to the above 9 or 10 is employed.

EFFECT OF THE INVENTION

[0008]

The present invention can provide a release film that can be prepared at low production cost, and have both good wettability of a slurry and a resin-dissolved solution for a sheet and an appropriate sheet peeling force even when the sheet to be formed is further thinned.

MODE FOR CARRYING OUT THE INVENTION

[0009]

Hereinafter, the present invention will be described in detail.

A release film of the present invention is preferably a release film including a release layer provided on at least one surface of a polyester film that is a substrate film. The polyester film is preferably a biaxially-oriented polyester film.

[0010]

In the present invention, the release layer is

obtained by curing a composition containing a resin having a long-chain alkyl group and at least one cross-linking agent selected from an oxazoline-based cross-linking agent or a carbodiimide-based cross-linking agent.

The hardness of the release layer according to the present invention is appropriately high, and the surface free energy of the release layer is in a predetermined range, whereby a good peeling force can be obtained.

[0011]

(Polyester film)

Polyester constituting the polyester film used as a substrate in the present invention is not particularly limited, and is polyester usually used generally as a release film substrate. 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 preferably polyethylene terephthalate, polyethylene-2,6-naphthalate, polybutylene terephthalate, or polytrimethylene terephthalate. The polyester may be a copolymer containing constituent components of these resins as main components. In particular, 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 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.

[0012]

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.

[0013]

In a method for production of a polyester film in the present invention, 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. In the present invention, it is preferable to use a so-called in-line coating method in which the release layer is applied in a polyester film producing step.

[0014]

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 longitudinal and transverse directions.

[0015]

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, there is no fear of the deformation of

the film due to heat during the production of the film, the processing step of the release layer, and the forming step of the 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.

[0016]

The polyester film substrate may be a single layer or a multilayer including two or more layers. For example, the polyester film substrate preferably includes a surface layer A substantially containing no 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 substantially containing no inorganic particles. As a laminated structure, a layer onto which the release layer is applied (laminated) 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 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. The surface layer B may contain no

particles. In that case, a coat layer 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.

[0017]

In the polyester film substrate of the present invention, the average area surface roughness (S_a) of the surface layer A is preferably 10 nm or less, and more preferably 7 nm or less. When S_a is 10 nm or less, pinholes and the like are less likely to occur when super-thin layer sheets to be laminated are formed, which are preferable. When S_a is 7 nm or less, pinholes and the like are further less likely to occur when super-thin layer sheets to be laminated are formed, which are preferable. The average area surface roughness (S_a) of the surface layer A is preferably smaller. For example, the average area surface roughness (S_a) of the surface layer A is 0.1 nm or more.

In one embodiment, the average area surface roughness (S_a) of the surface layer A is 0.1 nm or more and 10 nm or less, is, for example, 0.1 nm or more and 7 nm or less, may be 0.1 nm or more and 5 nm or less, or may be 0.5 nm or more and 3 nm or less.

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 (Sa) 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 the inorganic particles is 50 ppm or less, preferably 10 ppm or less, and most preferably equal to or less than the detection limit when an inorganic element is quantified by fluorescent X-ray analysis. This is because, even if the 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 steps may be peeled off, and mixed into the film.

[0018]

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. When the total content of silica particles and/or calcium carbonate

particles is 5000 ppm 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 layer sheet. When the total content of silica particles and/or calcium carbonate particles is 15000 ppm 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 layer sheet to be produced is stable, which is preferable.

[0019]

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. At this time, the average area surface roughness (S_a) 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 (S_a) is in a range of 5 to 35 nm. When the S_a 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 layer sheet. When 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 layer sheet to be produced is stable, which is preferable.

[0020]

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.

[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. When the average particle size is 2.0 μm or less, there is no fear of the occurrence of pinholes in the sheet due to coarse particles on the release layer surface, which is preferable.

[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 diameters.

[0023]

It is preferable that, when the surface layer B does not contain particles, a coat layer containing particles on the surface layer B is formed to have slipperiness. The coat layer is not particularly limited, and the coat layer is preferably provided by in-line coating in which the coat layer is coated during the formation of the polyester film. When the surface layer B does not contain particles and a coat layer containing particles is provided on the surface layer B, the surface of the coat layer preferably has average area surface roughness (S_a) of 1 to 40 nm for the same reason as that of the above-mentioned average area

surface roughness (Sa) of the surface layer B. More preferably, the average area surface roughness (Sa) is in a range of 5 to 35 nm.

[0024]

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.

[0025]

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 Sa 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.

[0026]

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 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.

[0027]

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

[0028]

(Release layer)

The release film of the present invention preferably includes a release layer provided on one surface of the polyester substrate film as described above.

The release layer is a layer obtained by curing a composition containing an acrylic resin having a long-chain alkyl group and at least one cross-linking agent selected from an oxazoline-based cross-linking agent and a

carbodiimide-based cross-linking agent.

The release film of the present invention including such a release layer can be prepared at low production cost. Furthermore, the release film of the present invention can have both good wettability of a slurry or a resin-dissolved solution for a sheet and an appropriate sheet peeling force even when the sheet is further thinned.

For example, the release layer preferably contains at least a binder resin, a cross-linking agent, and an additive.

The release layer is a layer formed by applying the composition containing a resin and a cross-linking agent according to the present invention, and may also be referred to as a release coating layer.

[0029]

(Binder resin in release layer)

[0030]

An acrylic resin is preferably contained as the binder resin constituting the release layer in the present invention. The acrylic resin is preferably an acrylic resin having at least one selected from the group consisting of a hydroxyl group, a carboxyl group, and a long-chain alkyl group in its molecule. In one embodiment, the acrylic resin is an acrylic resin having a long chain alkyl group. In the present specification, these acrylic

resins may be simply referred to as an acrylic resin.

Structural units having a hydroxyl group are more preferably contained in an amount of 5 to 90 mol% in 100 mol% of all structural units. If the amount of the structural units having a hydroxyl group is 5 mol% or more, the water solubility of the acrylic resin can be moderately kept, which is preferable. Meanwhile, when the amount is 90 mol% or less, the hydroxyl group of the acrylic resin and the particles contained in the release layer cause no extreme interaction to provide the uniform dispersion of the particles, which is preferable.

In one embodiment, the amount of the structural units having a hydroxyl group is 5 to 50 mol%, and for example 5 to 45 mol in 100 mol% of all structural units.

[0031]

In order to introduce the hydroxyl group into the acrylic resin, monomers having a hydroxy group such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, and 4-hydroxybutyl(meth)acrylate, and a ring-opening adduct of γ -butyrolactone or ϵ -caprolactone to 2-hydroxyethyl(meth)acrylate, and the like may be used as a copolymerization component. Among these, 2-hydroxyethyl(meth)acrylate is preferable since 2-hydroxyethyl(meth)acrylate does not inhibit water solubility. These may be used in combination of two or

more thereof.

[0032]

The hydroxyl value of the acrylic resin is preferably 2 mgKOH/g or more, more preferably 5 mgKOH/g or more, and still more preferably 10 mgKOH/g or more. If the hydroxyl value of the acrylic resin is 2 mgKOH/g or more, the water solubility of the acrylic resin is good, which is preferable.

[0033]

The hydroxyl value of the acrylic resin is preferably 250 mgKOH/g or less, more preferably 230 mgKOH/g or less, and still more preferably 200 mgKOH/g or less. If the hydroxyl value of the acrylic resin is 250 mgKOH/g or less, the hydroxyl group of the acrylic resin and the particles contained in the release layer cause no extreme interaction to provide the uniform dispersion of the particles, which is preferable.

[0034]

The acrylic resin used in the present invention may contain a resin having a hydroxyl group. The acrylic resin may also contain a resin having a carboxyl group. In another embodiment, the acrylic resin may contain both a resin having a hydroxyl group and a resin having a carboxyl group. The acrylic resin has the carboxyl group, whereby a crosslinked structure with a cross-linking agent can be

formed, and water solubility can be easily imparted. Examples thereof include monomers containing carboxy groups such as (meth)acrylic acid, crotonic acid, itaconic acid, maleic acid, and fumaric acid, and monomers containing acid anhydride groups such as maleic anhydride and itaconic anhydride.

[0035]

The amount of the monomer having a carboxyl group is preferably 4 mol% or more, and more preferably 10 mol% or more in 100 mol% of all the structural units of the acrylic resin. When the amount is 4 mol% or more, it is easy to form a crosslinked structure in the release layer and to impart water solubility, which is preferable. The amount of the monomer having a carboxyl group is preferably 65 mol% or less, and more preferably 50 mol% or less. If the amount is 65 mol% or less, the Tg of a coating film to be obtained is not too high with respect to a suitable range to be described later, and film-forming properties and stretching suitability in in-line coating are good, which is preferable.

[0036]

In order to exhibit good water solubility, it is preferable to neutralize the carboxyl group introduced into the acrylic resin by the copolymerization of acrylic acid or methacrylic acid. Examples of basic neutralizing agents

include amine compounds such as ammonia, trimethylamine, triethylamine, and dimethylaminoethanol, and inorganic basic substances such as potassium hydroxide and sodium hydroxide. Among these, an amine compound is preferably used as the neutralizing agent for the ease of the volatilization of the neutralizing agent and the ease of the formation of the crosslinked structure. Among these, ammonia is most preferable because the aggregation of particles does not occur when the particles are contained in the release layer. A neutralization rate is preferably 30 mol% to 95 mol%, and more preferably 40 mol% to 90 mol%. When the neutralization rate is 30 mol% or more, the water solubility of the acrylic resin is sufficient; the acrylic resin is easily dissolved during the preparation of an applying solution; and there is no fear of blanching of the coating surface after drying, which is preferable. Meanwhile, when the neutralization rate is 95 mol% or less, the water solubility is not too high, and alcohol and the like is easily mixed during the preparation of the applying solution, which is preferable.

[0037]

The acid value of the acrylic resin is preferably, for example, 40 mgKOH/g or more, more preferably 50 mgKOH/g or more, and still more preferably 60 mgKOH/g or more. If the acid value of the acrylic resin is, for example, 40

mgKOH/g or more, the number of crosslinking points with the oxazoline cross-linking agent or the carbodiimide cross-linking agent increases, whereby a robust coating film having a higher crosslinking density can be obtained, which is preferable.

[0038]

The acid value of the acrylic resin is preferably, for example, 400 mgKOH/g or less, more preferably 350 mgKOH/g or less, and still more preferably 300 mgKOH/g or less.

In one embodiment, the acid value of the acrylic resin is 200 mgKOH/g or less, and is, for example, 150 mgKOH/g or less.

If the acid value of the acrylic resin is 400 mgKOH/g or less, the crosslinking density with the oxazoline cross-linking agent or the carbodiimide cross-linking agent is not too high, whereby cracks do not occur during stretching, which is preferable.

It is considered that such a tendency can be obtained even in an aspect in which the oxazoline cross-linking agent and the carbodiimide cross-linking agent are used in combination.

If the acid value of the acrylic resin is 400 mgKOH/g or less, the carboxyl group of the acrylic resin and the particles contained in the release layer cause no extreme

interaction to provide the uniform dispersion of the particles, which is preferable. If the dispersibility of the particles is good, coarse protrusions do not occur in the release coating surface, and no pinholes occur in a sheet, which is preferable.

In one embodiment, the acid value of the acrylic resin having a long chain alkyl group is 40 mgKOH/g or more and 400 mgKOH/g or less, and is, for example, 40 mgKOH/g or more and 300 mgKOH/g or less.

[0039]

The acrylic resin used in the present invention is preferably a resin having at least one selected from the group consisting of a hydroxyl group, a carboxyl group, and a long-chain alkyl group. The acrylic resin has the long-chain alkyl group, whereby the sheet peeling force can be made light, which is preferable. The acrylic resin having the long-chain alkyl group preferably has an alkyl group having 8 to 25 carbon atoms in the side chain of the acrylic resin, more preferably an alkyl group having 12 to 22 carbon atoms in the side chain of the acrylic resin, and still more preferably an alkyl group having 16 to 20 carbon atoms in the side chain of the acrylic resin.

A copolymer that is a polymer having a (meth)acrylic acid ester as a main repeating unit, and contains a long-chain alkyl group having 8 to 20 carbon atoms in a

transesterified portion can also be suitably used. Examples thereof include lauryl (meth)acrylate and stearyl (meth)acrylate. Among these, stearyl methacrylate is suitably used because of availability, cost, and a good peeling force.

For example, the acrylic resin used in the present invention is a resin formed by further using at least one selected from the group consisting of methyl methacrylate (MMA), hydroxyethyl methacrylate (HEMA), and methacrylic acid (MAA) in addition to stearyl methacrylate (SMA).

The release film of the present invention contains such an acrylic resin, whereby the release film does not have a too high crosslinking density between the acrylic resin and the oxazoline cross-linking agent or the carbodiimide cross-linking agent in the release layer, whereby cracks occurring in the release film when stretched can be suppressed.

Furthermore, the release film contains such an acrylic resin, whereby the release film can be prepared at low production cost. Furthermore, the release film of the present invention can have both good wettability of a slurry or a resin-dissolved solution for a sheet and an appropriate sheet peeling force even when the sheet is further thinned.

[0040]

The glass transition temperature (T_g) of the acrylic resin is preferably 50°C or higher, more preferably 55°C or higher, and still more preferably 60°C or higher. If the glass transition temperature of the acrylic resin is 50°C or higher, the hardness of the release layer becomes moderately high, which is preferable.

[0041]

The glass transition temperature (T_g) of the acrylic resin is preferably 110°C or lower, more preferably 105°C or lower, and still more preferably 100°C or lower. If the glass transition temperature of the acrylic resin is 110°C or lower, uniform stretching is provided without causing cracks to occur in the coating film in a stretching step after the release layer is coated, which is preferable.

[0042]

As a T_g adjusting monomer copolymerized to set the T_g to the above range, (meth)acrylic monomers and non-acrylic vinyl monomers can be utilized. Specific examples of the (meth)acrylic monomers include (meth)acrylic acid alkyl esters such as methyl(meth)acrylate, ethyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate, isobutyl(meth)acrylate, n-amyl(meth)acrylate, n-hexyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, n-octyl(meth)acrylate, decyl(meth)acrylate, dodecyl(meth)acrylate, cyclohexyl(meth)acrylate, and

isobornyl(meth)acrylate; nitrogen-containing acrylic monomers such as (meth)acrylamide, diacetone acrylamide, n-methylolacrylamide, and (meth)acrylonitrile; and vinyl methacrylate. One or two or more of the (meth)acrylic monomers can be used.

[0043]

Examples of the non-acrylic vinyl monomers include styrene-based monomers such as styrene, α -methylstyrene, vinyltoluene (a mixture of m-methylstyrene and p-methylstyrene), and chlorostyrene; vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl caproate, vinyl caprylate, vinyl caprate, vinyl laurate, vinyl myristate, vinyl palmitate, vinyl stearate, vinyl cyclohexanecarboxylate, vinyl pivalate, vinyl octylate, vinyl monochloroacetate, divinyl adipate, vinyl crotonate, vinyl sorbate, vinyl benzoate, and vinyl cinnamate; and vinyl halide monomers such as vinyl chloride and vinylidene chloride. One or two or more of the non-acrylic vinyl monomers can be used.

[0044]

The amount of the monomer having a long-chain alkyl group is preferably 60 mol% or less, and more preferably 50 mol% or less in 100 mol% of all the structural units of the acrylic resin. When the amount is 60 mol% or less, the T_g of the coating film to be obtained is not too low with

respect to a suitable range, and the hardness of the coating film can be highly maintained, which is preferable. The amount of the monomer having a long-chain alkyl group is preferably 5 mol% or more, and more preferably 15 mol% or more in 100 mol% of all the structural units of the acrylic resin. If the amount is 5 mol% or more, a decrease in surface free energy provides a light peeling force, which is preferable.

[0045]

It is preferable that, after the appropriate amounts of a hydroxyl group-containing monomer, a carboxyl group-containing monomer, and a long-chain alkyl group-containing monomer are determined, the Tg adjusting monomer is the remainder. The Tg of the copolymer is determined by the following Fox formula.

[0046]

[Equation 1]

$$\frac{1}{Tg} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2} + \dots + \frac{W_n}{Tg_n}$$

W_n : Mass fraction of each monomer (mass%)

Tg_n : Tg (K) of homopolymer of each monomer

[0047]

The acrylic resin used in the present invention can be obtained by known radical polymerization. Any of emulsion polymerization, suspension polymerization,

solution polymerization, and bulk polymerization and the like can be employed. From the viewpoint of handleability, the solution polymerization is preferable. Examples of water-soluble organic solvents that can be used for the solution polymerization include ethylene glycol n-butyl ether, isopropanol, ethanol, n-methylpyrrolidone, tetrahydrofuran, 1,4-dioxane, 1,3-oxolane, methyl cellosolve, ethyl cellosolve, ethyl carbitol, butyl carbitol, propylene glycol monopropyl ether, and propylene glycol monobutyl ether. These may be used in mixture with water.

[0048]

A polymerization initiator may be any known compound that generates radicals, but a water-soluble azo-based polymerization initiator such as 2,2-azobis-2-methyl-N-2-hydroxyethylpropionamide is preferable. The temperature and time and the like of the polymerization are appropriately selected.

[0049]

The mass average molecular weight (Mw) of the acrylic resin is preferably about 10,000 to 200,000. The range of the mass average molecular weight is more preferably 20,000 to 150,000. When the Mw is 10,000 or more, there is no fear of thermal decomposition in a tenter, which is preferable. If the Mw is 200,000 or less, the viscosity of

the applying solution does not significantly increase to provide good coating performance, which is preferable.

[0050]

As a binder of the release layer in the present invention, other binder resins may be used in combination in addition to the acrylic resin. Examples of the other binder resins include a polyester resin, an urethane resin, a polyvinyl-based resin (polyvinyl alcohol and the like), polyalkylene glycol, polyalkyleneimine, methylcellulose, hydroxycellulose, and starch.

[0051]

The content of the acrylic resin in the release layer is preferably 20 mass% or more and 95 mass% or less in the total solid content. The content is more preferably 30 mass% or more and 90 mass% or less. If the content is 20 mass% or more, the content of the carboxyl group as a crosslinking component is not too small, whereby the crosslinking density does not decrease, which is preferable. If the content is 95 mass% or less, the amount of the cross-linking agent to be crosslinked is not too small, whereby the crosslinking density does not decrease, which is preferable.

[0052]

(Cross-linking agent)

In the present invention, in order to form the

crosslinked structure in the release layer, the release layer preferably contains at least one cross-linking agent selected from an oxazoline-based cross-linking agent or a carbodiimide-based cross-linking agent. The inclusion of the oxazoline-based cross-linking agent or the carbodiimide-based cross-linking agent provides improvement in adhesion with a PET substrate and promotion of crosslinking of the acrylic resin with the carboxyl group to allow the coating film strength of the release layer to be improved. As a result, a light peeling force can be provided. Other cross-linking agents may be used in combination, and specific examples of the cross-linking agents that can be used in combination include urea-based, epoxy-based, melamine-based, isocyanate-based, and silanol-based cross-linking agents. In order to promote a crosslinking reaction, a catalyst and the like can be appropriately used as needed.

[0053]

Examples of the cross-linking agent having an oxazoline group include a polymer having an oxazoline group. The polymer is obtained by copolymerizing a polymerizable unsaturated monomer having an oxazoline group and other polymerizable unsaturated monomer as needed by a conventionally known method (for example, solution polymerization or emulsion polymerization or the like).

[0054]

Examples of the polymerizable unsaturated monomer having an oxazoline group include 2-vinyl-2-oxazoline, 2-vinyl-4-methyl-2-oxazoline, 2-vinyl-5-methyl-2-oxazoline, 2-isopropenyl-2-oxazoline, 2-isopropenyl-4-methyl-2-oxazoline, and 2-isopropenyl-5-ethyl-2-oxazoline. These monomers may be used alone or in combination of two or more thereof.

[0055]

Examples of the other polymerizable unsaturated monomer include alkyl or cycloalkyl esters of (meth)acrylic acid that each have 1 to 24 carbon atoms such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, cyclohexyl(meth)acrylate, lauryl(meth)acrylate, and isobornyl(meth)acrylate; hydroxyalkyl esters of (meth)acrylic acid that each have 2 to 8 carbon atoms such as 2-hydroxyethyl(meth)acrylate and hydroxypropyl(meth)acrylate; vinyl aromatic compounds such as styrene and vinyltoluene; (meth)acrylamide, dimethylaminopropyl(meth)acrylamide, dimethylaminoethyl(meth)acrylate, and any adduct of glycidyl(meth)acrylate and an amine; polyethylene glycol(meth)acrylate; and N-vinylpyrrolidone, ethylene, butadiene, chloroprene, vinyl propionate, vinyl acetate,

and (meth)acrylonitrile. These monomers may be used alone or in combination of two or more thereof.

[0056]

In order to render the obtained cross-linking agent having an oxazoline group a water-soluble cross-linking agent, the other polymerizable unsaturated monomer is preferably a hydrophilic monomer from the viewpoint of improvements in compatibility with other resins, wettability, and crosslinking reaction efficiency and the like. Examples of the hydrophilic monomer include 2-hydroxyethyl(meth)acrylate, methoxy polyethylene glycol(meth)acrylate, monomers each having a polyethylene glycol chain, such as a monoester compound made of (meth)acrylic acid and polyethylene glycol, 2-aminoethyl(meth)acrylate and salts thereof, (meth)acrylamide, N-methylol(meth)acrylamide, N-(2-hydroxyethyl)(meth)acrylamide, (meth)acrylonitrile, and sodium styrenesulfonate. Among these, preferred are methoxy polyethylene glycol(meth)acrylate, and monomers each having a polyethylene glycol chain, such as a monoester compound made of (meth)acrylic acid and polyethylene glycol, which have a high solubility in water.

[0057]

The cross-linking agent having an oxazoline group preferably has an oxazoline group content of 3.0 to 9.0

mmol/g. More preferably, the oxazoline group content is in a range of 4.0 to 8.0 mmol/g. If the oxazoline group content is in the range of 3.0 to 9.0 mmol/g, an appropriate crosslinked structure can be formed, and a light peeling force is provided, which is preferable. When the content of the oxazoline cross-linking agent is in the above range, an appropriate cross-linked structure with the acrylic resin can be formed, and no cracks occur during stretching, which is preferable.

[0058]

Examples of the carbodiimide-based cross-linking agent include a monocarbodiimide compound and a polycarbodiimide compound. Examples of the monocarbodiimide compound include dicyclohexylcarbodiimide, diisopropylcarbodiimide, dimethylcarbodiimide, diisobutylcarbodiimide, dioctylcarbodiimide, t-butylisopropylcarbodiimide, diphenylcarbodiimide, di-t-butylcarbodiimide, and di- β -naphthylcarbodiimide. As the polycarbodiimide compound, polycarbodiimide compounds produced by a conventionally known method can be used. For example, the polycarbodiimide compound can be produced by synthesizing an isocyanate-terminated polycarbodiimide in a condensation reaction involving decarboxylation of diisocyanate.

[0059]

Examples of the diisocyanate that is the synthetic raw material of the polycarbodiimide compound include isomers of toluylene diisocyanate, aromatic diisocyanates such as 4,4-diphenylmethane diisocyanate, aromatic aliphatic diisocyanates such as xylylene diisocyanate, alicyclic diisocyanates such as isophorone diisocyanate, 4,4-dicyclohexylmethane diisocyanate and 1,3-bis(isocyanatomethyl)cyclohexane, and aliphatic diisocyanates such as hexamethylene diisocyanate and 2,2,4-trimethylhexamethylene diisocyanate. From the problem of yellowing, the aromatic aliphatic diisocyanates, the alicyclic diisocyanates, and the aliphatic diisocyanates are preferable.

[0060]

The diisocyanate may be used as a molecule controlled to an appropriate degree of polymerization using a compound that reacts with a terminal isocyanate such as monoisocyanate. Examples of the monoisocyanate for blocking the terminals of the polycarbodiimide to control the degree of polymerization thereof include phenyl isocyanate, toluylene isocyanate, dimethylphenyl isocyanate, cyclohexyl isocyanate, butyl isocyanate, and naphthyl isocyanate. In addition, a compound having an OH group, -NH₂ group, a COOH group, or a SO₃H group can be used as a terminal blocking agent.

[0061]

The condensation reaction involving decarboxylation of diisocyanate proceeds in the presence of a carbodiimidization catalyst. Examples of the catalyst include phospholene oxides such as 1-phenyl-2-phospholene-1-oxide, 3-methyl-2-phospholene-1-oxide, 1-ethyl-2-phospholene-1-oxide, 3-methyl-1-phenyl-2-phosphorene-1-oxide, and 3-phospholene isomers, and 3-methyl-1-phenyl-2-phospholene-1-oxide is preferable from the viewpoint of reactivity. The amount of the catalyst used may be a catalyst amount.

[0062]

The mono or polycarbodiimide compound described above is desirably kept in a uniform dispersed state when blended with an aqueous coating material. For this purpose, the mono or polycarbodiimide compound emulsified with an appropriate emulsifier is preferably used as an emulsion, or the mono or polycarbodiimide compound is blended with a coating material in the form of a self-emulsified product or in the form of a self-dissolved product by adding a hydrophilic segment into the molecular structure of the polycarbodiimide compound.

[0063]

Examples of the carbodiimide-based cross-linking agent used in the present invention include water-

dispersible and water-soluble carbodiimide-based cross-linking agents. The water-soluble carbodiimide-based cross-linking agent is preferable since the cross-linking agent has good compatibility with other water-soluble resins and improves the crosslinking reaction efficiency of the release layer. The water-soluble carbodiimide compound can be produced by synthesizing an isocyanate-terminated polycarbodiimide in a condensation reaction involving decarboxylation of isocyanate, and thereafter adding a hydrophilic moiety having a functional group having reactivity with an isocyanate group.

[0064]

Examples of the hydrophilic moiety include (1) quaternary ammonium salts of dialkylamino alcohols and quaternary ammonium salts of dialkylaminoalkylamines, and the like, (2) alkyl sulfonates having at least one reactive hydroxyl group, and the like, and (3) poly(ethylene oxide) terminal-blocked with an alkoxy group, and a mixture of poly(ethylene oxide) and poly(propylene oxide). The carbodiimide compound becomes (1) cationic, (2) anionic, and (3) nonionic when the hydrophilic moiety is introduced. Among these, regardless of the ionicity of other water-soluble resin, a compatible nonionic carbodiimide compound is preferable.

[0065]

The content of the cross-linking agent in the release layer is preferably 5 mass% or more and 80 mass% or less in the total solid content. The content is more preferably 10 mass% or more and 70 mass% or less. If the content is 5 mass% or more, the crosslinking density of the resin of the applying layer does not decrease, which is preferable. If the content is 80 mass% or less, the amount of the carboxyl groups of the acrylic resin to be crosslinked is not too small, whereby the crosslinking density does not decrease, which is preferable.

[0066]

(Particles in release layer)

The release layer may contain lubricant particles in order to control the peeling force of a sheet peeling starting point part and a peeling force during steady peeling, and to impart slipperiness to the surface. 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 particles, 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.

[0067]

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.

[0068]

The average particle size of the particles is preferably 500 nm or less, more preferably 400 nm or less, and still more preferably 300 nm or less. If the average particle size of the particles is 500 nm or less, pinholes are less likely to occur during sheet processing, and the particles do not fall off, which is preferable.

[0069]

In a method for measuring the average particle size

of particles, the particles in the cross section of the processed film are observed with a transmission electron microscope or a scanning electron microscope, and the 100 particles that do not aggregate are observed. The average value of the particle sizes of the particles is determined as the average particle size.

[0070]

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 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 π , calculating the square root, and doubling the value of the square root.

[0071]

The ratio of the particles to the total solid content of the release layer is preferably 50 mass% or less, more preferably 30 mass% or less, and still more preferably 10 mass% or less. If the ratio of the particles to the total solid content of the release layer is 50 mass% or less, pinholes are less likely to occur during sheet processing, and the falling-off of the particles from the release layer does not significantly occur, which is preferable. The

ratio may be 0 mass%.

[0072]

As a method for measuring the content rate of particles contained in a release layer, for example, the following method can be used when the release layer contains an organic component resin and inorganic particles. First, a release layer provided on a processed film is extracted from the processed film using a solvent or the like, and dried to take out the release layer. Next, only an inorganic component can be obtained by applying heat to the obtained release layer and burning off an organic component contained in the release layer with heat. By measuring the weights of the obtained inorganic component and the release layer before burning off, the mass% of the particles contained in the release layer can be measured. At this time, the measurement can be performed with high accuracy by using a commercially available differential heat-thermogravimetric simultaneous measurement device. The ratio of the particles in the total solid content of the release layer means the ratio of the total amount of multiple types of existing particles.

[0073]

(Additive)

In the present invention, releasability can be exhibited by using the acrylic resin having a long-chain

alkyl group, but an additive may be added in order to further improve the releasability. As the additive used in the release layer, silicone-based additives and non-silicone-based additives such as olefin-based, long-chain alkyl-based and fluorine-based additives, and the like can be used. It is preferable to use the silicone-based additives from the viewpoint of peelability. The silicone-based additive used in the present invention is effective not only in improving the releasability but also in improving leveling properties during application and defoaming an applying solution.

[0074]

(Silicone-based additive in release layer)

In the present invention, the silicone-based additive used in the release layer is a compound having a silicone structure in its molecule, and is not particularly limited as long as the effects of the present invention can be obtained. Polyorganosiloxanes and the like can be suitably used. Among the polyorganosiloxanes, polydimethylsiloxane (abbreviation, PDMS) can be suitably used, and those having a functional group as a part of polydimethylsiloxane are also preferable. The polydimethylsiloxane has the functional group, whereby an intermolecular interaction such as a hydrogen bond with a binder resin is likely to be exhibited, to cause difficult transition of the component

to the sheet, which is preferable.

[0075]

The functional group introduced into polydimethylsiloxane is not particularly limited, and may be a reactive functional group or a non-reactive functional group. The functional group may be introduced into one terminal, both terminals, or a side chain of polydimethylsiloxane. The functional group may be introduced into one position or each of a plurality of positions.

[0076]

As the reactive functional group to be introduced into polydimethylsiloxane, an amino group, an epoxy group, a hydroxyl group, a mercapto group, a carboxyl group, a methacryl group, and an acrylic group and the like can be used. As the non-reactive functional group, a polyether group, an aralkyl group, a fluoroalkyl group, a long-chain alkyl group, an ester group, an amide group, and a phenyl group and the like can be used. Although not particularly bound by theory, those having an epoxy group, a carboxyl group, a polyether group, a methacryl group, an acrylic group, and an ester group are preferable.

[0077]

As the functional group to be introduced into the polydimethylsiloxane, a polyether group and an ester group

that do not react with the binder resin, is likely to be oriented on the surface of the release layer, and have less transition properties to the green sheet are preferable.

[0078]

The silicone-based additive used in the present invention preferably has a molecular weight of 40,000 or less. More preferably, the molecular weight is 30,000 or less. When the molecular weight is 40,000 or less, the silicone-based additive is likely to segregate on the surface of the release layer to provide good peelability, which is preferable.

[0079]

(Long-chain alkyl-based additive in release layer)

As the long-chain alkyl-based additive, a long-chain alkyl-modified resin can be used, and a long-chain alkyl-based additive having an alkyl group having about 8 to 20 carbon atoms in its side chain such as polyvinyl alcohol or an acrylic resin is preferable. A copolymer that is a polymer having a (meth)acrylic acid ester as a main repeating unit, and contains a long-chain alkyl group having 8 to 20 carbon atoms in a transesterified portion can also be suitably used. The releasability may be improved by using a long-chain alkyl-based additive that is different from the acrylic resin having a long-chain alkyl group as a base compound. Examples of commercially

available products include Peroyl (registered trademark)
406 (Lion Specialty Chemicals Co., Ltd.).

[0080]

(Other additives in release layer)

In order to impart other functionality to the release layer, various additives other than the silicone additive may be contained in the release layer as long as the applying appearance is not impaired. Examples of the additives include a fluorescent dye, a fluorescent whitener, a plasticizer, an ultraviolet absorbent, a pigment disperser, a foam-restraining agent, an anti-foaming agent, and a preservative.

[0081]

The release layer may contain an additive other than the silicone additive for the purpose of improving leveling properties during applying and defoaming the applying solution. The additive may be any of cationic, anionic, and nonionic additives and the like, but the additive is preferably an acetylene glycol-based or fluorine-based additive. These additives are preferably contained in the release layer as long as the abnormality of the applying appearance does not occur when the additives are excessively added.

[0082]

The amount of the additive used in the present

invention is preferably 20 mass% or less. When the amount of the additive is 20 mass% or less, the transition of the additive to the sheet does not excessively occur, which is preferable. The amount of the additive may be 0 mass%.

[0083]

As the applying method, any of a so-called in-line coating method in which an applying solution is simultaneously applied when a polyester substrate film is formed and a so-called off-line coating method in which a polyester substrate film is formed, and an applying solution is then separately applied with a coater can be applied. The in-line coating method is more efficient, and more preferable.

[0084]

A method for applying the applying solution to a polyethylene terephthalate (hereinafter sometimes abbreviated as PET) film may be any known method. Examples thereof include reverse roll-coating, gravure coating, kiss coating, die coating, roll brushing, spray coating, air knife coating, wire bar coating, pipe doctor, impregnation coating, and curtain coating methods. The applying is attained by using these methods alone or in combination.

[0085]

In the present invention, examples of a method for providing a release layer on a polyester film include a

method for applying an applying solution containing a solvent, particles, and a resin on a polyester film, and then drying the coating solution. Examples of the solvent include an organic solvent such as toluene, water, and a mixed solvent of water and a water-soluble organic solvent, but preferred is water alone, or a so-called water-based solvent of water and a water-soluble organic solvent from the viewpoint of environmental issues.

[0086]

The concentration of the solid content of the release coating solution is preferably 0.5 mass% or more, and more preferably 1 mass% or more, depending on the type of the binder resin and the type of the solvent, and the like. The concentration of the solid content of the applying solution is preferably 35 mass% or less, and more preferably 20 mass% or less. The release coating solution may be described as a release coating solution.

[0087]

A drying temperature after applying is also preferably 70°C or higher, and preferably 250°C or lower depending on the type of the binder resin, the type of the solvent, the presence or absence of the cross-linking agent, and the solid content concentration, and the like.

[0088]

In the case of in-line coating, a coating solution

may be coated on an un-stretched film before stretching in a longitudinal direction or may be coated on a uniaxially stretched film before stretching in a transverse direction after stretching in the longitudinal direction. When the coating solution is coated before stretching in the longitudinal direction, it is preferable to provide a drying step before roll stretching. When the coating solution is coated on the uniaxially stretched film before stretching in the transverse direction, a film heating step in the tenter can also serve as the drying step, so that it is not necessary to separately provide a drying step. The same applies to simultaneous biaxial stretching.

[0089]

The film thickness of the release layer is preferably 0.001 μm or more, more preferably 0.01 μm or more, still more preferably 0.02 μm or more, and particularly preferably 0.03 μm or more. If the film thickness of the release layer is 0.001 μm or more, the film-forming properties of the applying film are maintained to provide a uniform applying film, which is preferable.

[0090]

The film thickness of the release 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 applying layer is

2 μm or less, there is no fear of blocking, which is preferable.

[0091]

When the surface roughnesses of both surfaces of the substrate polyester film are different, the release layer may be laminated on any surface, but the surface roughness of the release surface to be obtained becomes smoother, whereby the release layer is preferably laminated on the smooth surface of the substrate.

[0092]

The outer surface of the film on which the release layer has been formed (the surface of the release layer of the entire applying film that is not brought into contact with the polyester film) is desirably flat so as not to cause defects in the sheet applied and formed thereon. It is preferable that the average area surface roughness (S_a) is 5 nm or less, and the maximum protrusion height (P) is 50 nm or less. More preferably, the average area surface roughness is 5 nm or less, and the maximum protrusion height is 40 nm or less. If the area surface roughness is 5 nm or less, and the maximum protrusion height is 50 nm or less, the defects such as pinholes do not occur when the sheet is formed, and the yield is good, which is preferable. It can be said that the average area surface roughness (S_a) 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.

In one embodiment, the average area surface roughness is less than 4.4 nm, and the maximum protrusion height is 40 nm or less. For example, the average area surface roughness is 4 nm or less, and the maximum protrusion height is 40 nm or less.

[0093]

The surface free energy of the release layer is preferably 45 mJ/m² or less, and more preferably 35 mJ/m² or less. When the surface free energy of the release layer is 45 mJ/m² or less, the peeling force of the sheet is light, which is preferable. The surface free energy of the release layer is preferably 20 mJ/m² or more, and more preferably 25 mJ/m² or more. When the surface free energy of the release layer is 20 mJ/m² or more, the peeling force of the sheet is not too light, and the cissing of the slurry and resin-dissolved solution is less likely to occur, which is preferable.

[0094]

(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.

[0095]

The release film of the present invention is particularly suitably used for producing such a multilayer ceramic capacitor. For example, the release film is produced 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. 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

[0096]

Next, the present invention will be described in detail with reference to Examples and Comparative Examples, but the present invention is naturally not limited to the following Examples. Evaluation methods used in the present invention are as follows.

[0097]

(NMR Measurement)

The ratio of a copolymer component introduced into an acrylic resin (for example, an acrylic polyol) was confirmed by using nuclear magnetic resonance spectrometry (^1H -NMR, ^{13}C -NMR: Varian Unity 400, manufactured by Agilent Technologies). The measurement was carried out by removing a solvent in the synthesized acrylic resin (acrylic polyol) with a vacuum dryer and then dissolving the dried product in deuterated chloroform. From the obtained NMR spectrum,

the peaks of chemical shifts δ (ppm) attributed to the moieties of groups were identified. The integrated intensity of each of the obtained peaks was obtained, and the composition ratio (mol%) of the copolymer component introduced into the acrylic resin (acrylic polyol) was confirmed from the number of hydrogens and integrated intensity of the moiety of each group.

[0098]

[Confirmation of Tg]

The Tg of each acrylic resin (acrylic polyol) was obtained from the composition ratio of the copolymer component obtained in the NMR measurement and the above-described Fox formula.

[0099]

(Stretching adequacy)

In order to evaluate the stretching adequacy of the acrylic resin (acrylic polyol) itself, the synthesized acrylic resins (acrylic polyols) (1) to (5) were charged into a mixed solvent (25°C) of 30 mass% of isopropanol and 70 mass% of water such that the solid content concentration was 12 mass%, to prepare a dissolved solution containing the acrylic resin (acrylic polyol) alone. Then, the dissolved solution was applied on the surface of the polyester film subjected to only longitudinal stretching with Mayer bar #5. Then, a film sample on which the

applying layer (thickness: 6.5 μm) has been formed was allowed to stand in a hot air circulating oven set at a temperature of 60°C for 30 seconds. Then, the film sample was taken out of the oven, and pre-dried. Then, the sample was set in a hand-turned stretching apparatus (manufactured by Toyobo Engineering Co., Ltd.). The stretching apparatus was placed in a hot air circulation oven at 100°C to slowly stretch the sample. The sample was stretched until the length was 4 times the length of the sample before stretching, and the stretching apparatus was taken out from the hot air circulation oven. Thereafter, the stretched coating film was observed with an optical microscope (magnification: 200 times), and the presence or absence of cracking due to stretching was determined according to the following criteria.

Good: No cracks are observed.

Moderate: Some cracks are observed (1 to 4).

Poor: 5 or more cracks, or cracks are observed in the entire surface.

[0100]

(Measurement of acid value)

About 0.2 g of a sample was precisely weighed in an Erlenmeyer flask with a side arm (A (g)), and 10 ml of benzyl alcohol was added thereto. The resin was dissolved by heating for 15 minutes with a heater at 230°C in a

nitrogen atmosphere. After naturally cooling to room temperature, 10 ml of benzyl alcohol, 20 ml of chloroform, and a few drops of a phenolphthalein solution were added thereto, and the solution was titrated with a 0.02 Normal KOH solution (titration amount=B (ml), titer of KOH solution=p). A blank measurement was similarly carried out (titration amount=C (ml)), and the acid value was calculated according to the following formula.

$$\text{Acid value (mg KOH/g)} = (B - C) \times 0.02 \times 56.11 \times p / A$$

[0101]

(Quantification of oxazoline group of resin having oxazoline group)

A resin having an oxazoline group was freeze-dried, and from ¹H-NMR analysis using a nuclear magnetic resonance analyzer (NMR) ("GEMINI-200", manufactured by Varian Inc.), the intensity of an absorption peak originating from the oxazoline group, and that of each of absorption peaks originating from the other monomers were obtained. From these peak intensities, the oxazoline group amount (mmol/g) was calculated.

[0102]

(Surface characteristics of applying film and unapplying substrate film)

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), the maximum value of five measurements was employed.

(Measurement conditions)

- Measurement mode: WAVE mode
- Objective lens: 50 times
- 0.5 × Tube lens
- Measurement area $187 \times 139 \mu\text{m}$ (S_a , P measurement)

[0103]

(Surface free energy)

Using a contact angle meter (automatic contact angle meter DM-701, manufactured by Kyowa Interface Science Co., Ltd.) under conditions of 25°C and 50% RH, droplets of water (droplet volume: 1.8 μL), diiodomethane (droplet volume: 0.9 μL), and ethylene glycol (droplet volume: 0.9 μL) were prepared on the release surface of the release film, and the contact angles thereof were measured. As the contact angle, a contact angle after 10 seconds from the dropping of each solution onto the release film was adopted. The contact angle data of water, diiodomethane, and ethylene glycol obtained by the above method were calculated from the "Kitasaki-Hata" theory to obtain the dispersion component γ_{sd} , polar component γ_{sp} , and hydrogen

bond component γ_{sh} of the surface free energy of the release film. The sum of the components was defined as the surface free energy γ_s . The present calculation was performed using calculation software in contact angle meter software (FAMAS).

[0104]

(Evaluation of pinholes of ceramic slurry)

The 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 to obtain a ceramic slurry.

Toluene: 38.3 parts by mass

Ethanol: 38.3 parts by mass

Barium titanate (HPBT-1, manufactured by Fuji Titanium Industry Co., Ltd.): 64.8 parts by mass

Polyvinyl butyral (S-LEK BM-S, manufactured by Sekisui Chemical Co., Ltd.): 6.5 parts by mass

DOP (dioctyl phthalate): 3.3 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 μm , and dried at 90°C for 1 minute to form a ceramic green sheet. 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 applying 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

Moderate: Almost no pinholes

Poor: Occurrence of a large number of pinholes

[0105]

(Evaluation of peelability of ceramic green sheet)

As with the evaluation of the coatability of the ceramic slurry, the ceramic slurry was applied such that the dried ceramic sheet had a thickness of 0.8 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.). 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 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 peeling 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 peeling forces was adopted for evaluation. Determination was made based on the following criteria from the obtained numerical values of the peeling forces.

Good: 3.5 mN/mm or less

Moderate: greater than 3.5 mN/mm and 6.0 mN/mm or less

Poor: Greater than 6.0 mN/mm

[0106]

(Evaluation of pinholes of resin sheet)

Three types of resin solutions for forming resin sheets were prepared using the following methods.

(Resin sheet (1))

A resin solution (1) was prepared by dissolving 0.5 parts by mass of a cyclic olefin resin (ARTON (registered trademark) G7810, manufactured by JSR Corporation, solid content: 100 mass%) in 80 parts by mass of toluene and 20 parts by mass of tetrahydrofuran.

The solution was coated on the release surface of the release film sample using an applicator such that the

thickness after drying was 0.5 μm , and dried at 100°C for 1 minute to form a cyclic olefin resin sheet. Next, the release film was peeled off from the release film including the formed cyclic olefin resin sheet to obtain a cyclic olefin resin sheet (1).

(Resin sheet (2))

10 parts by mass of an ion exchange resin (20% Nafion (registered trademark) 20 Dispersion Solution DE2021 CS type, manufactured by Wako Pure Chemical Industries, Ltd., solid content: 20 mass%), 10 parts by mass of water, and 20 parts by mass of isopropyl alcohol were mixed to prepare a resin solution (2). The solution was coated on the release surface of the release film sample using an applicator such that the thickness after drying was 0.5 μm , and dried at 100°C for 1 minute to form an ion exchange resin sheet. Next, the release film was peeled off from the release film including the formed ion exchange resin sheet to obtain an ion exchange resin sheet (2).

(Resin sheet (3))

20 parts by mass of a UV curable resin (urethane acrylate, product name: 8UX-015A, manufactured by Taisei Fine Chemical Co., Ltd., solid content: 100 mass%), 40 parts by mass of methyl ethyl ketone, 39 parts by mass of isopropyl alcohol, and 1 part by mass of an optical radical initiator (Irgacure (registered trademark) 907,

manufactured by BASF SE) were mixed to prepare a resin solution (3). The solution was coated on the release surface of the release film sample using an applicator such that the thickness after drying was 1.0 μm , dried at 90°C for 15 seconds, and then irradiated with ultraviolet rays at 300 mJ/cm² using a high-pressure mercury lamp, to form an ultraviolet curable resin sheet. Next, the release film was peeled off from the release film including the formed ultraviolet curable resin sheet to obtain an ultraviolet curable resin sheet (3).

All three types of the obtained resin sheets were evaluated by the following methods.

In the central region of the obtained resin sheet in the film transverse direction, light was applied from the opposite surface of the applying surface of the resin 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

Moderate: Almost no pinholes

Poor: Occurrence of a large number of pinholes

[0107]

(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 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 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 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 mass% of synthetic calcium carbonate having an average particle size of 0.6 μm and obtained by attaching 1 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 mass%.

[0108]

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

Meanwhile, in the production 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)).

[0109]

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

Meanwhile, a PET chip having an intrinsic viscosity of 0.62 dl/g was obtained (hereinafter abbreviated as PET (III)) in the same manner as in the production of the PET (I) chip except that particles made of calcium carbonate and silica and the like were changed to porous colloidal silica having an average particle size of 0.2 μm and synthetic calcium carbonate having an average particle size of 0.1 μm .

[0110]

(Production of acrylic resin (acrylic polyol) A-1)

103 parts by mass of methyl methacrylate (MMA), 173 parts by mass of stearyl methacrylate (SMA), 100 parts by mass of hydroxyethyl methacrylate (HEMA), 22 parts by mass of methacrylic acid (MAA), and 929 parts by mass of isopropyl alcohol (IPA) 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 0.5 parts by mass of 2,2-azobis-2-methyl-N-2-hydroxyethylpropionamide 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 decompression operation of 1.5 kPa was performed at 120°C to remove unreacted raw materials and solvent, thereby obtaining an acrylic resin (acrylic polyol). The inside of the flask was returned to atmospheric pressure, and cooled to room temperature. 1592 parts by mass of an IPA aqueous solution (water content: 50 mass%) was added and mixed. Thereafter, ammonia was added using a dropping funnel during stirring, and the acrylic resin (acrylic polyol) was neutralized until the pH of the solution was in a range of 5.5 to 7.5, to obtain an acrylic resin (acrylic polyol) (A-1) having a solid content concentration of 20 mass%. The composition ratio, Tg, stretching adequacy, and acid value of the acrylic resin (acrylic polyol) (A-1) as measured by NMR were also shown in Table 1.

[0111]

(Production of acrylic resins (acrylic polyols) (A-2) to (A-6))

As shown in Table 1, acrylic polyols (A-2) to (A-6) having a solid content concentration of 20 mass% were obtained in the same manner as in the production of the acrylic resin (acrylic polyol) 1 except that the amounts of MMA, SMA, HEMA, MAA, IPA during charging, and IPA aqueous solution during dilution were changed.

The composition ratio, Tg, stretching adequacy, and acid value of each of the acrylic resins (acrylic polyols) (A-2) to (A-6) as measured by NMR were also shown in Table 1. The composition ratios were expressed as n1 (unit) for MMA, n2 (unit) for SMA, n3 (unit) for HEMA, and n4 (unit) for MAA.

[0112]

[Table 1]

Number	Acrylic Resin Raw Material								
	n1		n2		n3		n4		Neutralizing Agent
	Material	Number of Parts to be Charged (parts by mass)	Material	Number of Parts to be Charged (parts by mass)	Material	Number of Parts to be Charged (parts by mass)	Material	Number of Parts to be Charged (parts by mass)	
A-1	MMA	103	SMA	173	HEMA	100	MAA	22	
A-2		231		130		100		33	NH3
A-3		38		0		100		11	NH3
A-4		231		1041		100		794	NH3
A-5		10		325		100		8	NH3
A-6		0		195		100		50	NH3

MMA Methyl Methacrylate

SMA Stearyl Methacrylate

HEMA Hydroxyethyl Methacrylate

MAA Methacrylic Acid

[Table 1] (continued)

Number	Solvent				Composition Ratio in Acrylic Resin (mol %)				Various Physical Properties		
	During Polymerization		During Dilution								
	Material	Number of Parts to be Charged (parts by mass)	Material	Number of Parts to be Charged (parts by mass)	n1	n2	n3	n4	Tg (°C)	Stretching Adequacy	Acid Value (mgKOH/g)
A-1	IPA	929	IPA Aqueous Solution	1592	40	20	30	10	73	Good	72
A-2		1153		1976	60	10	20	10	88	Good	87
A-3		349		598	30	0	60	10	66	Good	96
A-4		5052		8660	15	20	5	60	125	Moderate	478
A-5		1034		1772	5	50	40	5	46	Good	24
A-6		804		1379	0	30	40	30	71	Good	188

[0113]

(Production of oxazoline-based cross-linking agent C-1)

460.6 parts of isopropyl alcohol 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 causing nitrogen gas to gently flow thereinto. A monomer mixture prepared beforehand and containing 126 parts of methyl methacrylate, 210 parts of 2-isopropenyl-2-oxazoline, and 84 parts of methoxy polyethylene glycol acrylate, and an initiator solution prepared beforehand and containing 21 parts of 2,2'-azobis(2-methylbutyronitrile) ("ABN-E", manufactured by Japan Finechem Inc.) that was a polymerization initiator, and 189 parts of isopropyl alcohol, 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. During the reaction, nitrogen gas was caused to continuously flow, 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 (C-1) having a solid content concentration of 10% and having an oxazoline group. The oxazoline group amount of the obtained resin (C-1) having an oxazoline group was 7.7 mmol/g, and the number-average molecular weight thereof measured by GPC (gel permeation chromatography) was 40000.

[0114]

(Production of oxazoline-based cross-linking agent C-2)

A resin (C-2) having a different composition (oxazoline group amount and molecular weight), having a solid content concentration of 25%, and having an oxazoline group was obtained in the same manner as in the synthesis of the resin (C-1) having an oxazoline group. The obtained resin (C-2) having an oxazoline group had an oxazoline group amount of 4.3 mmol/g, and the number-average molecular weight thereof measured by GPC was 20,000.

[0115]

(Production of carbodiimide cross-linking agent D-1)

168 parts by mass of hexamethylene diisocyanate and 220 parts by mass of polyethylene glycol monomethyl ether (M400, average molecular weight: 400) were charged into a flask equipped with a stirrer, a thermometer, and a reflux condenser, and stirred at 120°C for 1 hour. Furthermore, 26 parts by mass of 4,4'-dicyclohexylmethane diisocyanate and 3.8 parts by mass of 3-methyl-1-phenyl-2-phospholene-1-oxide (2 mass% based on the total isocyanate) as a carbodiimidization catalyst were added thereto, followed by stirring at 185°C under nitrogen flow for another 5 hours. The infrared spectrum of the reaction solution was measured, and the absorption at a wavelength of 2200 to 2300 cm⁻¹ was confirmed to disappear. The mixture was allowed to cool to

60°C, and 567 parts by mass of ion-exchanged water was added thereto to obtain a carbodiimide water-soluble resin (D-1) having a solid content of 40 mass%.

[0116]

(Production of isocyanate cross-linking agent E-1)

100 parts by mass of a polyisocyanate compound obtained by using hexamethylene diisocyanate as a raw material and having an isocyanurate structure (Duranate TPA, manufactured by Asahi Kasei Chemicals), 55 parts by mass of propylene glycol monomethyl ether acetate, and 30 parts by mass of polyethylene glycol monomethyl ether (average molecular weight: 750) were charged into a flask equipped with a stirrer, a thermometer, and a reflux condenser, and kept under a nitrogen atmosphere at 70°C for 4 hours. Thereafter, the reaction solution temperature was lowered to 50°C, and 47 parts by mass of methyl ethyl ketoxime was added dropwise. The infrared spectrum of the reaction solution was measured, and the absorption of the isocyanate group was confirmed to disappear. A block polyisocyanate water dispersion solution (E-1) having a solid content of 75 mass% was obtained.

[0117]

(Silica particle F-1)

Colloidal silica (trade name: Snowtex XL, manufactured by Nissan Chemical Corporation, average

particle size: 40 nm, solid content concentration: 40

mass%)

[0118]

(Example 1)

(Preparation of release coating solution 1)

A release coating solution 1 having the following composition was prepared.

(Release coating solution 1)

Water:

48.01 parts by mass

Isopropyl alcohol:

25.95 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%):

14.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid content concentration: 10 mass%):

12.00 parts by mass

Additive G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive, manufactured by Dow Corning Toray Co., Ltd., solid content concentration: 100 mass%)

[0119]

(Production of polyester film)

The PET chips were dried, then melted at 285°C, melted at 290°C by separate melt extruders, 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. PET (I) and 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. The layer ratio was adjusted such that PET (I)/ PET (II) = 60 mass%/40 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 longitudinal direction at a roll temperature of 80°C according to the speed difference between rolls.

[0120]

Then, the release coating solution was applied on the surface layer A 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 0.07 μm.

Subsequently, using 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 4 seconds in a state where the length of the film in the transverse direction was fixed. The film was further subjected to a loosening treatment in the transverse direction by 3% at 170°C to obtain an in-line release coating polyester film having a thickness of 31 μm . Sa of the surface layer B (opposite side layer to release surface) of the obtained film was 28 nm, and P thereof was 754 nm. Here, a PET substrate that does not contain a release layer is taken as Z. The intrinsic viscosity of the obtained PET substrate was 0.59 dl/g. Sa of the surface layer A of the PET substrate not containing the release layer was 1 nm, and P thereof was 16 nm.

[0121]

(Example 2)

A release polyester film was obtained in the same manner as in Example 1 except that a release coating solution 1 was changed to the following release coating solution 2.

(Release coating solution 2)

Water:

54.03 parts by mass

Isopropyl alcohol:

23.93 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%):

18.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid content concentration: 10 mass%):

4.00 parts by mass

Additive G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive, manufactured by Dow Corning Toray Co., Ltd., solid content concentration: 100 mass%)

[0122]

(Example 3)

A release polyester film was obtained in the same manner as in Example 1 except that a release coating solution 1 was changed to the following release coating solution 3.

(Release coating solution 3)

Water:

51.01 parts by mass

Isopropyl alcohol:

24.95 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%):

16.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid
content concentration: 10 mass%):

8.00 parts by mass

Additive G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive,
manufactured by Dow Corning Toray Co., Ltd., solid content
concentration: 100 mass%)

[0123]

(Example 4)

A release polyester film was obtained in the same
manner as in Example 1 except that a release coating
solution 1 was changed to the following release coating
solution 4.

(Release coating solution 4)

Water:

41.99 parts by mass

Isopropyl alcohol:

27.97 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid
content concentration: 20 mass%):

10.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid
content concentration: 10 mass%):

20.00 parts by mass

Additive G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive, manufactured by Dow Corning Toray Co., Ltd., solid content concentration: 100 mass%)

[0124]

(Example 5)

A release polyester film was obtained in the same manner as in Example 1 except that an acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%) in a release coating solution 1 used in Example 1 was changed to an acrylic resin (acrylic polyol resin) A-2 (solid content concentration: 20 mass%).

[0125]

(Example 6)

A release polyester film was obtained in the same manner as in Example 1 except that a release coating solution 6 was used, in which a cross-linking agent in a release coating solution 1 used in Example 1 was changed to an oxazoline-based cross-linking agent C-2 (solid content concentration: 25 mass%).

(Release coating solution 6)

Water:

55.23 parts by mass

Isopropyl alcohol:

25.93 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%):

14.00 parts by mass

Oxazoline-based cross-linking agent C-2 (solid content concentration: 25 mass%):

4.80 parts by mass

Additive G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive, manufactured by Dow Corning Toray Co., Ltd., solid content concentration: 100 mass%)

[0126]

(Example 7)

A release polyester film was obtained in the same manner as in Example 1 except that a release coating solution 7 was used, in which an acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%) in a release coating solution 1 used in Example 1 was changed to an acrylic resin (acrylic polyol resin) A-2 (solid content concentration: 20 mass%), and a cross-linking agent was changed to an oxazoline-based cross-linking agent C-2 (solid content concentration: 25 mass%).

(Release coating solution 7)

Water:

55.23 parts by mass

Isopropyl alcohol:

25.93 parts by mass

Acrylic resin (acrylic polyol resin) A-2 (solid
content concentration: 20 mass%):

14.00 parts by mass

Oxazoline-based cross-linking agent C-2 (solid
content concentration: 25 mass%):

4.80 parts by mass

Additive G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive,
manufactured by Dow Corning Toray Co., Ltd., solid content
concentration: 100 mass%)

[0127]

(Example 8)

A release polyester film was obtained in the same
manner as in Example 1 except that a release coating
solution 8 was used, in which a cross-linking agent in a
release coating solution 1 used in Example 1 was changed to
a carbodiimide-based cross-linking agent D-1 (solid content
concentration: 40 mass%).

(Release coating solution 8)

Water:

56.63 parts by mass

Isopropyl alcohol:

26.97 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%): 12.00 parts by mass

Carbodiimide-based cross-linking agent D-1 (solid content concentration: 40 mass%):

4.00 parts by mass

Additive G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive, manufactured by Dow Corning Toray Co., Ltd., solid content concentration: 100 mass%)

[0128]

(Example 9)

A release polyester film was obtained in the same manner as in Example 1 except that a release coating solution 1 was changed to the following release coating solution 9.

(Release coating solution 9)

Water:

47.51 parts by mass

Isopropyl alcohol:

25.95 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%):

14.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid
content concentration: 10 mass%):

12.00 parts by mass

Silica particle F-1:

0.50 parts by mass

(Average particle size: 40 nm, solid content
concentration: 40 mass%)

Additive G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive,
manufactured by Dow Corning Toray Co., Ltd., solid content
concentration: 100 mass%)

[0129]

(Example 10)

A release polyester film was obtained in the same
manner as in Example 1 except that a release coating
solution 1 was changed to the following release coating
solution 10.

(Release coating solution 10)

Water:

47.01 parts by mass

Isopropyl alcohol:

25.95 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid

content concentration: 20 mass%):

14.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid

content concentration: 10 mass%):

12.00 parts by mass

Silica particle F-1:

1.00 part by mass

(Average particle size: 40 nm, solid content

concentration: 40 mass%)

Additive G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive,

manufactured by Dow Corning Toray Co., Ltd., solid content

concentration: 100 mass%)

[0130]

(Example 11)

A release polyester film was obtained in the same manner as in Example 1 except that a release coating solution 11 was used, in which an additive in a release coating solution 1 used in Example 1 was changed to polyester-modified polydimethylsiloxane G-2 (solid content concentration: 25 mass%).

(Release coating solution 11)

Water:

47.90 parts by mass

Isopropyl alcohol:

25.93 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid
content concentration: 20 mass%):

14.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid
content concentration: 10 mass%):

12.00 parts by mass

Additive G-2:

0.17 parts by mass

(Polyester-modified polydimethylsiloxane, BYK-315N,
manufactured by BYK Japan KK, solid content concentration:
25 mass%)

[0131]

(Example 12)

A release polyester film was obtained in the same
manner as in Example 1 except that a release coating
solution 12 was used, in which an additive in a release
coating solution 1 used in Example 1 was changed to a long-
chain alkyl additive G-1 (solid content concentration: 15
mass%).

(Release coating solution 12)

Water:

47.80 parts by mass

Isopropyl alcohol:

25.93 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid
content concentration: 20 mass%):

14.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid
content concentration: 10 mass%):

12.00 parts by mass

Additive H-1:

0.27 parts by mass

(Peroyl (registered trademark) 406, manufactured by
Lion Specialty Chemicals Co., Ltd., solid content
concentration: 15 mass%)

[0132]

(Example 13)

A release polyester film was obtained in the same
manner as in Example 1 except that the following release
coating solution 13 containing no additive in a release
coating solution 1 used in Example 1 was used.

(Release coating solution 13)

Water:

48.05 parts by mass

Isopropyl alcohol:

25.95 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid
content concentration: 20 mass%):

14.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid content concentration: 10 mass%):

12.00 parts by mass

[0133]

(Example 14)

A release polyester film was obtained in the same manner as in Example 1 except that the thickness of a release layer was changed to 0.035 μm .

[0134]

(Example 15)

A release polyester film was obtained in the same manner as in Example 1 except that the thickness of a release layer was changed to 0.100 μm .

[0135]

(Example 16)

A release polyester film was obtained in the same manner as in Example 1 except that the thickness of a release layer was changed to 0.140 μm .

[0136]

(Example 17)

A release polyester film was obtained in the same manner as in Example 1 except that an acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%) in a release coating solution 1 used in Example 1

was changed to an acrylic resin (acrylic polyol resin) A-4 (solid content concentration: 20mass%).

[0137]

(Example 18)

A release polyester film was obtained in the same manner as in Example 1 except that an acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%) in a release coating solution 1 used in Example 1 was changed to an acrylic resin (acrylic polyol resin) A-5 (solid content concentration: 20mass%).

[0138]

(Example 19)

A release polyester film was obtained in the same manner as in Example 1 except that PET (II) of a surface layer A of a PET substrate was changed to PET (III).

Here, a PET substrate that does not contain a release layer is taken as Y. The intrinsic viscosity of the obtained PET substrate was 0.59 dl/g. Sa of the surface layer A of the PET substrate Y before the release layer is laminated was 10 nm, and P thereof was 130 nm.

[0139]

(Example 20)

A release polyester film was obtained in the same manner as in Example 1 except that a release coating solution 1 was changed to the following release coating

solution 16.

(Release coating solution 16)

Water:

47.85 parts by mass

Isopropyl alcohol:

25.95 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid
content concentration: 20 mass%):

14.00 parts by mass

Oxazoline-based cross-linking agent C-1 (solid
content concentration: 10 mass%):

12.00 parts by mass

Additive G-1:

0.20 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive,
manufactured by Dow Corning Toray Co., Ltd., solid content
concentration: 100 mass%)

[0140]

(Example 21)

A release polyester film was obtained in the same
manner as in Example 1 except that a release coating
solution 17 was used, in which an acrylic resin (acrylic
polyol resin) A-1 (solid content concentration: 20 mass%)
in a release coating solution 1 used in Example 1 was
changed to an acrylic resin (acrylic polyol resin) A-6

(solid content concentration: 20 mass%).

[0141]

(Comparative Example 1)

A release polyester film was obtained in the same manner as in Example 1 except that a release coating solution 1 was changed to the following release coating solution 18.

(Release coating solution 18)

Water:

76.76 parts by mass

Isopropyl alcohol:

19.19 parts by mass

Curable silicone water-based emulsion B-1:

4.01 parts by mass

(KM3951, manufactured by Shinetsu Silicones, solid content concentration: 40%)

Platinum catalyst B-2:

0.04 parts by mass

(CAT-PM-10A, manufactured by Shinetsu Silicones)

[0142]

(Comparative Example 2)

A release polyester film was obtained in the same manner as in Example 1 except that a release coating solution 19 was used, in which an acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%)

in a release coating solution 1 used in Example 1 was changed to an acrylic resin (acrylic polyol resin) A-3 (solid content concentration: 20 mass%).

[0143]

(Comparative Example 3)

A polyester film was obtained in the same manner as in Example 1 except that a release coating solution 1 was changed to the following release coating solution 20.

(Release coating solution 20)

Water:

58.30 parts by mass

Isopropyl alcohol:

25.95 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%):

14.00 parts by mass

Isocyanate cross-linking agent E-1 (solid content concentration: 75 mass%):

1.72 parts by mass

Surfactant G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive, manufactured by Dow Corning Toray Co., Ltd., solid content concentration: 100 mass%)

[0144]

(Comparative Example 4)

A polyester film was obtained in the same manner as in Example 1 except that a release coating solution 1 was changed to the following release coating solution 21.

(Release coating solution 21)

Water:

57.04 parts by mass

Isopropyl alcohol:

22.93 parts by mass

Acrylic resin (acrylic polyol resin) A-1 (solid content concentration: 20 mass%):

20.00 parts by mass

Surfactant G-1:

0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67Additive, manufactured by Dow Corning Toray Co., Ltd., solid content concentration: 100 mass%)

[0145]

Table 2 shows the evaluation results of Examples and Comparative Examples.

[0146]

[Table 2]

	PET Substrate	Release Coating Solution								
		(Composition Ratio is Represented by Parts by Mass of Each Solid Content)								
		Applying Solution	Resin		Cross-Linking Agent or Catalyst	Resin/Cross-Linking Agent or Catalyst Ratio (parts by mass)	Particle	Particle Ratio (parts by mass)	Additive	Additive Ratio (parts by mass)
			Type	SMA Ratio mol%						
Example 1	Z	1	A-1	20	C-1	70/30	-	-	G-1	1.0
Example 2	Z	2	A-1	20	C-1	90/10	-	-	G-1	1.0
Example 3	Z	3	A-1	20	C-1	80/20	-	-	G-1	1.0
Example 4	Z	4	A-1	20	C-1	50/50	-	-	G-1	1.0
Example 5	Z	5	A-2	10	C-1	70/30	-	-	G-1	1.0
Example 6	Z	6	A-1	20	C-2	70/30	-	-	G-1	1.0
Example 7	Z	7	A-2	10	C-2	70/30	-	-	G-1	1.0
Example 8	Z	8	A-1	20	D-1	60/40	-	-	G-1	1.0
Example 9	Z	9	A-1	20	C-1	70/30	F-1	5	G-1	1.0
Example 10	Z	10	A-1	20	C-1	70/30	F-1	10	G-1	1.0
Example 11	Z	11	A-1	20	C-1	70/30	-	-	G-2	1.0
Example 12	Z	12	A-1	20	C-1	70/30	-	-	H-1	1.0
Example 13	Z	13	A-1	20	C-1	70/30	-	-	-	-
Example 14	Z	1	A-1	20	C-1	70/30	-	-	G-1	1.0
Example 15	Z	1	A-1	20	C-1	70/30	-	-	G-1	1.0
Example 16	Z	1	A-1	20	C-1	70/30	-	-	G-1	1.0
Example 17	Z	14	A-4	20	C-1	70/30	-	-	G-1	1.0
Example 18	Z	15	A-5	50	C-1	70/30	-	-	G-1	1.0
Example 19	Y	1	A-1	20	C-1	70/30	-	-	G-1	1.0
Example 20	Z	16	A-1	20	C-1	70/30	-	-	G-1	5.0
Example 21	Z	17	A-6	30	C-1	70/30	-	-	G-1	1.0
Comparative Example 1	Z	18	B-1	0	B-2	98/2	-	-	-	-
Comparative Example 2	Z	19	A-3	0	C-1	70/30	-	-	G-1	1.0
Comparative Example 3	Z	20	A-1	20	E-1	70/30	-	-	G-1	1.0
Comparative Example 4	Z	21	A-1	20	-	100/0	-	-	G-1	1.0

SMA Stearyl Methacrylate

[Table 2] (continued)

	Release Layer						Ceramic Green Sheet	Resin Sheet
	Ceramic Peeling Force (mN/mm)	Ceramic Peeling Force Determination	Average Area Surface Roughness Sa (nm)	Maximum Protrusion Height P (nm)	Thickness of Release Coating Layer (nm)	Surface Free Energy γ_s (mJ/m ²)	Pinhole	Pinhole
Example 1	1.9	Good	0.9	35.4	70	34.5	Good	Good
Example 2	5.4	Moderate	0.9	35.6	70	32.3	Good	Good
Example 3	2.5	Good	1.0	35.9	70	33.5	Good	Good
Example 4	2.0	Good	0.9	34.7	70	35.7	Good	Good
Example 5	3.2	Good	0.9	34.2	70	39.6	Good	Good
Example 6	2.5	Good	0.9	34.5	70	32.9	Good	Good
Example 7	4.3	Moderate	0.9	34.6	70	38.5	Good	Good
Example 8	3.5	Good	1.0	37.8	70	35.8	Good	Good
Example 9	1.7	Good	2.1	46.0	70	36.8	Good	Good
Example 10	1.7	Good	2.9	48.2	70	34.8	Good	Good
Example 11	2.0	Good	0.9	35.4	70	34.7	Good	Good
Example 12	1.9	Good	1.0	38.6	70	33.2	Good	Good
Example 13	2.1	Good	1.0	36.3	70	35.7	Good	Good
Example 14	2.0	Good	0.8	30.1	35	35.5	Good	Good
Example 15	2.0	Good	1.0	38.2	100	34.1	Good	Good
Example 16	2.0	Good	1.2	39.4	140	35.1	Good	Good
Example 17	1.9	Good	4.4	70.0	70	34.6	Moderate	Moderate
Example 18	5.1	Moderate	0.9	34.7	70	31.2	Good	Good
Example 19	1.9	Good	10.5	152.0	70	34.5	Moderate	Moderate
Example 20	2.1	Good	0.9	35.5	70	34.5	Good	Good
Example 21	1.7	Good	0.9	36.7	70	34.5	Good	Good
Comparative Example 1	1.7	Good	0.9	48.2	70	18.0	Poor	Poor
Comparative Example 2	10.5	Poor	0.9	32.8	70	63.2	Poor	Poor
Comparative Example 3	8.5	Poor	0.9	37.2	70	34.3	Poor	Poor
Comparative Example 4	No Measurable	Poor	0.9	35.6	70	31.5	Poor	Poor

[0147]

In Table 2 above, for the resin, the cross-linking agent, the particles, and the additive in the release coating solution, respective compositions are described as parts by mass of the solid content. The sum of parts by mass of the solid contents of the resin, the cross-linking agent, the particles, and the additive present in the release coating solution is parts by mass of the total solid content of the release layer. By dividing parts by mass of the solid content of each of the resin, the cross-linking agent, the particles, and the additive by parts by mass of the total solid content of the release layer, the mass percentages of the resin, the cross-linking agent, the particles, and the additive in the total solid content of the release layer can be obtained.

[0148]

In Examples 1 to 21, the release film could be prepared at low production cost by in-line coating, and good wettability of a slurry or a resin-dissolved solution for a sheet and an appropriate sheet peeling force were exhibited even when the sheet to be formed was further thinned. Meanwhile, in Comparative Example 1, when a sheet was further thinned, wettability of a slurry or a resin-dissolved solution for a sheet was poor, so that pinholes occurred. In Comparative Example 2, an acrylic resin did

not contain a long-chain alkyl component, so that surface free energy increased, which caused an increased sheet peeling force. The heavy sheet peeling force caused pinholes to occur in the sheet during peeling. In Comparative Examples 3 and 4, an oxazoline-based cross-linking agent or a carbodiimide-based cross-linking agent was not used, so that a coating film was insufficiently cured, which caused an increased sheet peeling force. The heavy sheet peeling force caused pinholes to occur in the sheet during peeling.

INDUSTRIAL APPLICABILITY

[0149]

The present invention can provide a release film that can be prepared at low production cost, and have both good wettability of a slurry and a resin-dissolved solution for a sheet and an appropriate sheet peeling force even when the sheet is further thinned.

CLAIMS

1. A release film comprising:
a polyester film; and
a release layer,
wherein the release film includes the release layer
provided on at least one surface of the polyester film
directly or with other layer therebetween; and
the release layer is obtained by curing a composition
containing an acrylic resin having a long-chain alkyl group
and at least one cross-linking agent selected from an
oxazoline-based cross-linking agent or a carbodiimide-based
cross-linking agent.
2. The release film according to claim 1, wherein
the acrylic resin contains a long-chain alkyl group-
containing acrylate monomer; and
a copolymerization ratio of the long-chain alkyl
group-containing acrylate monomer in the acrylic resin is 5
mol% or more and 60 mol% or less.
3. The release film according to claim 1 or 2,
wherein
the cross-linking agent is the oxazoline-based cross-
linking agent; and

the oxazoline-based cross-linking agent contains 3.0 to 9.0 mmol/g of an oxazoline group.

4. The release film according to any one of claims 1 to 3, wherein the acrylic resin having the long-chain alkyl group has an acid value of 40 mgKOH/g or more and 400 mgKOH/g or less.

5. The release film according to any one of claims 1 to 4, wherein the release layer has a thickness of 0.001 μm or more and 2 μm or less.

6. The release film according to any one of claim 1 to 5, wherein the release film is a release film for production of a ceramic green sheet.

7. A method for production of a release film comprising a polyester film and a release layer,

wherein the release film includes the release layer provided on at least one surface of the polyester film directly or with other layer therebetween;

the release layer is obtained by curing a composition containing an acrylic resin having a long-chain alkyl group and at least one cross-linking agent selected from an oxazoline-based cross-linking agent or a carbodiimide-based

cross-linking agent; and

the method comprises:

coating a release coating solution on a film being an un-stretched film or a uniaxially stretched film;

then stretching the film in at least a uniaxial direction in which the film is un-stretched; and

heat-treating the film.

8. The method for production of a release film according to claim 7, wherein the method is a method for production of a release film for production of a ceramic green sheet.

9. A method for production of a ceramic green sheet, wherein the ceramic green sheet is formed by using the release film for production of a ceramic green sheet according to claim 6 or the method for production of a release film for production of a ceramic green sheet according to claim 8.

10. The method for production of a ceramic green sheet according to claim 9, wherein the ceramic green sheet to be produced has a thickness of 0.2 μm or more and 2.0 μm or less.

11. A method for production of a ceramic capacitor,
wherein the method for production of a ceramic green sheet
according to claim 9 or 10 is employed.