

DESCRIPTION

TITLE OF THE INVENTION: RELEASE FILM AND METHOD FOR
PRODUCING SAME

[0001]

The present invention relates to a release film and a method for producing the same.

BACKGROUND ART

[0002]

Release films are members to be used for uniformly forming and peeling sheet to be peeled without causing damage.

Examples of the sheet to be peeled include a ceramic green sheet, a sheet containing particles and a resin, and a resin sheet or the like.

[0003]

For example, Patent Document 1 discloses a release polyester film having a layer obtained by applying silicone on an outermost layer.

Patent Document 2 discloses a release film comprising a support substrate, an intermediate layer, and a release layer, wherein the release layer is formed of a cured product of a coating composition for a release layer comprising a silicone-based resin and a cellulose

derivative.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004]

Patent Document 1: JP-A-2016-30343

Patent Document 2: JP-A-2019-147274

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

In each of the release films disclosed in Patent Documents 1 and 2, since the release layer contains a silicone-based resin or the like as its main component, the surface free energy of the release layer tends to be low.

In recent years, further thinning of ceramic green sheets has been required. For example, when such a release film is used for the production of a ceramic green sheet, there is a possibility that "cissing" of a slurry, a resin solution, and the like occurs, and there is a possibility that pinholes occur in the resulting ceramic green sheet or the like.

[0006]

The present invention has been devised in view of the problems of the conventional technique. That is, an object

of the present invention is to be able to exhibit superior wettability for, for example, a slurry, a resin solution, and the like for ceramic green sheets, and to suppress generation of pinholes in ceramic green sheets and the like to be obtained. In addition, another object of the present invention is to provide a release film that has good releasability and makes it possible to further reduce the thickness of a ceramic green sheet, a resin thin film, and the like.

MEANS FOR SOLVING THE PROBLEMS

[0007]

Here, since the release films shown in the prior art use a silicone-based compound as a main component of a release layer, the release films tend to repel a slurry, a resin solution, and the like for ceramic green sheets. For this reason, when "cissing" of a slurry, a resin solution, or the like for ceramic green sheets, the film thickness of a ceramic green sheet or the like to be formed is not uniform, and pinholes may be generated. In particular, in the technical field where thinning of sheets is required, not only thinning of a sheet but also high required characteristics must be satisfied. Therefore, there is a demand for solving various problems that may occur due to "cissing".

[0008]

On the other hand, when an attempt is made to improve wettability in order to suppress "cissing" of a slurry, a resin solution, and the like for ceramic green sheets, the peeling force of a resulting ceramic green sheet increases, and the ceramic green sheet may be damaged at the time of peeling.

In particular, in a technical field where thinning of sheets is required, there is a high possibility that a sheet is damaged when the obtained sheet or the like is peeled off, and it is required to solve such a problem.

[0009]

As described above, there is a trade-off relationship between the improvement in wettability for a slurry, a resin solution, and the like for ceramic green sheets and the peelability of a formed sheet, and especially in the technical field aiming at thinning of ceramic green sheets and the like, it is required to solve these problems together.

In order to solve such problems, the inventors of the present application have extensively studied for achieving not only suppression of pinholes in ceramic green sheets, resin thin films, and the like and significant reduction in breakage of sheets, resin thin films, and the like at the time of peeling, but also further thinning of resulting

ceramic green sheets, resin thin films, and the like, and as a result, have accomplished the present invention.

[0010]

In order to solve the above problems, in one aspect of the present invention is provided

[1] A release film having a release layer on at least one surface of a polyester film directly or with another layer interposed between the release layer and the polyester film, wherein

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

the composition for forming a release layer comprises an acrylic resin,

the acrylic resin has a hydroxyl value of 150 mgKOH/g or more and 450 mgKOH/g or less,

the acrylic resin is a resin prepared by copolymerizing two or more types of acrylic monomers selected from the group consisting of:

an acrylic monomer having a hydroxyl group as a first acrylic monomer,

an acrylic monomer having a carboxyl group as a second acrylic monomer,

an acrylic monomer having a long chain alkyl group as a third acrylic monomer, and

a radically polymerizable acrylic monomer other than

the first to third acrylic monomers as a fourth acrylic monomer.

[2] In one embodiment, the composition for forming a release layer further comprises an oxazoline-based crosslinking agent, and the hydroxyl value of the acrylic resin is 190 mgKOH/g or more and 450 mgKOH/g or less.

[3] In one embodiment, the release layer has a surface free energy of 30 mJ/m² or more on a surface opposite from the polyester film.

[4] In one embodiment, the acrylic resin has an acid value of 20 mgKOH/g or more and 300 mgKOH/g or less.

[5] In one embodiment, the acrylic resin has a glass transition temperature (T_g) of 40°C or higher and 110°C or lower.

[6] In one embodiment, the acrylic resin comprises, as one of copolymerized constituents, an acrylic monomer having a carboxyl group, which is the second acrylic monomer, and a composition ratio of the second acrylic monomer is 0.1 mol% or more and 35 mol% or less based on 100 mol% of a total amount of the copolymerized constituents in the acrylic resin.

[7] In one embodiment, the acrylic resin comprises, as a copolymerized constituent, an acrylic monomer having a hydroxyl group, which is the first acrylic monomer and a composition ratio of the first acrylic monomer is

25 mol% or more and 95 mol% or less based on 100 mol% of a total amount of the copolymerized constituents in the acrylic resin.

[8] In one embodiment, the acrylic resin comprises, as a copolymerized constituent, an acrylic monomer having a hydroxyl group, which is the first acrylic monomer, and

the acrylic resin further comprises, as a copolymerized constituent, an acrylic monomer having a carboxyl group, which is the second acrylic monomer, and

a relationship between a composition ratio of the first acrylic monomer and a composition ratio of the second acrylic monomer is represented by

(composition ratio of first acrylic monomer/composition ratio of second acrylic monomer) ≥ 1.5 .

[9] In one embodiment, the oxazoline-based crosslinking agent contains an oxazoline group in an amount of 3.0 to 9.0 mmol/g.

[10] In one embodiment, the release layer has a thickness of 0.001 μm or more and 2 μm or less.

[11] In one aspect, the release film is a release film for producing a ceramic green sheet.

[12] In another aspect, the present invention provides a method for producing a release film described herein. In one embodiment, the production method of the present invention comprises:

applying a composition for forming a release layer to an unstretched film or a uniaxially stretched film, and

after applying the composition for forming a release layer, in an unstretched state or after stretching in at least a uniaxial direction, performed heat-setting in a range of 80°C to 270°C.

[13] In one embodiment, the method for producing a release film is a method for producing a release film for producing a ceramic green sheet.

[14] In one aspect, the present invention provides a method for producing a ceramic green sheet, comprising forming a ceramic green sheet using the release film for producing a ceramic green sheet described in the present description, or the method for producing a release film for producing a ceramic green sheet described in the present disclosure.

[15] In one embodiment, the ceramic green sheet to be produced has a thickness of 0.2 μm or more and 2.0 μm or less.

[16] In one aspect, the present invention provides a method for producing a ceramic capacitor employing the method for producing a ceramic green sheet described in the present description.

EFFECT OF THE INVENTION

[0011]

The release film according to the present invention can improve wettability for a slurry, a resin solution, and the like for ceramic green sheets, and can greatly reduce breakage of a sheet, a resin thin film, and the like at the time of peeling. In addition, the release film according to the present invention can suppress generation of pinholes in a ceramic green sheet, a resin thin film, and the like to be obtained, can provide a uniform film thickness, and can achieve further reduction in thickness.

MODE FOR CARRYING OUT THE INVENTION

[0012]

Hereinafter, the present invention will be described in detail.

The release film according to the present invention is a release film having a release layer on at least one surface of a polyester film directly or with another layer interposed between the release layer and the polyester film, wherein

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

the composition for forming a release layer comprises an acrylic resin,

the acrylic resin has a hydroxyl value of 150 mgKOH/g

or more and 450 mgKOH/g or less,

the acrylic resin is a resin prepared by copolymerizing two or more types of acrylic monomers selected from the group consisting of:

an acrylic monomer having a hydroxyl group as a first acrylic monomer,

an acrylic monomer having a carboxyl group as a second acrylic monomer,

an acrylic monomer having a long chain alkyl group as a third acrylic monomer, and

a radically polymerizable acrylic monomer other than the first to third acrylic monomers as a fourth acrylic monomer.

[0013]

Any release film of the present invention can exhibit good wettability for, for example, a slurry, a resin solution, and the like for ceramic green sheets, so that it can suppress cissing.

In addition, generation of pinholes in ceramic green sheets or the like to be obtained can be suppressed.

Furthermore, any release film according to the present invention can have a moderate peelability while suppressing cissing. Therefore, it is possible to suppress the breakage of an obtained ceramic green sheet, resin thin film, or the like when peeling it off from the release

film.

With the release film of the present invention, a required ceramic green sheet and a required resin thin film can be also formed with a uniform film thickness, and thinning can also be achieved.

In addition, the release film according to the present invention can be produced by an in-line coating process, and the production cost can be suppressed. In addition, it is possible to reduce waste loss of ceramic green sheets, resin thin films, and the like, and it is possible to contribute to reduction of environmental load.

The release film of the present invention can be used especially for a release film for producing a ceramic green sheet. When the hydroxyl value of the acrylic resin is within the above range and the acrylic resin is a resin obtained by copolymerizing a specific acrylic monomer, superior wettability can be exhibited for a slurry for ceramic green sheets, a required ceramic green sheet can be formed with a uniform film thickness, and thinning can be achieved.

[0014]

(Polyester Film)

The release film of the present invention is a release film having a release layer on at least one surface of a polyester film as a substrate film directly or with

another layer interposed therebetween, and the polyester film is desirably a biaxially oriented polyester film. By virtue of having the polyester film, the hardness of the release layer is moderately increased and a good peeling force can be obtained.

[0015]

The polyester constituting the polyester film to be used as the substrate in the present invention is not particularly limited, and may be a polyester used as a substrate for a release film, and is preferably a crystalline linear saturated polyester composed of an aromatic dibasic acid component and a diol component. For example, polyethylene terephthalate, polyethylene-2,6-naphthalate, polybutylene terephthalate, and polytrimethylene terephthalate are more preferable, or copolymers containing constituents of these resins as main components may be used. Especially, polyethylene terephthalate is particularly suitable.

Polyethylene terephthalate contains ethylene terephthalate repeating units preferably in an amount of 90 mol% or more, more preferably 95 mol% or more, and other dicarboxylic acid components and diol components may be copolymerized in small amounts. For example, a copolymer produced from only terephthalic acid and ethylene glycol is preferable in view of capability of increasing the hardness

of the release layer and contributing to high smoothness, and cost.

Further, known additives, such as an antioxidant, a light stabilizer, an ultraviolet absorber, and a crystallizing agent, may be added as long as the effects of the film of the present invention are not impaired. The polyester film is preferably a biaxially oriented polyester film because of its elastic modulus in both directions, and the like.

[0016]

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, it is preferable because breakage does not often occur in a stretching process. Conversely, when the intrinsic viscosity is 0.70 dl/g or less, it is preferable because the cuttability of the polyester film at the time of being cut into a predetermined product width is good and dimensional defects do not occur.

It is also preferable that the raw material pellets are sufficiently vacuum-dried.

[0017]

In the present invention, a polyester film can be obtained by, for example, melting the polyester with an extruder, extruding the molten polyester into a film,

cooling the film with a rotary cooling drum to obtain an unstretched film, and uniaxially or biaxially stretching the unstretched film. A biaxially stretched film can be obtained by a method in which a film uniaxially stretched in the machine direction or the transverse direction is sequentially stretched biaxially in the transverse direction or the machine direction, or a method in which an unstretched film is simultaneously stretched biaxially in the machine direction and the transverse direction.

In the present invention, the composition for forming a release layer can be applied in the process of producing a polyester film, and it is preferable to use a so-called in-line coating method. Of course, the release film may be produced using an off-line coating method in which a polyester film is produced and then a release layer is formed.

[0018]

In the present invention, the stretching temperature when stretching the polyester film is preferably set equal to or higher than a secondary transition point (T_g) of the polyester. It is preferable to stretch the film 1 to 8 times, particularly 2 to 6 times, in each of the machine and transverse directions. For example, the film may be stretched at a temperature of 80°C or more and 200°C or less.

[0019]

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, it is preferable because there is no risk that the film is deformed by heat during the film production, a step of processing the release layer, or sheet forming. Whereas, when the thickness of the film is 50 μm or less, it is preferable to reduce the environmental load because the amount of the film to be disposed after use is not extremely large.

[0020]

The polyester film substrate may have a single layer or two or more layers. For example, the polyester film preferably has a surface layer A substantially free of inorganic particles on at least one surface. In the case of a laminated polyester film having a multilayer configuration including two or more layers, the polyester film preferably has a surface layer B that can contain particles and the like on the surface opposite from the surface layer A substantially free of inorganic particles. As the laminated configuration, the layer configuration in the thickness direction may be a laminated structure of release layer/A/B, release layer/A/C/B, or the like where a layer to which the composition for forming a release layer

is applied is named a surface layer A, a layer located opposite from the surface layer A is named a surface layer B, and a core layer other than these layers is named a layer C. As a matter of course, the layer C may have a configuration including a plurality of layers. The surface layer B may be free of particles. In that case, a coating 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.

[0021]

In the polyester film substrate in the present invention, the average area surface roughness (S_a) of the surface layer A is preferably 10 nm or less. When the S_a of the surface layer A is 10 nm or less, it is preferable because pinholes and the like are less likely to occur during forming an ultrathin sheet to be laminated.

It can be said that the smaller the average area surface roughness (S_a) of the surface layer A is, the more preferable it is. For example, the S_a of the surface layer A may be 0.1 nm or more.

In one embodiment, the average area surface roughness (S_a) of the surface layer A may be 0.1 nm or more and 7 nm or less, for example, 0.1 nm or more and 5 nm or less. Within such a range, generation of pinholes and the like at the time of forming an ultrathin sheet can be more

effectively suppressed.

[0022]

The maximum protrusion height (P) of the surface layer A not including the release layer is, for example, 1 nm or more and 130 nm or less, and may be 3 nm or more and 80 nm or less, or may be 5 nm or more and 40 nm or less. When the maximum protrusion height (P) of the surface layer A is within such a range, the release film according to the present invention can have a release layer having higher smoothness.

Further, for example, the maximum protrusion height (P) of the surface layer A may be 7 nm or more and 25 nm or less. When the maximum protrusion height (P) of the surface layer A is within such a range, the release layer according to the present invention can also have a preferable average area surface roughness (Sa) and a preferable maximum protrusion height (P), and a release film having high smoothness can be obtained. Furthermore, it can also contribute to thinning of ceramic green sheets, resin thin films, and the like.

[0023]

Here, when an anchor coating layer described later or the like is provided on the surface layer A, it is preferable that the anchor coating layer is substantially free of inorganic particles and it is preferable that the

average area surface roughness (Sa) after the lamination of a coating layer falls within the range described above. In addition, it is preferable that the maximum protrusion height (P) also falls within the range described above.

In the present invention, the phrase "substantially free of inorganic particles" means a content that is 50 ppm or less, preferably 10 ppm or less, and most preferably equal to or less than the detection limit when an inorganic element is quantitatively determined by fluorescent X-ray analysis. This is because, even if the inorganic particles are not intentionally added to the film, contamination components derived from foreign substances, raw material resins, and stains adhered to the lines and devices in the film production process may peel off and mixed into the film.

[0024]

In the polyester film substrate in the present invention, the surface layer B forming the surface opposite from the surface to which the composition for forming a release layer is applied preferably contains particles, and especially, silica particles and/or calcium carbonate particles are preferably used, from the viewpoint of maintaining good slipperiness of the film, improving the ease of air release, and the like. As to the content of particles contained, the particles are preferably contained

in the surface layer B in an amount of 5000 to 15000 ppm in total. When the total content of the silica particles and/or the calcium carbonate particles is 5000 ppm or more, air can be uniformly released when the film is wound up into a roll shape, and the film is suitable for the production of an ultrathin sheet because of its good winding appearance and good flatness. In addition, when the total content of the silica particles and/or the calcium carbonate particles is 15000 ppm or less, it is preferable because aggregation of the lubricant hardly occurs and coarse protrusions are not formed, so that the quality is stabilized in the production of an ultrathin sheet.

[0025]

In the polyester film substrate in the present invention, the surface layer B forming the surface opposite from the surface to which the composition for forming a release layer is applied preferably contains particles, and especially, silica particles and/or calcium carbonate particles are preferably used, from the viewpoint of improvement in the slipperiness of the film and the ease of air release. At this time, the average area surface roughness (S_a) of the film of the surface layer B is preferably within a range of 1 to 40 nm. More preferably, it is within a range of 5 to 35 nm. When the S_a is 1 nm or

more, air can be uniformly released when the film is wound up into a roll shape, and the film is suitable for the production of an ultrathin sheet because of its good winding appearance and good flatness. In addition, when the Sa is 40 nm or less, it is preferable because aggregation of the lubricant hardly occurs and coarse protrusions are not formed, so that the quality is stabilized at the time of producing an ultrathin sheet.

[0026]

As the particles to be contained in the surface layer B, inert inorganic particles and/or heat-resistant organic particles other than silica and/or calcium carbonate can be used. From the viewpoint of transparency and cost, it is more preferable to use silica particles and/or calcium carbonate particles, and examples of other inorganic particles that can be used include alumina-silica complex oxide particles and hydroxyapatite particles. Examples of the heat-resistant organic particles include crosslinked polyacrylic particles, crosslinked polystyrene particles, and benzoguanamine-based particles. When silica particles are used, porous colloidal silica is preferable, whereas when calcium carbonate particles are used, light calcium carbonate surface-treated with a polyacrylic acid-based polymeric compound is preferable from the viewpoint of preventing the lubricant from falling off.

[0027]

The average particle diameter of the particles to be added to the surface layer B is preferably 0.1 μm or more and 2.0 μm or less, and particularly preferably 0.5 μm or more and 1.0 μm or less. When the average particle diameter of the particles is 0.1 μm or more, it is preferable because the slipperiness of the release film is good. In addition, when the average particle diameter is 2.0 μm or less, it is preferable because there is no risk that pinholes of the sheet due to coarse particles on a surface of the release layer are generated.

[0028]

The surface layer B may contain two or more types of particles made of different materials. Also, the same type of particles having different average particle diameters may be contained.

[0029]

When the surface layer B is free of particles, it is preferable to impart lubricity to the surface layer B with a coating layer containing particles. This coating layer is not particularly limited, but is preferably provided by in-line coating, in which application is performed during the formation of a polyester film. When the surface layer B is free of particles and has a coating layer containing particles on the surface layer B, the surface of the

coating layer preferably has an average area surface roughness (Sa) within a range of 1 to 40 nm for the same reason as that of the average area surface roughness (Sa) of the surface layer B described above. More preferably, it is within a range of 5 to 35 nm.

[0030]

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

[0031]

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

that the environmental load is reduced.

[0032]

For a layer other than the surface layer A (the surface layer B or the intermediate layer C described above), 50 to 90% by mass of film scraps and recycled raw materials of PET bottles can be used. In the present invention, since such film scraps and recycled raw materials of PET bottles can be used, the environmental load can be greatly reduced. In addition, also in an embodiment including film scraps and recycled raw materials of PET bottles, it is possible to improve the slipperiness of a film and maintain the ease of air release, and it is possible to set the average area surface roughness (S_a) to a desired range.

For example, for a layer other than the surface layer A (the surface layer B or the intermediate layer C described above), polyester films used in various applications can be appropriately recovered, treated, and reused.

Even in this case, it is preferable that the type, the amount, and the particle size of the lubricant contained in the surface layer B, and the average area surface roughness (S_a) of the surface layer B satisfy the above ranges.

[0033]

In addition, in order to improve adhesion of the composition for forming a release layer to be applied, and the like, and in order to prevent electrification, a coating layer may be provided on the surface of the surface layer A and/or the surface layer B before stretching or after uniaxial stretching in the film forming step, and corona treatment or the like may also be performed.

[0034]

(Composition for Forming Release Layer)

The release film of the present invention has a release layer on at least one surface of a polyester film directly or with another layer interposed therebetween. The release layer is a layer formed by curing the composition for forming a release layer, and the composition for forming a release layer according to the present invention comprises an acrylic resin, and in one embodiment, further comprises an oxazoline-based crosslinking agent.

[0035]

(Binder Resin in Composition for Forming Release Layer)

The composition for forming a release layer in the present invention comprises an acrylic resin as a binder resin. The hydroxyl value of the acrylic resin according to the present invention is 150 mgKOH/g or more and 450 mgKOH/g or less.

When the hydroxyl value of the acrylic resin contained in the release layer is within such a range, the release sheet of the present invention can have a high hardness release layer, and for example, can exhibit good releasability for a ceramic green sheet, a resin thin film, and the like. In addition, it can have good wettability for a slurry, a resin solution, and the like for ceramic green sheets. In addition, it can suppress generation of pinholes, and it can contribute to thinning of a resulting ceramic green sheet, resin thin film, and the like. By virtue of containing such an acrylic resin, the present invention can more favorably exert the effect described above especially for a slurry for ceramic green sheets, and is suitable for a release sheet for producing a ceramic green sheet.

The hydroxyl value of the acrylic resin is more preferably 190 mgKOH/g or more, and for example, may be 210 mgKOH/g or more.

[0036]

In one embodiment, the hydroxyl value of the acrylic resin is 220 mgKOH/g or more, for example, more than 250 mgKOH/g, and more preferably 255 mgKOH/g or more.

The hydroxyl value of the acrylic resin may be 270 mgKOH/g or more, for example, 280 mgKOH/g or more, and is preferably 280 mgKOH/g or more.

When the hydroxyl value of the acrylic resin is 220 mgKOH/g or more, the release sheet of the present invention can have a release layer with higher hardness and can exhibit better releasability to a ceramic green sheet, a resin thin film, and the like. In addition, it can have better wettability for a slurry, a resin solution, and the like for ceramic green sheets.

In addition, it can suppress generation of pinholes, and it can contribute to thinning of a resulting ceramic green sheet, resin thin film, and the like.

For example, in one embodiment, the composition for forming a release layer according to the present invention may further comprise an oxazoline-based crosslinking agent. Also in such an embodiment, the hydroxyl value of the acrylic resin may be within the above range. When the composition for forming a release layer comprises an oxazoline-based crosslinking agent, it is preferable because the reactivity between the acrylic resin according to the present invention and the oxazoline-based crosslinking agent is improved. In one embodiment, when the hydroxyl value of the acrylic resin is more than 250 mgKOH/g, the reactivity is improved, so that a release layer having higher hardness is obtained. In addition, good wettability can be exhibited for a slurry, a resin solution, and the like for ceramic green sheets, so that

cissing can be suppressed. In addition, lightening release can also be achieved at the time of peeling of a ceramic green sheet, a resin thin film, and the like. As a result, for example, a ceramic green sheet having a thickness of 0.2 μm can be favorably formed and can be favorably peeled off, which is preferable.

[0037]

The hydroxyl value of the acrylic resin is preferably 450 mgKOH/g or less, more preferably 400 mgKOH/g or less, and still more preferably 350 mgKOH/g or less. When the hydroxyl value of the acrylic resin is 450 mgKOH/g or less, good wettability for a slurry, a resin solution, and the like for ceramic green sheets can be exhibited, and cissing can be suppressed. In addition, lightening release can also be achieved at the time of peeling of a ceramic green sheet, a resin thin film, and the like.

In one embodiment, when particles are contained in the composition for forming a release layer, it is preferable because it is considered that the contained particles hardly cause an interaction with hydroxyl groups or the like of the acrylic resin, and the particles are uniformly dispersed.

For example, when the composition for forming a release layer according to the present invention contains a plurality of types of acrylic resins included in the scope

of the present invention, the hydroxyl value is an average value of the plurality of types of acrylic resins.

[0038]

The acrylic resin according to the present invention is a resin prepared by copolymerizing two or more types of acrylic monomers selected from the group consisting of:

- an acrylic monomer having a hydroxyl group as a first acrylic monomer,

- an acrylic monomer having a carboxyl group as a second acrylic monomer,

- an acrylic monomer having a long chain alkyl group as a third acrylic monomer, and

- a radically polymerizable acrylic monomer other than the first to third acrylic monomers as a fourth acrylic monomer.

[0039]

(First Acrylic Monomer)

In one embodiment, the acrylic resin comprises, as a copolymerized constituent, an acrylic monomer having a hydroxyl group as a first acrylic monomer. The composition ratio of the first acrylic monomer is, for example, 25 mol% or more and 95 mol% or less, and preferably 40 mol% or more, for example, more than 40 mol% and 95 mol% or less, based on 100 mol% of the total amount of the copolymerized constituents in the acrylic resin.

When the composition ratio of the first acrylic monomer is 25 mol% or more, a release layer having high hardness can be obtained, and this can contribute to lightening release at the time of peeling of a ceramic green sheet, a resin thin film, and the like. In addition, for example, in the release film having the surface layer A substantially free of inorganic particles described in the present description, the release layer can exhibit higher smoothness, and can contribute to thinning of a ceramic green sheet, a resin thin film, and the like.

In one embodiment, when the composition ratio of the first acrylic monomer is within the above range and the composition for forming a release layer further comprises an oxazoline-based crosslinking agent, it is preferable because the reactivity between the acrylic resin according to the present invention and the oxazoline-based crosslinking agent is improved. By improving the reactivity, a release layer having high hardness can be obtained, and this can more effectively contribute to lightening release at the time of peeling of a ceramic green sheet, a resin thin film, and the like.

Whereas, when the composition ratio is 95 mol% or less and particles are contained in the composition for forming a release layer, it is preferable because the contained particles can be suppressed from causing extreme

interaction with the hydroxyl groups of the acrylic resin, so that the particles can be uniformly dispersed.

[0040]

As the acrylic monomer having a hydroxyl group as the first acrylic monomer, a monomer having a hydroxyl group such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, or 4-hydroxybutyl (meth)acrylate, a ring-opening adduct of γ -butyrolactone or ϵ -caprolactone to 2-hydroxyethyl (meth)acrylate, or the like may be used as a copolymerized constituent. Among them, 2-hydroxyethyl (meth)acrylate is preferable from the viewpoint of not inhibiting water solubility. Two or more of them may be used in combination.

[0041]

(Second Acrylic Monomer)

In one embodiment, the acrylic resin comprises, as a copolymerized constituent, an acrylic monomer having a carboxyl group as a second acrylic monomer. By virtue of having the second acrylic monomer, especially a carboxyl group, a crosslinked structure with a crosslinking agent can be favorably formed, and furthermore, it becomes possible to impart water solubility to the acrylic resin in the present invention. Examples of the second acrylic monomer include monomers containing a carboxyl group such as (meth)acrylic acid, crotonic acid, itaconic acid, maleic

acid, and fumaric acid, and monomers containing an acid anhydride group such as maleic anhydride and itaconic anhydride.

[0042]

The composition ratio of the second acrylic monomer is, for example, 0.1 mol% or more and 35 mol% or less based on 100 mol% of the total amount of the copolymerized constituents in the acrylic resin.

The composition ratio of the second acrylic monomer is preferably 0.1 mol% or more and 20 mol% or less based on 100 mol% of the total amount of the copolymerized constituents in the acrylic resin. The composition ratio is more preferably 1 mol% or more and 15 mol% or less. When the composition ratio is 0.1 mol% or more, the composition for forming a release layer is likely to form a crosslinked structure and can impart water solubility. When the composition ratio is 35 mol% or less, it is preferable because the Tg of a resulting release layer is not excessively high with respect to a suitable range described later and the film formability and the stretch aptitude in a coating step such as in-line coating are good.

[0043]

In order to develop good water solubility, it is preferable to neutralize carboxyl groups introduced into

the acrylic resin by copolymerization of acrylic acid or methacrylic acid. Examples of a basic neutralizing agent include amine compounds such as ammonia, trimethylamine, triethylamine, and dimethylaminoethanol, and inorganic basic substances such as potassium hydroxide and sodium hydroxide, and among these, it is preferable to use an amine compound as a neutralizing agent for ease of volatilization of the neutralizing agent and ease of formation of a crosslinked structure. Among them, ammonia is most preferable from the viewpoint that aggregation of particles does not occur when particles are incorporated in the composition for forming a release layer. The neutralization ratio is preferably 30 mol% to 95 mol%, and more preferably 40 mol% to 90 mol%. When the neutralization ratio is 30 mol% or more, it is preferable because the water solubility of the acrylic resin is sufficient, the acrylic resin is easily dissolved in the preparation of the composition for forming a release layer, and there is no risk of whitening the coating film surface after drying. Whereas, when the neutralization ratio is 95 mol% or less, it is preferable because water solubility is not excessively high and it is easy to mix alcohol and the like in the preparation of the composition for forming a release layer.

[0044]

The acrylic resin comprises, as a copolymerized constituent, an acrylic monomer having a hydroxyl group as the first acrylic monomer, and the acrylic resin further comprises, as a copolymerized constituent, an acrylic monomer having a carboxyl group as the second acrylic monomer. In this embodiment, the relationship between the composition ratio of the first acrylic monomer and the composition ratio of the second acrylic monomer is preferably $(\text{composition ratio of first acrylic monomer})/(\text{composition ratio of second acrylic monomer}) \geq 1.5$. For example, $(\text{composition ratio of first acrylic monomer})/(\text{composition ratio of second acrylic monomer}) \geq 3.0$. More preferably, $(\text{composition ratio of first acrylic monomer})/(\text{composition ratio of second acrylic monomer}) \geq 6.0$.

When $(\text{composition ratio of first acrylic monomer})/(\text{composition ratio of second acrylic monomer}) \geq 1.5$, light release of a ceramic green sheet is enabled, and cissing of a slurry for ceramic green sheet formation can be favorably suppressed.

When $(\text{composition ratio of first acrylic monomer})/(\text{composition ratio of second acrylic monomer}) \geq 3.0$, the peeling force can be further reduced. When $(\text{composition ratio of first acrylic monomer})/(\text{composition ratio of second acrylic monomer}) \geq 6.0$, light release and

generation of pinholes can be suppressed even when a thinner 0.2 μm ceramic sheet is used.

[0045]

In one embodiment, the relationship between the composition ratio of the first acrylic monomer and the composition ratio of the second acrylic monomer is $(\text{composition ratio of first acrylic monomer})/(\text{composition ratio of second acrylic monomer}) \leq 20$, for example, $(\text{composition ratio of first acrylic monomer})/(\text{composition ratio of second acrylic monomer}) \leq 12$, or $(\text{composition ratio of first acrylic monomer})/(\text{composition ratio of second acrylic monomer}) \leq 11.5$.

By virtue of having such a relationship, it is possible to have a good peeling force and to favorably suppress cissing, and for example, it is possible to suppress generation of pinholes in a ceramic green sheet and a resin sheet.

Furthermore, light release is possible even when a thinner 0.2 μm ceramic sheet is used, and generation of pinholes can be suppressed.

[0046]

(Third Acrylic Monomer)

In one embodiment, the acrylic resin comprises, as a copolymerized constituent, an acrylic monomer having a long chain alkyl group as a third acrylic monomer. It is

preferable to have a long chain alkyl group because the peeling force can be reduced. The acrylic resin into which a long chain alkyl group is introduced preferably has an alkyl group having 8 to 25 carbon atoms in the side chain of the acrylic resin, more preferably has an alkyl group having 12 to 22 carbon atoms, and still more preferably has an alkyl group having 16 to 20 carbon atoms.

In addition, 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 them, stearyl methacrylate is suitably used in terms of availability, cost, and good peeling force.

[0047]

The composition ratio of the third acrylic monomer is, for example, 40 mol% or less based on 100 mol% of the total amount of the copolymerized constituents in the acrylic resin.

The composition ratio of the third acrylic monomer is preferably 25 mol% or less based on 100 mol% of the total amount of the copolymerized constituents in the acrylic resin. The composition ratio is more preferably 1 mol% or more and 20 mol% or less. When the composition ratio of

the third acrylic monomer is within such a range, it is preferable because the surface free energy of the release layer is not excessively lowered and the wettability is not lowered. The composition ratio of the long chain alkyl group may be 0 mol%.

[0048]

(Fourth Acrylic Monomer)

In one embodiment, the acrylic resin contains, as a copolymerized constituent, a radically polymerizable acrylic monomer other than the first to third acrylic monomers as a fourth acrylic monomer.

Examples of the fourth monomer include (meth)acrylic monomers and a non-acrylic vinyl monomers. 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-methylol acrylamide, and (meth)acrylonitrile; and vinyl methacrylate, which may be used singly or in combination of two or more of them.

For example, by incorporating such a monomer as a copolymerized constituent in the acrylic resin according to the present invention, it is possible to adjust the glass transition temperature (T_g) of the acrylic resin to within a desired range. In addition, in a stretching step or the like after applying the composition for forming a release layer, generation of cracks in the coating film (release layer) can be more effectively suppressed, and the release film can be uniformly stretched.

[0049]

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; vinyl halide monomers such as vinyl chloride and vinylidene chloride; which may be used singly or in combination of two or more of them.

[0050]

The fourth acrylic monomer is preferably the

remainder resulting from the determination of appropriate amounts of the first acrylic monomer, the second acrylic monomer, and the third acrylic monomer according to the present invention. The Tg of the copolymer is determined by the following Fox's equation.

[0051]

[Math 1]

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

W_n: mass fraction (% by mass) of each monomer

Tg_n: Tg (K) of homopolymer of each monomer

[0052]

The acrylic resin has a glass transition temperature (Tg) of preferably 40°C or higher, more preferably 45°C or higher, and still more preferably 50°C or higher. When the glass transition temperature of the acrylic resin is 40°C or higher, it is preferable because the hardness of the release layer is moderately increased.

[0053]

The acrylic resin has a glass transition temperature (Tg) of preferably 110°C or lower, more preferably 105°C or lower, and still more preferably 100°C or lower. The glass transition temperature (Tg) of the acrylic resin may be 80°C or lower.

When the glass transition temperature of the acrylic

resin is 110°C or lower, it is preferable because generation of cracks in the coating film can be effectively suppressed in a stretching process after applying the composition for forming a release layer, and the coating film can be uniformly stretched.

[0054]

The acid value of the acrylic resin is preferably 20 mgKOH/g or more, for example, more than 20 mgKOH/g, more preferably 40 mgKOH/g or more, and still more preferably 60 mgKOH/g or more. When the acid value of the acrylic resin is 20 mg KOH/g or more, it is preferable because, for example, the number of crosslinking points with an oxazoline crosslinking agent, a carbodiimide crosslinking agent, or the like increases, so that a strong coating film with a higher crosslinking density can be obtained.

[0055]

The acid value of the acrylic resin is preferably 300 mgKOH/g or less, more preferably 250 mgKOH/g or less, for example, less than 250 mgKOH/g, and still more preferably 200 mgKOH/g or less. When the acid value of the acrylic resin is 300 mgKOH/g or less, it is preferable because cracks are not generated when the release film is stretched. For example, the crosslinking density with the oxazoline crosslinking agent does not become excessively high, and the release film can be stretched well.

When the acrylic resin has an acid value of 300 mgKOH/g or less, it is preferable because when particles are contained in the composition for forming a release layer, the contained particles are uniformly dispersed without causing extreme interaction with, for example, carboxyl groups of the acrylic resin. In the present invention, when the dispersibility of the particles is good, it is preferable because it is possible to suppress generation of coarse protrusions on the release surface, and pinholes of the sheet hardly occur. When the acid value is 200 mgKOH/g or less, it is more preferable because generation of pinholes can be well suppressed even for a thin 0.2 μm ceramic sheet.

[0056]

The acrylic resin to be used in the present invention can be obtained by known radical polymerization. Any of emulsion polymerization, suspension polymerization, solution polymerization, bulk polymerization, and the like can be employed. From the viewpoint of handleability, solution polymerization is preferable. Examples of the water-soluble organic solvent that can be used for 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 combination with water.

[0057]

The polymerization initiator may be any known compound that generates radicals, and for example, a water-soluble azo-based polymerization initiator such as 2,2-azobis-2-methyl-N-2-hydroxyethyl propionamide is preferable. The temperature, time, and the like of the polymerization are appropriately chosen.

[0058]

The mass average molecular weight (M_w) of the acrylic resin is preferably about 10,000 to about 200,000. A more preferable range is 20,000 to 150,000. When the M_w is 10,000 or more, it is preferable because there is no risk of thermal decomposition in a tenter. When the M_w is 200,000 or less, it is preferable because the coating liquid does not significantly increase in viscosity and the coating property thereof is good.

[0059]

As the binder of the release layer in the present invention, a binder resin other than the acrylic resin may be used in combination. Examples of the other binder resin include polyester resins, urethane resins, polyvinyl-based resins (polyvinyl alcohol and the like), polyalkylene glycols, polyalkyleneimines, methylcellulose,

hydroxycellulose, and starches.

[0060]

The content of the acrylic resin in the composition for forming a release layer is preferably 20% by mass or more and 95% by mass or less in the total solid content. The content is more preferably 30% by mass or more and 90% by mass or less. When the content is 20% by mass or more, it is preferable because the amount of carboxyl groups as crosslinking components is not excessively small and the crosslinking density does not decrease. When the content is 95% by mass or less, it is preferable because the amount of the crosslinking agent to be crosslinked is not excessively small and the crosslinking density is not lowered.

[0061]

(Crosslinking Agent)

In the present invention, the composition for forming a release layer may comprise a crosslinking agent in order to form a crosslinked structure in the composition for forming a release layer. As the crosslinking agent, for example, at least one crosslinking agent selected from oxazoline-based crosslinking agents and carbodiimide-based crosslinking agents is preferably contained. By incorporating an oxazoline-based crosslinking agent and/or a carbodiimide-based crosslinking agent, for example,

adhesion to a PET substrate is improved and crosslinking with carboxyl groups that may be contained in the acrylic resin is promoted, whereby the coating film strength of the release layer can be improved and, as a result, the peeling force can be reduced. In one embodiment, an oxazoline-based crosslinking agent may be contained as the crosslinking agent.

In addition, other crosslinking agents may be used in combination, and examples of specific crosslinking agents that can be used in combination include urea-based crosslinking agents, epoxy-based crosslinking agents, melamine-based crosslinking agents, isocyanate-based crosslinking agents, and silanol-based crosslinking agents. In order to promote a crosslinking reaction, a catalyst or the like may be appropriately used, as necessary.

[0062]

Examples of the crosslinking agent having an oxazoline group include polymers having an oxazoline group obtained by (co)polymerizing a polymerizable unsaturated monomer having an oxazoline group with, as necessary, other polymerizable unsaturated monomer by a conventionally known method (for example, solution polymerization or emulsion polymerization).

[0063]

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 may be used singly or two or more of them may be used in combination.

[0064]

Examples of the other polymerizable unsaturated monomer include alkyl or cycloalkyl esters of (meth)acrylic acid wherein the alkyl or cycloalkyl has 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, wherein the hydroxyalkyl has 2 to 8 carbon atoms, such as 2-hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate; vinyl aromatic compounds, such as styrene and vinyltoluene; adducts of (meth)acrylamide, dimethylaminopropyl (meth)acrylamide, dimethylaminoethyl (meth)acrylate, and glycidyl (meth)acrylate with amines; polyethylene glycol (meth)acrylate; and N-vinylpyrrolidone, ethylene, butadiene, chloroprene, vinyl propionate, vinyl acetate, and (meth)acrylonitrile. These may be used singly or two or more of them may be used in combination.

[0065]

From the viewpoint of rendering a resulting crosslinking agent having an oxazoline group a water-soluble crosslinking agent to improve compatibility with other resins, wettability, and crosslinking reaction efficiency, and the like, the other polymerizable unsaturated monomer is preferably a hydrophilic monomer. Examples of the hydrophilic monomer include 2-hydroxyethyl(meth)acrylate, monomers each having a polyethylene glycol chain, such as methoxy polyethyleneglycol(meth)acrylate and 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 them, monomers having a polyethylene glycol chain, such as methoxy polyethylene glycol (meth)acrylate, which has a high solubility in water, and monoester compounds made of (meth)acrylic acid and polyethylene glycol, are preferable.

[0066]

The crosslinking agent having an oxazoline group preferably has an oxazoline group content of 3.0 to 9.0 mmol/g. The oxazoline group content is more preferably within a range of 4.0 to 8.0 mmol/g. When the content is

within the range of 3.0 to 9.0 mmol/g, it is preferable because a moderate crosslinked structure can be formed and the peeling force is reduced.

[0067]

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

[0068]

The content of the crosslinking agent in the composition for forming a release layer is preferably 5% by mass or more and 80% by mass or less in the total solid content. The content is more preferably 10% by mass or more and 70% by mass or less. When the content is 5% by mass or more, it is preferable because the crosslinking density of the resin of the coating layer does not

decrease. When the content is 80% by mass or less, it is preferable because the amount of carboxyl groups or the like in the acrylic resin that can be crosslinked is not excessively small and the crosslinking density is not lowered.

In one embodiment, the content of the crosslinking agent in the composition for forming a release layer is preferably smaller than the content of the acrylic resin.

The total solid content means that the total content of a resin solid component contained in the composition for forming a release layer, a solid component of the crosslinking agent added as necessary, and a catalyst added as necessary is 100 parts by mass.

[0069]

(Particles in Composition for Forming Release Layer)

The composition for forming a release layer may comprise lubricant particles. By containing lubricant particles, it is possible to control the peeling force of a sheet peeling starting point part, control the peeling force at the time of steady peeling, and more favorably impart slipperiness to a release layer 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, magnesium hydroxide, and barium sulfate, and (2) organic particles such as 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 particles.

[0070]

The average particle diameter of the particles is preferably 10 nm or more, more preferably 20 nm or more, and still more preferably 30 nm or more. When the average particle diameter of the particles is 10 nm or more, it is preferable because the particles are less likely to aggregate and slipperiness can be secured.

[0071]

The average particle diameter of the particles is preferably 500 nm or less, more preferably 400 nm or less, and still more preferably 300 nm or less. When the average

particle diameter of the particles is 500 nm or less, it is preferable because pinholes are hardly generated during sheet processing and the particles do not fall off.

[0072]

The average particle diameter of the particles was measured by a method in which particles in a cross section of a processed film were observed with a transmission electron microscope or a scanning electron microscope, 100 particles that were not aggregated were observed, and the average value thereof was taken as the average particle diameter.

[0073]

The shape of the particles is not particularly limited as long as it satisfies the object of the present invention, and spherical particles and non-spherical particles having an indefinite shape can be used. The particle diameter of the particles having an indefinite shape can be calculated as an equivalent circle diameter. The equivalent circle diameter is a value obtained by dividing the area of the observed particles by π , calculating the square root, and doubling the square root.

[0074]

The ratio of the particles to the total solid content of the composition for forming a release layer is preferably 50% by mass or less, more preferably 30% by mass

or less, and still more preferably 10% by mass or less. When the ratio of the particles to the total solid content of the composition for forming a release layer is 50% by mass or less, it is preferable because pinholes are hardly generated during sheet processing and falling off of the particles from the release layer does not significantly occur. The ratio of the particles may be 0% by mass. For example, the ratio of the particles to the total solid content of the composition for forming a release layer may be 0.5% by mass or more.

[0075]

As a method for measuring the content of particles contained in a release layer, for example, when the release layer contains an organic component resin and inorganic particles, the following method can be used. 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 the inorganic component can be obtained by applying heat to the obtained release layer and burning off the organic component contained in the release layer by heat. By measuring the weights of the obtained inorganic component and the release layer before burning off, the amount in % by 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 thermogravimetry / differential thermal analyzer. When there are a plurality of types of particles, the ratio of the particles in the total solid content of the release layer means the ratio of the total amount of the plurality of types of particles.

[0076]

(Additive)

In the present invention, by the use of an acrylic resin having a hydroxyl value of 150 mgKOH/g to 450 mgKOH/g, good wettability can be exhibited for a slurry, a resin solution, and the like to ceramic green sheets, cissing can be suppressed, and good releasability can be exhibited in a well-balanced manner. Furthermore, an additive may be added in order to improve releasability. As the additive to be contained in the composition for forming a release layer, a silicone-based additive, a non-silicone-based additive such as an olefin-based additive, a long chain alkyl-based additive, or a fluorine-based additive, or the like can be used. For example, in view of peelability, it is preferable to use a silicone-based additive. The silicone-based additive to be used in the present invention is effective not only in improving the releasability but also in improving a leveling property during application and defoaming a coating liquid.

[0077]

(Silicone-Based Additive in Composition for Forming Release Layer)

In the present invention, the silicone-based additive contained in the composition for forming a release layer is any 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. For example, polyorganosiloxanes and the like can be suitably used. Among the polyorganosiloxanes, polydimethylsiloxane (abbreviated as PDMS) can be suitably used, and those having a functional group as a part of polydimethylsiloxane are also preferable. It is preferable that the polyorganosiloxane has a functional group because due to the presence of the functional group, an intermolecular interaction such as hydrogen bonding is easily exhibited with the binder resin and the binder resin is hardly transferred to the sheet.

[0078]

The functional group to be introduced into the polydimethylsiloxane is not particularly limited, and may be a reactive functional group or a non-reactive functional group. In addition, the functional group may be introduced to one end of the polydimethylsiloxane, or may be introduced to both ends or side chains. In addition, the

functional group may be introduced to one position or to a plurality of positions.

[0079]

As the reactive functional group to be introduced into the polydimethylsiloxane, an amino group, an epoxy group, a hydroxyl group, a mercapto group, a carboxyl group, a methacrylic group, an acrylic group, and the like may 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, a phenyl group, and the like may be used. Although not particularly bound by a theory, those having an epoxy group, a carboxyl group, a polyether group, a methacrylic group, an acrylic group, or an ester group among the above groups are preferable.

[0080]

As the functional group to be introduced into the polydimethylsiloxane, a polyether group and an ester group are preferable, which do not react with a binder resin, is easily oriented on a surface of the release layer, and has little migration to a green sheet.

[0081]

The silicone-based additive to be used in the present invention preferably has a molecular weight of 40000 or less. More preferably, the molecular weight is 30000 or

less. When the molecular weight is 40000 or less, it is preferable because peelability is good.

[0082]

(Long Chain Alkyl-Based Additive in Composition for Forming Release Layer)

As the long chain alkyl-based additive, a long chain alkyl-modified resin can be used, and

polyvinyl alcohol, an acrylic resin, or the like having an alkyl group having about 8 to about 20 carbon atoms in a side chain is preferable. The acrylic resin described in this paragraph means an acrylic resin other than the acrylic resin having a specific hydroxyl value according to the present invention.

In addition, 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.

For example, by using a long chain alkyl-based additive different from the acrylic resin having a hydroxyl value of 150 mgKOH/g to 450 mgKOH/g, which is a main agent in the composition for forming a release layer, releasability is sometimes improved. Examples of commercially available products include PEEL0IL (registered trademark) 406 (available from Lion Specialty Chemicals

Co., Ltd.).

[0083]

(Other Additives in Composition for Forming Release Layer)

In order to impart other functionalities to the composition for forming a release layer, various additives other than the silicone additive may be incorporated as long as the characteristics of the present invention are not impaired, for example, as long as the applied appearance is not impaired. Examples of the additives include a fluorescent dye, a fluorescent whitener, a plasticizer, an ultraviolet absorber, a pigment dispersant, a foam-restraining agent, an anti-foaming agent, and a preservative.

[0084]

The composition for forming a release layer may comprise additives other than silicone additives for the purpose of improving a leveling property during application and defoaming a coating liquid. The additive may be any of a cationic additive, an anionic additive, and a nonionic additive, but an acetylene glycol-based additive or a fluorine-based additive is preferable. It is preferable that these additives are incorporated in the composition for forming a release layer in such a range that an abnormality in a coating appearance does not occur due to excessive addition of these additives.

[0085]

For example, the ratio of the additive based on 100% by mass of the total solid content of the composition for forming a release layer is preferably 20% by mass or less. When the ratio of the additive is 20% by mass or less, it is preferable because migration of the additive to the sheet does not excessively occur. The amount of the additive may be 0% by mass.

[0086]

As the application method, any of a so-called in-line coating method in which a coating liquid 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 a coating liquid is then separately applied with a coater can be applied. The in-line coating method is more efficient, and more preferable.

[0087]

As a method for applying a coating liquid to, for example, a polyethylene terephthalate (hereinafter sometimes abbreviated as PET) film, any known method can be used. Examples thereof include a reverse roll-coating method, a gravure coating method, a kiss coating method, a die coating method, a roll brushing method, a spray coating method, an air knife coating method, a wire bar coating method, a pipe doctor method, an impregnation coating

method, and a curtain coating method. The application is performed using these methods singly or in combination.

[0088]

In the present invention, examples of a method for providing a release layer on a polyester film include a method in which a composition for forming a release layer comprising a solvent, particles, and a resin is applied to a polyester film and dried. Examples of the solvent include an organic solvent such as toluene, water, or a mixed system of water and a water-soluble organic solvent, and from the viewpoint of environmental problems, water alone or a so-called aqueous solvent prepared by mixing water with a water-soluble organic solvent is preferable.

[0089]

The solid concentration of the composition for forming a release layer in a state of containing a solvent is preferably 0.5% by mass or more, and more preferably 1% by mass or more although it depends on the type of a binder resin, the type of the solvent, and the like. The solid concentration of the coating liquid is preferably 35% by mass or less, and more preferably 20% by mass or less.

[0090]

The drying temperature after application is preferably 70°C or higher, and preferably 250°C or lower, depending on the type of a binder resin, the type of the

solvent, the presence or absence of a crosslinking agent, the solid concentration, and the like.

[0091]

In the case of in-line coating, a coating liquid may be applied to an un-stretched film before stretching in a machine direction or may be applied to a uniaxially stretched film before stretching in a transverse direction after stretching in a machine direction. When the application is performed before stretching in the machine direction, it is preferable to provide a drying step before roll stretching. When applying to a uniaxially stretched film before stretching in the transverse direction, a film heating step in a tenter can also serve as a drying step, and therefore it is not always necessary to separately provide a drying step. The same applies to the case of simultaneous biaxial stretching.

[0092]

The 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. When the thickness of the release layer is 0.001 μm or more, it is preferable because the film formability of a coating film is maintained, so that a uniform coating film is obtained.

[0093]

The 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, particularly preferably 0.5 μm or less. When the thickness of the release layer is 2 μm or less, it is preferable because blocking does not occur.

[0094]

When both the surfaces of the substrate polyester film are different in surface roughness, the release layer may be laminated on any of the surfaces, but because a smoother release surface will be obtained, the release layer is preferably laminated on a smoother surface of the substrate.

[0095]

The outer film surface on which the release layer has been formed (the release layer surface that is not in contact with the polyester film) is desirably flat so as not to allow defects to occur in a sheet, a resin thin film, or the like to be applied and formed thereon. It is preferable that the average area surface roughness (S_a) is 10 nm or less and the maximum protrusion height (P) is 155 nm or less.

When the outer surface of the release layer satisfies such conditions, generation of pinholes tends to be suppressed.

In one embodiment, 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. Furthermore, it is more preferable that the average area surface roughness is 5 nm or less and the maximum protrusion height is 40 nm or less. When the area surface roughness is 5 nm or less and the maximum protrusion height is 50 nm or less, it is preferable because the generation of defects such as pinholes can be more effectively suppressed during sheet formation and the yield is favorable. It can be said that it is more preferable as the average area surface roughness (S_a) is smaller, but the average area surface roughness (S_a) may be 0.1 nm or more or may be 0.3 nm or more. It also can be said that it is more preferable as the maximum protrusion height (P) is smaller, but the maximum protrusion height (P) may be 1 nm or more or may be 3 nm or more.

[0096]

The surface free energy of the release layer is preferably 30 mJ/m² or more, more preferably 32 mJ/m² or more, and still more preferably 35 mJ/m² or more.

When the surface free energy of the release layer is 28 mJ/m² or more, it is preferable because cissing of a slurry, a resin solution, and the like for forming a ceramic green sheet hardly occurs.

Furthermore, when the surface free energy of the

release layer is more than 35 mJ/m², for example, 37 mJ/m² or more, good peelability and suppression of cissing of a slurry, a resin solution, and the like for forming ceramic green sheets can be exhibited in a more balanced manner.

In one embodiment, the surface free energy of the release layer may be 45 mJ/m² or more, for example, is 50 mJ/m² or more, for example, may be 60 mJ/m² or more.

When the surface free energy is set within such a range, it is more preferable because cissing is less likely to occur even when a slurry or a resin solution for forming ceramic green sheets is applied so as, for example, to form a 0.2 μm thin film is formed. In addition, generation of pinholes in a resulting ceramic green sheet or a resulting resin thin film can be effectively suppressed.

[0097]

(Method for Producing Release Film)

The method for producing a release film of the present invention comprises:

applying a composition for forming a release layer to an unstretched polyester film or a uniaxially stretched polyester film, and

after applying the composition for forming a release layer, in an unstretched state or after stretching in at least a uniaxial direction, performed heat-setting in a range of 80°C to 270°C.

[0098]

(Ceramic Green Sheet and Ceramic Capacitor)

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

[0099]

The release film of the present invention is particularly suitably used for producing such a multilayer ceramic capacitor. For example, a multilayer ceramic capacitor 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 the first or second internal electrode is printed on the applied and

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

[0100]

The release film of the present invention may be used when a resin thin film is formed. Examples of the resin thin film (also referred to as a resin sheet) include a cyclic olefin film (sheet), an ion exchange resin sheet, an ultraviolet-cured resin sheet, a urethane sheet, a polymer electrolyte film, and a pressure sensitive adhesive sheet.

EXAMPLES

[0101]

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.

[0102]

(NMR Measurement)

The ratio of a copolymerized constituent introduced into an acrylic resin 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 with a vacuum dryer and then dissolving the dried resin in deuterated chloroform. From the obtained NMR spectrum, the peak of the chemical shift δ (ppm) assigned to the moiety of each group was identified. The integrated intensity of each of the peaks obtained was determined, and the composition ratio (mol%) of the copolymerized constituent introduced into the acrylic resin was confirmed from the number of hydrogen atoms and the integrated intensity of the moiety of each group.

[0103]

(Confirmation of Tg)

The Tg of each acrylic resin was determined from the composition ratios of the copolymerized constituents determined by the NMR measurement and the above-described Fox's equation.

[0104]

(Stretching Adequacy)

In order to evaluate the stretching adequacy of an acrylic resin itself, the synthesized acrylic resins (A-1) to (A-11) were each charged into a mixed solvent (25°C) of 30% by mass of isopropanol and 70% by mass of water such that the solid concentration was 12% by mass, to prepare a solution containing the acrylic resin alone. Then, the solution was applied with Mayer bar #5 to a surface of a polyester film subjected to only longitudinal stretching. Then, a film sample on which a coating layer (thickness: 6.5 μm) had been formed was allowed to stand in a hot air circulation 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 TOYOB0 Engineering Co., Ltd.). The stretching apparatus was then placed in a hot air circulation oven at 100°C to slowly stretch the sample. The stretching operation was performed until the length became four times the length before stretching, and the stretching apparatus was taken out of 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 judged according to the following criteria.

○: No cracks are observed.

△: Some cracks are observed (one to four cracks).

×: Five or more cracks are observed or cracks are observed in the entire surface.

[0105]

(Acid Value, Hydroxyl Value)

The acid value is the number of mg of potassium hydroxide required to neutralize acid components such as free fatty acid and resin acid contained in 1 g of a sample. The measurement was performed according to JIS-K0070. The hydroxyl value is the number of mg of potassium hydroxide required to neutralize acetic acid bonded to the hydroxyl value when 1 g of a sample is acetylated. The measurement was performed according to JIS-K0070.

[0106]

(Quantitative Determination of Oxazoline Group in Resin Having Oxazoline Group)

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

[0107]

(Surface Characteristics of Coating Film and Uncoated

Substrate Film)

The surface characteristics of the coating film are represented by values measured under the following conditions using a noncontact surface profilometer system (VertScan R550H-M100). As the average area surface roughness (S_a), an average value of five measurements was adopted, and as the maximum protrusion height (P), a maximum value of five measurements was adopted.

(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)

[0108]

(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 a release surface of a release film, and the contact angles thereof were measured. As the contact angle, a contact angle after 10 seconds from the dropping of each liquid 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 a dispersion component γ_{sd} , a polar component γ_{sp} , and a 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 included in contact angle meter software (FAMAS).

[0109]

(Evaluation of Coating Property of Ceramic Slurry)

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

(Slurry Composition I)

Toluene 22.3 parts by mass

Ethanol 18.3 parts by mass

Barium titanate (average particle diameter: 100 nm)

57.5 parts by mass

HOMOGENOL L-18 (manufactured by Kao Corporation)

1.9 parts by mass

(Slurry Composition II)

Toluene 39.6 parts by mass

Ethanol 39.6 parts by mass

Dioctyl phthalate 3.3 parts by mass

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

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

Subsequently, the ceramic slurry was applied to a release surface of the obtained release film sample by using an applicator such that a ceramic green sheet after being dried might be 1.0 μm , 0.5 μm , or 0.2 μm , and then was dried at 60°C for 1 minute, and a coating property was evaluated according to following criteria.

In Table 3, it is simply expressed as "cissing".

⊙: At both 1.0 μm and 0.5 μm , the surface was coated without cissing or the like. In addition, even at 0.2 μm , the surface was coated without cissing or the like.

○: At both 1.0 μm and 0.5 μm , the surface was coated without cissing or the like.

△: At 1.0 μm , the surface was coated without cissing or the like. Whereas, at 0.5 μm , cissing partially occurred.

×: Sheet defects such as cissing were observed at all of 1.0 μm , 0.5 μm , and 0.2 μm .

[0110]

(Evaluation of Pinholes of Ceramic Green Sheet)

Ceramic green sheets having thicknesses of 1.0 μm and 0.2 μm were formed each on a release surface of a release film in the same manner as in the evaluation of the coating property of a ceramic slurry. Subsequently, the release film was peeled off from the formed release film with the ceramic green sheet to obtain the ceramic green sheet. In a range of 25 cm^2 in a central region of each of the obtained ceramic green sheet in the film transverse direction, light was applied to a surface opposite from a surface to which a ceramic slurry was applied, and the generation status of pinholes viewed due to passing of light was visually observed.

○: No pinholes are generated.

△: No pinholes are generated at 1.0 μm , and pinholes are generated at 0.2 μm .

×: Pinholes are generated at 1.0 μm and 0.2 μm

[0111]

(Evaluation of Peelability of Ceramic Green Sheet)

Slurry composition I composed of the materials shown below was stirred and mixed for 10 minutes, and dispersed for 10 minutes with zirconia beads having a diameter of 0.5

mm using a bead mill to obtain a primary dispersion.

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

(Slurry Composition I)

Toluene 22.3 parts by mass

Ethanol 18.3 parts by mass

Barium titanate (average particle diameter: 100 nm)
57.5 parts by mass

HOMOGENOL L-18 (manufactured by Kao Corporation)
1.9 parts by mass

(Slurry Composition II)

Toluene 39.6 parts by mass

Ethanol 39.6 parts by mass

Dioctyl phthalate 3.3 parts by mass

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

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

[0112]

Subsequently, the ceramic slurry was applied to a release surface of the obtained release film sample by

using an applicator such that the slurry after being dried might have a thickness of 1.0 μm , and then was dried at 60°C for 1 minute to form a ceramic green sheet on the release film. The obtained release film with the ceramic green sheet was statically eliminated using astatic eliminator (SJ-F020, manufactured by Keyence Corporation), and then peeled off at a peeling angle of 90°, a peeling temperature of 25°C, and a peeling speed of 10 m/min using a peeling tester (VPA-3, manufactured by Kyowa Interface Science Co., Ltd., load cell load: 0.1 N). As a direction of peeling, a double-sided adhesive tape (No. 535A, manufactured by Nitto Denko Corporation) was attached on a SUS plate attached to the peeling tester, and the release film was fixed with the ceramic green sheet side bonded 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 the peeling force at a peel distance of 20 mm to 70 mm was calculated, and the value was taken as the peeling force. The measurement was performed five times in total, and the average value of the peeling force was adopted and evaluated. Determination was made according to the following criteria based on the obtained numerical value of the peeling force.

⊙: 0.5 mN/mm or more, and 1.0 mN/mm or less

○: More than 1.0 mN/mm, and 2.0 mN/mm or less

△: More than 2.0 mN/mm, and 2.5 mN/mm or less

×: Less than 0.5 mN/mm or more than 2.5 mN/mm

[0113]

(Evaluation of Pinholes of Resin Sheet)

Three resin solutions for resin sheet formation were prepared using the following method.

(Resin Sheet (1))

0.5 parts by mass of a cyclic olefin resin (ARTON (registered trademark) G7810, manufactured by JSR Corporation, solid content: 100% by mass) was dissolved in 80 parts by mass of toluene and 20 parts by mass of tetrahydrofuran to prepare resin solution (1). The resin solution was applied to 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. Subsequently, the release film was peeled off from the release film with the formed cyclic olefin resin sheet to obtain cyclic olefin resin sheet (1).

[0114]

(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% by mass), 10 parts by mass of water, and

20 parts by mass of isopropyl alcohol were mixed to prepare resin solution (2). The resin solution was applied to 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. Subsequently, the release film was peeled off from the release film with the formed ion exchange resin sheet to obtain ion exchange resin sheet (2).

[0115]

(Resin Sheet (3))

20 parts by mass of an ultraviolet-curable resin (urethane acrylate, product name: 8UX-015A, manufactured by Taisei Fine Chemical Co., Ltd., solid content: 100% by mass), 40 parts by mass of methyl ethyl ketone, 39 parts by mass of isopropyl alcohol, and 1 part by mass of a photoradical initiator (Irgacure (registered trademark) 907, manufactured by BASF SE) were mixed to prepare resin solution (3). The resin solution was applied to 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-cured resin sheet. Subsequently, the release film was peeled off from the release film with the formed ultraviolet-cured resin sheet

to obtain ultraviolet-cured resin sheet (3).

All the three resin sheets obtained were evaluated by the following method.

In a range of 25 cm² in a central region of each of the obtained resin sheet in the film transverse direction, light was applied to a surface opposite from a surface to which a resin slurry was applied, and the generation status of pinholes viewed due to passing of light was visually observed.

○: No pinholes are generated in any resin sheet.

△: Almost no pinholes are generated.

×: There are a large number of pinholes.

[0116]

(Preparation of Polyethylene Terephthalate Pellets (PET (I)))

As an esterification reactor, a continuous esterification reactor composed of a three-stage complete mixing tank having a stirrer, a partial condenser, a raw material inlet and a product outlet was used. The amount of TPA (terephthalic acid) was set to 2 tons/hour, and the amount of EG (ethylene glycol) was set to 2 mol per 1 mol of TPA. The amount of antimony trioxide was set such that the amount of Sb atoms with respect to the produced PET was set to 160 ppm. These slurries were continuously fed 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. Subsequently, the reaction product in the first esterification reaction can was continuously taken out of the system, and fed to a second esterification reaction can. 8% by mass of EG distilled off from the first esterification reaction can with respect to the produced PET was fed into the second esterification reaction can. Furthermore, an EG solution containing magnesium acetate tetrahydrate in an amount set such that the amount of Mg atoms with respect to the produced PET was set to 65 ppm and an EG solution containing TMPA (trimethyl phosphate) in an amount set such that the amount of P atoms with respect to the produced PET was set to 40 ppm were added, and reacted at 260°C at normal pressure for an average residence time of 1 hour. Subsequently, the reaction product of the second esterification reaction can was continuously taken out of the system, and fed to a third esterification reaction can. 0.2% by mass of porous colloidal silica having an average particle diameter of 0.9 μm and subjected to dispersion treatment with the average number of treatments of 5 passes under pressure of 39 MPa (400 kg/cm²) using a high pressure disperser (manufactured by Nippon Seiki Co., Ltd.), and 0.4% by mass of synthetic calcium carbonate having an average particle diameter of 0.6 μm and obtained by

attaching 1% by mass of a polyacrylic acid ammonium salt per calcium carbonate were added in the form of 10% EG slurries, and reacted at 260°C at normal pressure for an average residence time of 0.5 hours. The esterification reaction product produced in the third esterification reaction can was continuously fed to a three-stage continuous polycondensation reaction apparatus to perform polycondensation, and the polycondensation product was filtered with a filter prepared by sintering stainless steel fibers having a 95% cut diameter of 20 μm , and then subjected to ultrafiltration, then, the filtered product was extruded into water, cooled, and then cut into a chip shape to obtain PET chips having an intrinsic viscosity of 0.60 dl/g (hereinafter abbreviated as PET (I)). The content of the lubricant in the PET chip was 0.6% by mass.

[0117]

(Preparation of Polyethylene Terephthalate Pellets (PET (II)))

Meanwhile, in the production of the PET (I) chips, PET chips having an intrinsic viscosity of 0.62 dl/g and containing no particles of calcium carbonate, silica, or the like were obtained (hereinafter abbreviated as PET (II)).

[0118]

(Preparation of Polyethylene Terephthalate Pellets (PET

(III)))

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

[0119]

(Production of Acrylic Resin A-1)

A four-necked flask equipped with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet tube was charged with 100 parts by mass of hydroxyethyl methacrylate (HEMA), 8 parts by mass of methacrylic acid (MAA), 33 parts by mass of stearyl methacrylate (SMA), 3 parts by mass of methyl methacrylate (MMA), and 336 parts by mass of isopropyl alcohol (IPA), and the temperature in the flask was raised to 80°C with stirring. Stirring was conducted for 3 hours while the temperature in the flask was maintained at 80°C, and then 0.5 parts by mass of 2,2-azobis-2-methyl-N-2-hydroxyethylpropionamide was added to the flask. The atmosphere in the flask was replaced by nitrogen while the temperature in the flask was raised to 120°C, and then the mixture was stirred at 120°C for 2

hours.

Subsequently, a decompression operation to 1.5 kPa was performed at 120°C to remove unreacted raw materials and the solvent, thereby obtaining an acrylic resin. The inside of the flask was returned to atmospheric pressure and cooled to room temperature, and 575 parts by mass of an aqueous IPA solution (water content: 50% by mass) was added and mixed. Thereafter, ammonia was added using a dropping funnel with stirring, and the acrylic resin was neutralized until the pH of the solution reached a range of 5.5 to 7.5 to obtain acrylic resin (A-1) having a solid concentration of 20% by mass. The composition ratio, Tg, stretching adequacy, and acid value of the acrylic resin (A-1) measured by NMR were also shown in Table 1.

[0120]

(Production of Acrylic Resins (A-2) to (A-11))

Acrylic resins (A-2) to (A-11) each having a solid concentration of 20% by mass were obtained in the same manner as in the production of the acrylic resin 1 except that the amounts of HEMA, MAA, SMA, MMA, IPA at the time of charging, and an aqueous IPA solution at the time of dilution were changed as shown in Table 1. The composition ratio, Tg, stretching adequacy, acid value, and hydroxyl value of the acrylic resins (A-2) to (A-11) measured by NMR were also shown in Table 1. The composition ratios were

expressed as n_1 (unit) for HEMA, n_2 (unit) for MAA, n_3 (unit) for SMA, and n_4 (unit) for MMA.

[0121]

[Table 1A]

Number	Acrylic resin									Solvent			
	n1		n2		n3		n4		Neutralizing agent	In polymerization	In dilution		
	Material	Number of parts charged (parts by mass)	Material	Number of parts charged (parts by mass)	Material	Number of parts charged (parts by mass)	Material	Number of parts charged (parts by mass)		Material	Number of parts charged (parts by mass)	Material	Number of parts charged (parts by mass)
A-1	HEMA	100	MAA	8	SMA	33	MMA	2	NH3	IPA	336	Aqueous IPA solution	575
A-2		100		9		0		31	NH3		327		560
A-3		100		13		52		46	NH3		493		846
A-4		100		13		87		10	NH3		490		841
A-5		100		7		0		1	NH3		251		430
A-6		100		6		152		0	NH3		600		1029
A-7		100		7		52		54	NH3		496		850
A-8		100		26		52		31	NH3		488		837
A-9		100		40		52		15	NH3		483		828
A-10		100		26		0		277	NH3		941		1614
A-11		0		10		42		100	NH3		353		605

HEMA Methyl methacrylate HEMA Hydroxyethyl methacrylate

SMA Stearyl methacrylate MAA Methacrylic acid

[0122]

[Table 1B]

Number	Composition ratio (mol%) in acrylic resin				Acrylic monomer ratio	Properties			
	n1	n2	n3	n4		Tg (°C)	Stretching adequacy	Acid value (mgKOH/g)	Hydroxyl value (mgKOH/g)
A-1	78	10	10	2	7.8	49	○	77	300
A-2	65	9	0	26	7.2	62	○	85	308
A-3	50	10	10	30	5.0	66	○	82	204
A-4	60	12	20	8	5.0	55	○	82	205
A-5	90	9	0	1	10.0	47	○	80	401
A-6	60	5	35	0	12.0	42	○	28	168
A-7	50	5	10	35	10.0	64	○	41	203
A-8	50	20	10	20	2.5	72	○	165	206
A-9	50	30	10	10	1.7	77	○	250	208
A-10	20	8	0	72	2.5	94	○	86	107
A-11	0	9	10	81	0.0	103	○	82	0

[0123]

(Production of Oxazoline-based Crosslinking Agent C-1)

A flask equipped with a stirrer, a reflux condenser, a nitrogen inlet tube, and a thermometer was charged with 460.6 parts of isopropyl alcohol, and heated to 80°C while gently flowing nitrogen gas. 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 conducted for 5 hours. During the reaction, nitrogen gas was continued to flow, and the temperature in the flask was kept at $80 \pm 1^{\circ}\text{C}$. Thereafter, the reaction solution was cooled, affording a resin (C-1) having an oxazoline group with a solid concentration of 10%. The obtained resin (C-1) having an oxazoline group had an oxazoline group amount of 7.7 mmol/g and a number average molecular weight measured by GPC (gel permeation chromatography) of 40000.

[0124]

(Production of Oxazoline-based Crosslinking Agent C-2)

A resin (C-2) having an oxazoline group with a solid concentration of 25% and having a different composition (oxazoline group amount and molecular weight) 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 a number average molecular weight measured by GPC of 20000.

[0125]

(Silica Particle D-1)

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

particle diameter: 40 nm, solid concentration: 40% by mass)

[0126]

(Additive E-1)

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

(Additive E-2)

OLFINE E1010 (solid concentration: 100% by mass,
manufactured by Nissin Chemical Industry Co., Ltd.)

(Additive E-3)

PEELOIL ® 406 (solid concentration: 15% by mass,
manufactured by Lion Specialty Chemicals Co., Ltd.)

[0127]

(Example 1)

(Preparation of Composition 1 for Forming Release Layer)

A composition 1 for forming a release layer having
the following composition was prepared.

(Composition 1 for Forming Release Layer)

Water 45.76 parts by mass

Isopropyl alcohol 28.20 parts by mass

Acrylic resin A-1 (solid concentration: 20% by mass)

14.00 parts by mass

Oxazoline-based crosslinking agent C-1 (solid
concentration: 10% by mass) 12.00 parts by mass

Additive E-1 0.04 parts by mass

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

[0128]

(Production of Polyester Film)

The PET chips were dried, then melted at 285°C, melted at 290°C with separate melt extruder, subjected to two-stage filtration with a filter prepared by sintering stainless steel fibers having a 95% cut diameter of 15 μm and a filter prepared 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 to be PET (I)/(II) = 60% by mass/40% by mass in the calculation of the discharge amounts of the respective extruders. Subsequently, the un-stretched sheet was heated with an infrared heater, and then stretched 3.5 times in the machine direction by a speed difference between rolls at a roll temperature of 80°C.

[0129]

Subsequently, the composition for forming a release layer was applied to the surface layer A of the PET film with a bar coater, and then dried at 80°C for 15 seconds. The coating amount after final stretching and drying was adjusted to be 0.07 μm . Subsequently, using a tenter, the film was stretched by 4.0 times in a transverse direction at 150°C, heated at 230°C for 0.5 seconds with the length of the film in the transverse direction fixed. The film was further subjected to relaxation treatment in the transverse direction by 3% at 230°C for 10 seconds to obtain an in-line release coated polyester film having a thickness of 31 μm . The surface layer B (anti-release surface side) of the obtained film had an Sa of 28 nm and a P of 754 nm. Here, the PET substrate containing no release layer is represented by Z. The obtained PET substrate had an intrinsic viscosity of 0.59 dl/g. The surface layer A of the PET substrate containing no release layer had an Sa of 1 nm and a P of 16 nm.

[0130]

(Example 2)

A release polyester film was obtained in the same manner as in Example 1 except that the composition 1 for forming a release layer was changed to the following composition 2 for forming a release layer.

(Composition 2 for Forming Release Layer)

Water 48.46 parts by mass

Isopropyl alcohol 27.50 parts by mass

Acrylic resin A-1 (solid concentration: 20% by mass)

16.00 parts by mass

Oxazoline-based crosslinking agent C-1 (solid
concentration: 10% by mass) 8.00 parts by mass

Additive E-1 0.04 parts by mass

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

[0131]

(Example 3)

A release polyester film was obtained in the same
manner as in Example 1 except that the composition 1 for
forming a release layer was changed to the following
composition 3 for forming a release layer.

(Composition 3 for Forming Release Layer)

Water 40.39 parts by mass

Isopropyl alcohol 29.57 parts by mass

Acrylic resin A-1 (solid concentration: 20% by mass)

10.00 parts by mass

Oxazoline-based crosslinking agent C-1 (solid
concentration: 10% by mass) 20.00 parts by mass

Additive E-1 0.04 parts by mass

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

[0132]

(Example 4)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition 1 for forming a release layer used in Example 1 was changed to an acrylic resin A-2 (solid concentration: 20% by mass).

[0133]

(Example 5)

A release polyester film was obtained in the same manner as in Example 1 except that a composition 5 for forming a release layer in which the crosslinking agent in the composition 1 for forming a release layer used in Example 1 was changed to an oxazoline-based crosslinking agent C-2 (solid concentration: 25% by mass) was used.

(Composition 5 for Forming Release Layer)

Water 52.96 parts by mass

Isopropyl alcohol 28.20 parts by mass

Acrylic resin A-1 (solid concentration: 20% by mass)
14.00 parts by mass

Oxazoline-based crosslinking agent C-2 (solid concentration: 25% by mass) 4.80 parts by mass

Additive E-1 0.04 parts by mass

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

[0134]

(Example 6)

A release polyester film was obtained in the same
manner as in Example 1 except that a composition 6 for
forming a release layer in which the acrylic resin A-1
(solid concentration: 20% by mass) in the composition 1 for
forming a release layer used in Example 1 was changed to an
acrylic resin A-2 (solid concentration: 20% by mass) and
the crosslinking agent was changed to an oxazoline-based
crosslinking agent C-2 (solid concentration: 25% by mass)
was used.

(Composition 6 for Forming Release Layer)

Water 52.96 parts by mass

Isopropyl alcohol 28.20 parts by mass

Acrylic resin A-2 (solid concentration: 20% by mass)
14.00 parts by mass

Oxazoline-based crosslinking agent C-2 (solid
concentration: 25% by mass) 4.80 parts by mass

Additive E-1 0.04 parts by mass

(Polyether-modified polydimethylsiloxane, 67 Additive,
solid concentration: 100% by mass, manufactured by Dow

Corning Toray Co., Ltd.)

[0135]

(Example 7)

A release polyester film was obtained in the same manner as in Example 1 except that the composition 1 for forming a release layer was changed to the following composition 7 for forming a release layer.

(Composition 7 for Forming Release Layer)

Water 45.26 parts by mass

Isopropyl alcohol 28.20 parts by mass

Acrylic resin A-1 (solid concentration: 20% by mass)
14.00 parts by mass

Oxazoline-based crosslinking agent C-1 (solid
concentration: 10% by mass) 12.00 parts by mass

Silica particle D-1 0.50 parts by mass

(Average particle diameter: 40 nm, solid concentration: 40%
by mass)

Additive E-1 0.04 parts by mass

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

[0136]

(Example 8)

A release polyester film was obtained in the same manner as in Example 1 except that the composition 1 for

forming a release layer was changed to the following composition 8 for forming a release layer.

(Composition 8 for Forming Release Layer)

Water 45.26 parts by mass

Isopropyl alcohol 28.20 parts by mass

Acrylic resin A-2 (solid concentration: 20% by mass)

14.00 parts by mass

Oxazoline-based crosslinking agent C-1 (solid concentration: 10% by mass) 12.00 parts by mass

Silica particle D-1 0.50 parts by mass

(Average particle diameter: 40 nm, solid concentration: 40% by mass)

Additive E-1 0.04 parts by mass

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

[0137]

(Example 9)

A release polyester film was obtained in the same manner as in Example 1 except that the composition 1 for forming a release layer was changed to the following composition 9 for forming a release layer.

(Composition 9 for Forming Release Layer)

Water 44.76 parts by mass

Isopropyl alcohol 28.20 parts by mass

Acrylic resin A-1 (solid concentration: 20% by mass)

14.00 parts by mass

Oxazoline-based crosslinking agent C-1 (solid
concentration: 10% by mass) 12.00 parts by mass

Silica particle D-1 1.00 part by mass

(Average particle diameter: 40 nm, solid concentration: 40%
by mass)

Additive E-1 0.04 parts by mass

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

[0138]

(Example 10)

A release polyester film was obtained in the same
manner as in Example 1 except that the composition 1 for
forming a release layer was changed to the following
composition 10 for forming a release layer.

(Composition 10 for Forming Release Layer)

Water 44.76 parts by mass

Isopropyl alcohol 28.20 parts by mass

Acrylic resin A-2 (solid concentration: 20% by mass)

14.00 parts by mass

Oxazoline-based crosslinking agent C-1 (solid
concentration: 10% by mass) 12.00 parts by mass

Silica particle D-1 1.00 part by mass

(Average particle diameter: 40 nm, solid concentration: 40% by mass)

Additive E-1 0.04 parts by mass

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

[0139]

(Example 11)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition for forming a release layer 1 used in Example 1 was changed to an acrylic resin A-3 (solid concentration: 20% by mass).

[0140]

(Example 12)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition for forming a release layer 1 used in Example 1 was changed to an acrylic resin A-4 (solid concentration: 20% by mass).

[0141]

(Example 13)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition for

forming a release layer 1 used in Example 1 was changed to an acrylic resin A-5 (solid concentration: 20% by mass).

[0142]

(Example 14)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition for forming a release layer 1 used in Example 1 was changed to an acrylic resin A-6 (solid concentration: 20% by mass).

[0143]

(Example 15)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition for forming a release layer 1 used in Example 1 was changed to an acrylic resin A-7 (solid concentration: 20% by mass).

[0144]

(Example 16)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition for forming a release layer 1 used in Example 1 was changed to an acrylic resin A-8 (solid concentration: 20% by mass).

[0145]

(Example 17)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition for forming a release layer 1 used in Example 1 was changed to an acrylic resin A-9 (solid concentration: 20% by mass).

[0146]

(Example 18)

A release polyester film was obtained in the same manner as in Example 1 except that the composition 1 for forming a release layer was changed to the following composition 18 for forming a release layer.

(Composition 18 for Forming Release Layer)

Water 45.76 parts by mass

Isopropyl alcohol 28.20 parts by mass

Acrylic resin A-1 (solid concentration: 20% by mass)

14.00 parts by mass

Oxazoline-based crosslinking agent C-1 (solid concentration: 10% by mass) 12.00 parts by mass

Additive E-2 0.04 parts by mass

(OLFINE E1010, solid concentration: 100% by mass, manufactured by Nissin Chemical Industry Co., Ltd.)

[0147]

(Example 19)

A release polyester film was obtained in the same manner as in Example 1 except that the thickness of the

release layer was changed to be 0.035 μm .

[0148]

(Example 20)

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

[0149]

(Example 21)

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

[0150]

(Example 22)

A release polyester film was obtained in the same manner as in Example 1 except that the following composition 20 for forming a release layer not containing the additive in the composition 1 for forming a release layer used in Example 1 was used.

(Composition 20 for Forming Release Layer)

Water 45.80 parts by mass

Isopropyl alcohol 28.20 parts by mass

Acrylic resin A-1 (solid concentration: 20% by mass)
14.00 parts by mass

Oxazoline-based crosslinking agent C-1 (solid
concentration: 10% by mass) 12.00 parts by mass

[0151]

(Example 23)

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

Here, the PET substrate containing no release layer is represented by Y. The obtained PET substrate had an intrinsic viscosity of 0.59 dl/g. The surface layer A of the PET substrate Y containing no release layer had an Sa of 10 nm and a P of 130 nm.

[0152]

(Comparative Example 1)

A release polyester film was obtained in the same manner as in Example 1 except that the composition 1 for forming a release layer was changed to the following composition 21 for forming a release layer.

(Composition 21 for Forming Release Layer)

Water 76.76 parts by mass

Isopropyl alcohol 19.19 parts by mass

Curable silicone aqueous emulsion B-1 4.01 parts
by mass

(manufactured by Shin-Etsu Chemical Co., Ltd., solid
concentration: 40%, KM3951)

Platinum-based catalyst B-2 (CAT-PM-10 A,
manufactured by Shin-Etsu Chemical Co., Ltd.) 0.04 parts

by mass

[0153]

(Comparative Example 2)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition 1 for forming a release layer used in Example 1 was changed to an acrylic resin A-10 (solid concentration: 20% by mass).

[0154]

(Comparative Example 3)

A release polyester film was obtained in the same manner as in Example 1 except that the acrylic resin A-1 (solid concentration: 20% by mass) in the composition 1 for forming a release layer used in Example 1 was changed to an acrylic resin A-11 (solid concentration: 20% by mass).

[0155]

The evaluation results of Examples and Comparative Examples are shown in Tables 2 and 3.

[0156]

[Table 2A]

	Substrate	Composition for forming release layer (The composition ratio is expressed in parts by mass of each solid content.)										
		Composition No.	Resin				Crosslinking agent or catalyst	Resin/(cross linking agent or catalyst) ratio (parts by mass)	Particles	Particle ratio (parts by mass)	Additive	Additive ratio (parts by mass)
			Type	SMA ratio mol %	Acid value mgKOH /g	Hydroxyl value mgKOH /g						
Example 1	Z	1	A-1	10	77	300	C-1	70/30	-	-	E-1	1.0
Example 2	Z	2	A-1	10	77	300	C-1	80/20	-	-	E-1	1.0
Example 3	Z	3	A-1	10	77	300	C-1	50/50	-	-	E-1	1.0
Example 4	Z	4	A-2	0	85	308	C-1	70/30	-	-	E-1	1.0
Example 5	Z	5	A-1	10	77	300	C-2	70/30	-	-	E-1	1.0
Example 6	Z	6	A-2	0	85	308	C-2	70/30	-	-	E-1	1.0
Example 7	Z	7	A-1	10	77	300	C-1	70/30	D-1	5	E-1	1.0
Example 8	Z	8	A-2	0	85	308	C-1	70/30	D-1	5	E-1	1.0
Example 9	Z	9	A-1	10	77	300	C-1	70/30	D-1	10	E-1	1.0
Example 10	Z	10	A-2	0	85	308	C-1	70/30	D-1	10	E-1	1.0
Example 11	Z	11	A-3	10	82	204	C-1	70/30	-	-	E-1	1.0
Example 12	Z	12	A-4	20	82	205	C-1	70/30	-	-	E-1	1.0
Example 13	Z	13	A-5	0	80	401	C-1	70/30	-	-	E-1	1.0
Example 14	Z	14	A-6	35	28	168	C-1	70/30	-	-	E-1	1.0

[0157]

[Table 2B]

	Substrate	Composition for forming release layer (The composition ratio is expressed in parts by mass of each solid content.)										
		Composition No.	Resin				Crosslinking agent or catalyst	Resin/(cross linking agent or catalyst) ratio (parts by mass)	Particles	Particle ratio (parts by mass)	Additive	Additive ratio (parts by mass)
			Type	SMA ratio mol %	Acid value mgKOH /g	Hydroxyl value mgKOH /g						
Example 15	Z	15	A-7	10	41	203	C-1	70/30	-	-	E-1	1.0
Example 16	Z	16	A-8	10	165	206	C-1	70/30	-	-	E-1	1.0
Example 17	Z	17	A-9	10	250	208	C-1	70/30	-	-	E-1	1.0
Example 18	Z	18	A-1	10	77	300	C-1	70/30	-	-	E-2	1.0
Example 19	Z	1	A-1	10	77	300	C-1	70/30	-	-	E-1	1.0
Example 20	Z	1	A-1	10	77	300	C-1	70/30	-	-	E-1	1.0
Example 21	Z	1	A-1	10	77	300	C-1	70/30	-	-	E-1	1.0
Example 22	Z	20	A-1	10	77	300	C-1	70/30	-	-	-	-
Example 23	Y	1	A-1	10	77	300	C-1	70/30	-	-	E-1	1.0
Comparative Example 1	Z	21	B-1	0	0	0	B-2	98/2	-	-	-	-
Comparative Example 2	Z	22	A-10	0	86	107	C-1	70/30	-	-	E-1	1.0
Comparative Example 3	Z	23	A-11	10	82	0	C-1	70/30	-	-	E-1	1.0

[0158]

[Table 3A]

	Evaluation of release layer						Ceramic green sheet		Resin sheet
	Ceramic peeling force (mN/mm)	Determination of ceramic peeling force	Sa (nm)	P (nm)	Thickness of release layer (nm)	γ_s (mJ/m ²)	Cissing	Pinhole	Pinhole
Example 1	0.8	⊙	0.7	13.7	70.0	40.3	○	○	○
Example 2	0.7	⊙	0.7	15.6	70.0	37.6	○	○	○
Example 3	1.2	○	0.8	17.3	70.0	44.2	○	○	○
Example 4	1.1	○	1.2	33.4	70.0	69.7	⊙	○	○
Example 5	1.0	⊙	0.8	13.2	70.0	35.8	○	○	○
Example 6	1.2	○	1.4	35.6	70.0	63.2	⊙	○	○
Example 7	0.7	⊙	2.2	46.0	70.0	38.9	○	○	○
Example 8	1.1	○	2.3	44.7	70.0	68.5	⊙	○	○
Example 9	0.7	⊙	2.7	48.3	70.0	38.6	○	○	○
Example 10	1.2	○	2.9	45.5	70.0	68.3	⊙	○	○
Example 11	1.3	○	0.9	12.4	70.0	39.0	○	○	○
Example 12	0.9	⊙	0.9	14.5	70.0	33.3	△	○	○
Example 13	1.0	⊙	1.4	36.2	70.0	71.9	⊙	○	○
Example 14	1.2	○	0.8	13.6	70.0	32.3	△	○	○

[0159]

[Table 3B]

	Evaluation of release layer						Ceramic green sheet		Resin sheet
	Ceramic peeling force (mN/mm)	Determination of ceramic peeling force	Sa (nm)	P (nm)	Thickness of release layer (nm)	γ_s (mJ/m ²)	Cissing	Pinhole	Pinhole
Example 15	1.4	○	0.8	12.9	70.0	36.4	○	○	○
Example 16	1.0	⊙	0.9	16.2	70.0	40.9	○	○	○
Example 17	1.1	○	0.8	13.8	70.0	41.5	○	△	△
Example 18	0.8	⊙	0.8	12.5	70.0	42.3	○	○	○
Example 19	0.8	⊙	0.8	16.2	35.0	39.8	○	○	○
Example 20	0.8	⊙	0.8	12.3	100.0	42.1	○	○	○
Example 21	0.9	⊙	0.8	11.2	140.0	43.0	○	○	○
Example 22	0.9	⊙	0.8	13.2	70.0	39.9	○	○	○
Example 23	0.8	⊙	10.5	152.0	70.0	40.3	○	△	△
Comparative Example 1	0.7	⊙	0.9	48.2	70.0	18.0	×	×	×
Comparative Example 2	3.5	×	0.9	14.4	70.0	60.7	⊙	×	×
Comparative Example 3	3.8	×	0.7	13.3	70.0	40.5	○	×	×

[0160]

In Tables 2 and 3 above, for the resin, the crosslinking agent, the particles, and the additives, each composition for forming a release layer is expressed by a solid content in parts by mass. The sum total of the solid contents in parts by mass of the resin, the crosslinking agent, the particles, and the additives present in the composition for forming a release layer is the solid content of the release layer in parts by mass. For the resin, the crosslinking agent, the particles, and the additives, each solid content in parts by mass is divided by the total solid content of the release layer in parts by mass, whereby the mass percent of the resin, the crosslinking agent, the particles, and the additives in the total solid content in the release layer can be determined.

[0161]

In Examples 1 to 24, it was possible to manufacture the products at a reduced production cost by in-line coating, and even when sheets were further thinned, good wettability for a slurry and a resin solution for sheet and a moderate sheet peeling force were exhibited.

On the other hand, in Comparative Example 1, since the acrylic resin according to the present invention was not contained, the wettability for a slurry and a resin solution for a sheet was poor, and pinholes were generated.

In Comparative Examples 2 and 3, since the hydroxyl value of the acrylic resin was smaller than the range of the present invention, for example, a lowered reaction rate with oxazoline was obtained, so that an increased sheet peeling force was exhibited. Since the sheet peeling force was large, pinholes were generated in the sheet during peeling.

[0162]

As described above, the release film of the present invention can exhibit good wettability for, for example, a slurry, a resin solution, and the like for ceramic green sheets, and can suppress cissing.

In addition, generation of pinholes in ceramic green sheets or the like to be obtained can be suppressed.

Furthermore, any release film according to the present invention can have a moderate peelability while suppressing cissing. Therefore, it is possible to suppress the breakage of an obtained ceramic green sheet, resin thin film, or the like when peeling it off from the release film.

In addition, with the release film of the present invention, a required ceramic green sheet, a required resin thin film, and the like can be formed with a film thickness more uniform than before, and thinning can also be achieved.

Furthermore, the release film according to the present invention can be produced by an in-line coating process, and the production cost can be suppressed. In addition, it is possible to reduce waste loss of ceramic green sheets, resin thin films, and the like, and it is possible to contribute to reduction of environmental load.

INDUSTRIAL APPLICABILITY

[0163]

By the present invention, it is possible to produce a release film which can be produced at a reduced production cost and can have all of good wettability for a slurry and a resin solution for sheet and a moderate sheet peeling force even when a sheet is further thinned.

CLAIMS

1. A release film having a release layer on at least one surface of a polyester film directly or with another layer interposed between the release layer and the polyester film, wherein

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

the composition for forming a release layer comprises an acrylic resin,

the acrylic resin has a hydroxyl value of 150 mgKOH/g or more and 450 mgKOH/g or less,

the acrylic resin is a resin prepared by copolymerizing two or more types of acrylic monomers selected from the group consisting of:

an acrylic monomer having a hydroxyl group as a first acrylic monomer,

an acrylic monomer having a carboxyl group as a second acrylic monomer,

an acrylic monomer having a long chain alkyl group as a third acrylic monomer, and

a radically polymerizable acrylic monomer other than the first to third acrylic monomers as a fourth acrylic monomer.

2. The release film according to claim 1, wherein the composition for forming a release layer further comprises an oxazoline-based crosslinking agent, and the hydroxyl value of the acrylic resin is 190 mgKOH/g or more and 450 mgKOH/g or less.

3. The release film according to claim 1 or 2, wherein the release layer has a surface free energy of 30 mJ/m² or more on a surface opposite from the polyester film.

4. The release film according to any one of claims 1 to 3, wherein the acrylic resin has an acid value of 20 mgKOH/g or more and 300 mgKOH/g or less.

5. The release film according to any one of claims 1 to 4, wherein the acrylic resin has a glass transition temperature (T_g) of 40°C or higher and 110°C or lower.

6. The release film according to any one of claims 1 to 4, wherein the acrylic resin comprises, as one of copolymerized constituents, an acrylic monomer having a carboxyl group, which is the second acrylic monomer, and a composition ratio of the second acrylic monomer is 0.1 mol% or more and 35 mol% or less based on 100 mol% of a

total amount of the copolymerized constituents in the acrylic resin.

7. The release film according to any one of claims 1 to 4, wherein the acrylic resin comprises, as one of copolymerized constituents, an acrylic monomer having a hydroxyl group, which is the first acrylic monomer, and a composition ratio of the first acrylic monomer is 25 mol% or more and 95 mol% or less based on 100 mol% of a total amount of the copolymerized constituents in the acrylic resin.

8. The release film according to any one of claims 1 to 7, wherein the acrylic resin comprises, as a copolymerized constituent, an acrylic monomer having a hydroxyl group, which is the first acrylic monomer, and the acrylic resin further comprises, as a copolymerized constituent, an acrylic monomer having a carboxyl group, which is the second acrylic monomer, and

a relationship between a composition ratio of the first acrylic monomer and a composition ratio of the second acrylic monomer is:

(composition ratio of first acrylic monomer/composition ratio of second acrylic monomer) ≥ 1.5 .

9. The release film according to any one of claims 2 to 8, wherein the oxazoline-based crosslinking agent comprises 3.0 to 9.0 mmol/g of an oxazoline group.

10. The release film according to any one of claims 1 to 9, wherein the release layer has a thickness of 0.001 μm or more and 2 μm or less.

11. The release film according to any one of claims 1 to 10, wherein the release film is a release film for the production of a ceramic green sheet.

12. A method for producing the release film according to any one of claims 1 to 11, the method comprising:

applying a composition for forming a release layer to an unstretched film or a uniaxially stretched film, and

after applying the composition for forming a release layer, in an unstretched state or after stretching in at least a uniaxial direction, performed heat-setting in a range of 80°C to 270°C.

13. The method for producing a release film according to claim 12, wherein the method for producing a release film is a method for producing a release film for

producing a ceramic green sheet.

14. A method for producing a ceramic green sheet, comprising forming a ceramic green sheet using the release film for producing a ceramic green sheet according to claim 11, or

the method for producing a release film for producing a ceramic green sheet according to claim 13.

15. The method for producing a ceramic green sheet according to claim 14, wherein a thickness of a ceramic green sheet to be produced is 0.2 μm or more and 2.0 μm or less.

16. A method for producing a ceramic capacitor, wherein the method for producing a ceramic green sheet according to claim 14 or 15 is employed.