

DESCRIPTION

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

TECHNICAL FIELD

[0001]

The present invention relates to a silicone release polyester film. More specifically, the present invention relates to a silicone release polyester film having releasability and adhesiveness suitable for molding ranging from light peeling to heavy peeling in, for example, ceramic green sheet forming or the like to be used in production of a stacked ceramic capacitor, and being capable of preventing the occurrence of breakage or deformation of the sheet or the like, a method for producing the same, and so on.

BACKGROUND ART

[0002]

A release film is used as a carrier film for forming a resin sheet or a ceramic sheet. As a substrate of the release film, a polyester film is used particularly in terms of dimensional stability and heat resistance. In recent years, particularly with the progress of miniaturization and reliability enhancement of stacked

ceramic capacitors, various types of ceramic green sheets ranging from thin one to thick one have been produced. Therefore, carrier films are required to have various characteristics suitable for the thickness of slurry. In production of stacked ceramic capacitors, reduction in thickness leads to decrease in the rigidity of a ceramic green sheet and occurrence of the breakage of the sheet in peeling the sheet, and therefore, light peelability has been required. In addition, since a green sheet having a relatively large thickness has high rigidity, lifting is generated between the sheet and a release film during process conveyance, and deformation of the sheet occurs. As described above, in ceramic sheet peeling, various peeling forces ranging from light peeling to heavy peeling may be required. In addition, regardless of the thickness of a green sheet, slight cissing defects generated during application of a ceramic slurry penetrate the sheet, whereby pinholes or thickness unevenness occurs, and the yield of a stacked ceramic capacitor is significantly deteriorated. Therefore, coating film uniformity of a release layer of a release film is required.

[0003]

Regarding these problems, it has been proposed to add a component composed of a silicone resin having a trifunctional unit siloxane or tetrafunctional unit

siloxane structure (see, for example, Patent Document 1), but the content of the silicone resin is not specifically presented, and there has been no description on an emulsion type release agent.

[0004]

Moreover, an aqueous coating composition including a silicone containing a Q unit in a prescribed mol% range and a silicone having an Si-H group has been described (see, for example, Patent Document 2), but there has been no particular description on the optimal molecular weight range of the silicone containing the Q unit.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0005]

Patent Document 1: JP-A-9-1527

Patent Document 2: JP-A-2021-11081

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006]

In view of the above circumstances, an object of the present invention is to provide a silicone release polyester film that can be suitably used as, for example, a carrier film or the like in the production of a stacked

ceramic capacitor and that is superior in peelability and adhesion suitable for sheet molding ranging from light peeling to heavy peeling, and a method for producing the same.

MEANS FOR SOLVING THE PROBLEMS

[0007]

As a result of intensive studies to solve the above problems, the present inventors have found that it is possible to provide a release film or the like having an appropriate peeling force ranging from light peeling to heavy peeling even when an emulsion type silicone is used under certain specific conditions, and have accomplished the present invention.

[0008]

That is, the present invention provides the following silicone release polyester films (silicone-releasable polyester films).

[0009]

[1]

A silicone release polyester film having, on at least one surface of the polyester film, a coating layer formed using a coating composition for release including an aqueous dispersion (1) of one or more silicones (A) containing an alkenyl group and/or a Q unit represented by

SiO_{4/2}, an aqueous dispersion (2) of a silicone (B) having a hydrogen atom directly bonded to a Si atom represented by an Si-H group, a crosslinking reaction inhibitor, a platinum-based catalyst, and a nonionic emulsifier,

wherein a number average molecular weight of the silicones (A) is 150000 or more, and

a content of Si atoms contained in the Q unit is 0.05 mol% or more and 60 mol% or less.

[0010]

[2]

The silicone release polyester film according to [1], wherein a content of the silicone (B) is 3 parts by mass or more and 45 parts by mass or less where a total content of the silicones (A) and the silicone (B) is 100 parts by mass.

[0011]

[3]

The silicone release polyester film according to [1] or [2], wherein the alkenyl group of the silicones (A) is a vinyl group.

[0012]

[4]

The silicone release polyester film according to any one of [1] to [3], wherein a peeling force after being attached to a polyester adhesive tape is 20 g/25 mm width

or more and 400 g/25 mm width or less.

[0013]

[5]

The silicone release polyester film according to any one of [1] to [4], which is to be used for ceramic green sheet forming in production of a stacked ceramic capacitor.

[0014]

The present invention also provides the following method for producing a silicone release polyester film.

[0015]

[6]

A method for producing a silicone release polyester film, the method comprising a step of forming a coating layer on at least one surface of a polyester film using a coating composition for release including an aqueous dispersion (1) of one or more silicones (A) containing an alkenyl group and/or a Q unit represented by $\text{SiO}_{4/2}$, an aqueous dispersion (2) of a silicone (B) having a hydrogen atom directly bonded to a Si atom represented by an Si-H group, a crosslinking reaction inhibitor, a platinum-based catalyst, and a nonionic emulsifier,

wherein a number average molecular weight of the silicones (A) is 150000 or more, and

a content of Si atoms contained in the Q unit is in a range of 0.05 mol% or more and 60 mol% or less.

[0016]

[7]

The method according to [6], wherein a content of the silicone (B) is 3 parts by mass or more and 45 parts by mass or less where a total content of the silicones (A) and the silicone (B) is 100 parts by mass.

[0017]

[8]

The method according to [6] or [7], wherein the alkenyl group of the silicones (A) is a vinyl group.

EFFECT OF THE INVENTION

[0018]

Owing to having the configuration described above, the silicone release polyester film of the present invention serves as a release film for sheet forming having a peeling force to sheet forming suitable for the thickness of a ceramic green sheet or the like and moderate releasability with little sheet deformation, and a sheet having a reduced defect rate and high reliability can be produced.

[0019]

In addition, the method for producing a silicone release polyester film of the present invention makes it possible to efficiently and easily obtain a silicone

release polyester film having the characteristics described above.

MODE FOR CARRYING OUT THE INVENTION

[0020]

Hereinafter, a detailed description is made of embodiments of the present invention, but the present invention is not limited to these embodiments.

[0021]

<Silicone release polyester film>

The silicone release polyester film of the present invention is a silicone release polyester film having, on at least one surface of the polyester film, a coating layer formed using a coating composition for release including an aqueous dispersion (1) of one or more silicones (A) containing an alkenyl group and/or a Q unit represented by $\text{SiO}_{4/2}$, an aqueous dispersion (2) of a silicone (B) having a hydrogen atom directly bonded to a Si atom represented by an Si-H group, a crosslinking reaction inhibitor, a platinum-based catalyst, and a nonionic emulsifier,

wherein a number average molecular weight of the silicones (A) is 150000 or more, and

a content of Si atoms contained in the Q unit is 0.05 mol% or more and 60 mol% or less.

[0022]

[Polyester film]

For the polyester film of the present invention, known polyesters can be appropriately used, and for example, those shown below can be suitably used.

[0023]

(Polyester)

The polyester that constitutes a polyester film to be used as the substrate film (hereinafter, sometimes referred to as "substrate") in the present invention is not particularly limited, and a film formed product of a polyester commonly used as a substrate for a release film can be used. A crystalline linear saturated polyester composed of an aromatic dibasic acid component and a diol component is preferable. For example, polyethylene terephthalate, polyethylene isophthalate, polyethylene-2,6-naphthalate, polybutylene terephthalate, poly(1,4-cyclohexylenedimethylene terephthalate), polytrimethylene terephthalate, or copolymers containing constituent components of these resins as main components are more preferable. In particular, polyester films formed from polyethylene terephthalate are particularly suitable. In polyethylene terephthalate, the content of repeating units of ethylene terephthalate is preferably 90 mol% or more, more preferably 95 mol% or more, and other dicarboxylic acid components and diol components may be copolymerized in

small amounts. For example, from the viewpoint of cost, a copolymer produced from only terephthalic acid and ethylene glycol is preferable.

[0024]

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

[0025]

The intrinsic viscosity of the polyester film is preferably 0.50 dl/g or more and 0.70 dl/g or less, and more preferably 0.52 dl/g or more and 0.65 dl/g or less. When the intrinsic viscosity is 0.50 dl/g or more, breakage does not often occur in a stretching step, which is preferable. Conversely, when the intrinsic viscosity is 0.70 dl/g or less, the cuttability of the polyethylene terephthalate film at the time of being cut into a predetermined product width is good and dimensional failure does not occur, which is preferable. In addition, it is preferable that the raw material pellets are sufficiently vacuum-dried.

[0026]

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

[0027]

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

[0028]

In the present invention, a stretching temperature when stretching the polyester film is preferably set to be equal to or higher than a secondary transition point (T_g) of the polyester. The polyester film is stretched in each of the machine direction and the transverse direction

preferably by once or more and 8 times or less, and particularly preferably by twice or more and 6 times or less.

[0029]

The thickness of the polyester film is preferably 12 μm or more and 100 μm or less, more preferably 16 μm or more and 50 μm or less, and still more preferably 19 μm or more and 33 μm or less. When the thickness of the film is 12 μm or more, there is no risk of deformation due to heat during film production, processing steps, and molding, which is preferable. When the thickness of the film of 100 μm or less, the amount of the film to be disposed after being used is not extremely large, which is preferable for reducing the environmental load.

[0030]

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

[0031]

In this aspect, particles having a particle size of

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

[0032]

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

[0033]

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

[0034]

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

[0035]

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

[0036]

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

[0037]

As the laminated configuration, when the layer on the side to which the release layer is applied is a layer A, the layer on the opposite surface thereof is a layer B, and

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

[0038]

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

[0039]

At this time, the average area surface roughness (S_a) of the film of the surface layer B is preferably in a range of 1 nm or more and 40 nm or less. More preferably, the average area surface roughness is in a range of 5 nm or

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

[0040]

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

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

[0041]

The average particle diameter of the inorganic particles to be added to the surface layer B is preferably 0.1 μm or more and 2.0 μm or less, and particularly preferably 0.3 μm or more and 1.0 μm or less. When the average particle diameter of the inorganic particles is 0.1 μm or more, the slipperiness of the release film is good, which is preferable. When the average particle diameter is 2.0 μm or less, there is no possibility of adversely affecting the smoothness of the surface of the release layer, and therefore there is no possibility of generating pinholes in the ceramic green sheet, which is preferable.

[0042]

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

to a corona treatment or the like.

[0043]

The silicone release polyester film of the present invention can have a peeling force of 20 g/25 mm width or more and 400 g/25 mm width or less after being attached to a polyester adhesive tape. The lower limit of the peeling force may be, for example, 30 g/25 mm width or more, 40 g/25 mm width or more, 50 g/25 mm width or more, 70 g/25 mm width or more, 100 g/25 mm width or more, 120 g/25 mm width or more, 150 g/25 mm width or more, or 180 g/25 mm width or more. The upper limit of the peeling force may be, for example, 380 g/25 mm or less, 350 g/25 mm or less, 330 g/25 mm or less, 300 g/25 mm or less, 280 g/25 mm or less, 250 g/25 mm or less, 230 g/25 mm or less, or 200 g/25 mm or less. The peeling strength is preferably 20 g/25 mm or more and 400 g/25 mm or less. Since the silicone release polyester film of the present invention has the configurations described above, as a result of, for example, the introduction of a silicone resin (Q unit resin) into a silicone main agent (silicone A), the silicone release polyester film not only has adhesion but also can have a controlled peeling force ranging from light peeling to heavy peeling through the adjustment of the amount of a crosslinking agent to be added; for example, the silicone release polyester film is releasable with a

moderate hardness as a release film for sheet formation even with a little amount of a crosslinking agent. Therefore, the silicone release polyester film has an extremely high industrial value.

[0044]

In the present invention, the adhesive tape peeling strength refers to a strength obtained by bonding a polyester adhesive tape (No. 31B produced by Nitto Denko Corporation) to the surface of the coating layer (release layer) of the release film, pressure-bonding the resultant with a 5 kg pressure-bonding roller, leaving the resultant for 30 minutes or more, and then measuring the peeling strength (peeling angle: 180 degrees, peeling rate: 300 mm/min, unit: g/25 mm width) between the release layer and the adhesive tape with a peeling strength tester.

[0045]

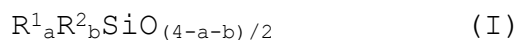
[Coating composition for release]

The coating composition for release of the present invention includes an aqueous dispersion (1) of one or more silicones (A) containing an alkenyl group and/or a Q unit represented by $\text{SiO}_{4/2}$, an aqueous dispersion (2) of a silicone (B) having a hydrogen atom directly bonded to a Si atom represented by an Si-H group, a crosslinking reaction inhibitor, a platinum-based catalyst, and a nonionic emulsifier.

[0046]

(One or more silicones (A) containing an alkenyl group and/or a Q unit represented by $\text{SiO}_{4/2}$)

Examples of the silicone (A) containing an alkenyl group and/or a Q unit represented by $\text{SiO}_{4/2}$ (hereinafter, this unit may be simply referred to as "Q unit") in the present invention include an organopolysiloxane having the following general formula (I) (hereinafter, this may be referred to as "silicone (A)").



(In the formula (I), R^1 represents an alkenyl group having 2 to 8 carbon atoms, R^2 represents a monovalent saturated hydrocarbon group having 1 to 16 carbon atoms selected from alkyl groups or aryl groups, a represents an integer of 0 to 3, b represents an integer of 0 to 3, provided that $a + b \leq 3$ is satisfied.)

[0047]

Examples of the alkenyl group having 2 to 8 carbon atoms represented by R^1 include a vinyl group, an allyl group, a butenyl group, a pentenyl group, and a hexenyl group, and among these groups, a vinyl group is particularly preferable. Examples of the alkyl group represented by R^2 include a methyl group, an ethyl group, a propyl group, and a butyl group, and examples of the aryl group include a phenyl group and a tolyl group. Among

them, for example, it is preferable that 50 mol% or more of the substituent of R² is a methyl group from the viewpoint of light peelability.

[0048]

The silicone (A) containing an alkenyl group and/or a Q unit is required to contain a Q unit. It is noted that when multiple types of silicones (A) containing an alkenyl group and/or a Q unit are contained, a Q unit is just required to be contained in any of them. Owing to the Q unit being contained in the silicone-based release layer, the coating film hardness of the silicone-based release layer increases, and viscosity loss at the time of peeling the sheet can be suppressed, leading to light peeling. In addition, when a silicone containing a Q unit is contained in the alkenyl group-containing silicone, wettability is also improved, so that the occurrence of pinhole defects during sheet coating can be inhibited. The content of Si atoms contained in the Q unit is 0.05 mol% or more and 60 mol%, preferably 0.1 mol% or more and 55 mol% or less, and more preferably 1.0 mol% or more and 50 mol% or less, with respect to all Si atoms in the silicones (A) containing an alkenyl group and/or a Q unit. When the content of the Si atoms contained in the Q unit is less than 0.05 mol%, sufficient coating film hardness cannot be exhibited, and light peeling is not attained, whereas when the content

exceeds 60 mol%, wettability is excessively imparted, so that strong adhesion to the sheet occurs, resulting in cohesive failure of the sheet surface (excessive heavy peeling).

[0049]

The number average molecular weight of the silicones (A) containing an alkenyl group and/or a Q unit is 150000 or more, for example, preferably 180000 or more, 200000 or more, 220000 or more, or the like. The number average molecular weight of the silicones (A) containing an alkenyl group and/or a Q unit may be, for example, 1000000 or less, and may be 900000 or less, 800000 or less, 700000 or less, 600000 or less, 500000 or less, 400000 or less, or the like. When the number average molecular weight is less than 150000, the formation of crosslinking of the release coating film is insufficient, and viscosity loss at the time of peeling the sheet cannot be suppressed, so that excessive heavy peeling occurs, and the amount of silicone transferred to the adherend also increases.

[0050]

The silicones (A) containing an alkenyl group and/or a Q unit in the present invention can be produced by a known method. The silicones (A) containing an alkenyl group and/or a Q unit in the present invention are preferably contained in the aforementioned composition in

the form of an aqueous dispersion (aqueous dispersion (1)).

[0051]

When the silicones (A) containing an alkenyl group and/or a Q unit is processed to form an aqueous dispersion (aqueous dispersion (1)), the % by mass of the silicones (A) containing an alkenyl group and/or a Q unit in the aqueous dispersion (1) may be, for example, 1% by mass or more and 50 % by mass or less, and may be 3% by mass or more and 40 % by mass or less, 5% by mass or more and 30 % by mass or less, 10 % by mass or more and 20 % by mass or less, or the like.

[0052]

(Silicone (B) having hydrogen atom directly bonded to Si atom represented by Si-H group)

Examples of the silicone (B) having a hydrogen atom directly bonded to a Si atom represented by an Si-H group (hereinafter, this may be referred to as "silicone (B)" or "Si-H group-containing silicone (B)") in the present invention include an organohydrogen polysiloxane having a structure represented by the following general formula (II).



(In the formula (II), R^3 represents a monovalent saturated hydrocarbon group having 1 to 16 carbon atoms selected from alkyl groups or aryl groups, c represents an

integer of 0 to 2, d represents an integer of 1 to 3, provided that $c + d \leq 3$ is satisfied.)

[0053]

Examples of the alkyl group represented by R^3 include a methyl group, an ethyl group, a propyl group, and a butyl group, and examples of the aryl group include a phenyl group and a tolyl group. Among them, it is preferable that 50 mol% or more of the substituent of R^3 is a methyl group from the viewpoint of light peelability.

[0054]

From the viewpoint of curing characteristics, the Si-H group-containing silicone (B) preferably has at least three, preferably five or more, hydrogen atoms bonded to Si atoms in one molecule of the silicone.

[0055]

The Si-H group-containing silicone (B) can be produced by a known method. The Si-H group-containing silicone (B) in the present invention is preferably contained in the aforementioned composition in the form of an aqueous dispersion (aqueous dispersion (2)).

[0056]

When the Si-H group-containing silicone (B) is processed to form an aqueous dispersion (aqueous dispersion (2)), the % by mass of the Si-H group-containing silicone (B) in the aqueous dispersion (2) may be, for example, 1%

by mass or more and 50% by mass or less, and may be 3% by mass or more and 40% by mass or less, 5% by mass or more and 30% by mass or less, 10% by mass or more and 20% by mass or less, or the like.

[0057]

In addition, the content of the Si-H group-containing silicone (B) is preferably 1 part by mass or more and 60 parts by mass or less, more preferably 2 parts by mass or more and 50 parts by mass or less, and still more preferably 3 parts by mass or more and 45 parts by mass or less where the total content of the silicones (A) containing an alkenyl group and/or a Q unit represented by $\text{SiO}_{4/2}$ and the Si-H group-containing silicone (B) is 100 parts by mass. When the content is less than 1 part by mass, a curing reaction is difficult to proceed, so that sufficient coating film hardness may not be obtained, whereas when the content exceeds 60 parts by mass, Si-H is excessively precipitated on a surface, and strongly adheres to a green sheet, so that heavy peeling may be caused as a result.

[0058]

(Silicone content)

In the coating composition for release in the present invention, the total of the solid content of the silicones (A) containing an alkenyl group and/or a Q unit represented

by $\text{SiO}_{4/2}$ and the solid content of the Si-H group-containing silicone (B) is preferably 70% by mass or more based on the solid mass of the composition. Each of the silicone solid contents is more preferably 80% by mass or more and 97% by mass or less. Here, the silicone solid content refers to the amount excluding the aqueous solvent, and the solid mass of the composition refers to the total amount of the solid contents of the respective additives. When the total amount of the silicone solid contents is less than the lower limit, the area covered with silicone is reduced with respect to the film surface on which the coating film is formed, the peeling force is increased, and unevenness may occur in the peeling force.

[0059]

(Aqueous solvent)

As the aqueous solvent for forming each of the aqueous silicone dispersions of the present invention, water is preferably used. By using the aqueous solvent, it is possible to form a silicone release layer without using an explosion-proof facility and an organic solvent recovery facility required for the organic solvent during the process of producing the release film.

[0060]

(Nonionic emulsifier)

Each of the aqueous dispersions is prepared using a

nonionic emulsifier to increase the stability or the shear resistance of the aqueous dispersion. As a result of intensive studies conducted by the inventors, it has been found that the emulsifier needs to be a nonionic emulsifier in order to prevent aggregation of the respective aqueous dispersions and not to affect the curing reactions of the silicones. A cationic emulsifier affects the curing reactions of the silicones, and is localized in a coating film, for example, bleeds out to the surface to affect releasability and lead to heavy peeling. In addition, although details are not clear, when a cationic emulsifier is used, the silicone-based aqueous dispersions are likely to aggregate.

[0061]

The nonionic emulsifier preferably has an HLB value in the range of 6 or more and 18 or less, and examples thereof include at least one selected from among higher alcohols and alkylene oxide adduct types including alkylene oxide adducts of higher fatty acids, esters of alkylene oxide adducts of higher fatty acids and alcohols, alkylene oxide adducts of alkanolamides, alkylene oxide adducts of sorbitan esters, and alkylene oxide adducts of higher fatty acid glycerides. These may be used alone or in combination of two or more kinds thereof. Here, the HLB value is a value calculated by Griffin's calculation formula.

[0062]

Examples of the alkylene oxide include ethylene oxide, propylene oxide, and butylene oxide, and either one of these or two or more of these may be used. When a plurality of alkylene oxides are used, the type of addition may be either block or random, and the HLB value is preferably in the range of 6 or more and 18 or less, and more preferably in the range of 10 or more and 15 or less. Among these nonionic emulsifiers, for example, polyoxyethylene lauryl ether, polyoxyethylene tridecyl ether, and the like are preferable. When a nonionic emulsifier having an HLB value outside the above range is used as an emulsifier of the aqueous silicone dispersion, the emulsifying and dispersing power and the stability of the aqueous dispersion may be deteriorated. The nonionic emulsifier is used preferably in a range of 0.1% by mass or more and 20% by mass or less, more preferably in a range of 0.2% by mass or more and 15% by mass or less, and still more preferably in a range of 0.5% by mass or more and 10% by mass or less, with respect to the total solid content. If it falls below this range, emulsification tends to fail, whereas if it exceeds this range, heavy peeling may occur.

[0063]

(Platinum-based catalyst)

In the coating composition for release constituting

the coating layer of the present invention, it is necessary to use a platinum-based catalyst in order to make one or more silicones (A) containing an alkenyl group and/or a Q unit undergo an addition reaction with the Si-H group-containing silicone (B).

[0064]

Known platinum-based catalysts can be used, and examples thereof include platinum chloride and chloroplatinic acid. In consideration of the dispersibility of the platinum-based catalyst in the silicone, a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane platinum complex (Karstedt catalyst) may be used, and uniform dispersibility can be secured by simultaneously dispersing silicone when emulsifying the silicone. These may be used alone or in combination of two or more kinds thereof.

[0065]

The platinum-based catalyst is preferably contained in such an amount that the mass of platinum element in a range of 10 ppm or more and 800 ppm or less with respect to 100 parts by mass of the total amount of the aqueous dispersion (1) of one or more silicones (A) containing an alkenyl group and/or a Q unit and the aqueous dispersion (2) of the Si-H group-containing silicone (B). Within the above range, the silicone can be sufficiently cured. In

addition, generation of a silicone aggregate can be inhibited, and a release polyester film superior in surface properties can be obtained. When the mass ratio of platinum element exceeds the above range, the addition reaction between an alkenyl group and an Si-H group is accelerated, and a silicone aggregate tends to be generated. From the above viewpoint, the amount of the platinum-based catalyst is more preferably 600 ppm or less, still more preferably 500 ppm or less, particularly preferably 200 ppm or less, and very preferably 150 ppm or less. When the mass ratio of platinum element is less than the lower limit, the addition reaction does not proceed, and poor curing of silicone tends to be caused. From the above viewpoint, the amount of the platinum catalyst is more preferably 15 ppm or more, still more preferably 20 ppm or more, particularly preferably 25 ppm or more, and most preferably 40 ppm or more.

[0066]

(Crosslinking reaction inhibitor)

A crosslinking reaction inhibitor is preferably contained in the aqueous coating composition in order to suppress the activity of the platinum-based catalyst at room temperature. The crosslinking reaction inhibitor is preferably a crosslinking reaction inhibitor having an alkynyl group. The crosslinking reaction inhibitor having

an alkynyl group is not particularly limited as long as the reaction inhibitor has an alkynyl group, and specific examples thereof include 1-ethynyl-1-cyclohexanol, 4-ethyl-1-octyn-3-ol, 3-methyl-1-dodecyn-3-ol, 3,7,11-trimethyl-1-dodecyn-3-ol, 1,1-diphenyl-2-propyn-3-ol, 3-ethyl-6-ethyl-1-nonyn-3-ol, 3-methyl-1-pentadecyn-3-ol, 2,5-dimethyl-3-hexyne-2,5-diol, and 3-phenyl-1-butyn-3-ol. These may be used alone or in combination of two or more kinds thereof. In the present invention, since an aqueous emulsion coating composition is adopted, use of any of the crosslinking reaction inhibitors having an alkynyl group and a hydroxyl group disclosed above as examples is preferable in terms of boiling point and balance between affinity solubility in water and coordination ability to platinum.

[0067]

The content of the crosslinking reaction inhibitor is preferably 5 ppm or more and 1,000 ppm or less, more preferably 10 ppm or more and 700 ppm or less, and still more preferably 20 ppm or more and 500 ppm or less, with respect to the mass of the aqueous coating composition to be used for the formation of the release layer. When the content of the crosslinking reaction inhibitor is equal to or greater than the lower limit, the pot life tends to be long, the addition curing reaction of silicone tends to hardly proceed at room temperature, and silicone aggregates

tend to be hardly generated. When the content of the crosslinking reaction inhibitor is equal to or less than the upper limit, silicone is less likely to migrate to a mating material after the mating material is peeled off, and the amount of the reaction inhibitor volatilized during a heat treatment is reduced, so that contamination inside an oven is less likely to occur.

[0068]

(Other components)

To the coating composition for release of the present invention may be further added, for example, an agent for imparting adhesiveness to a substrate, a coloring agent, an ultraviolet absorber, particles, or an anti-static agent as long as the object of the present invention is not impaired.

[0069]

(Preparation of aqueous silicone dispersion)

In preparing each of the aqueous silicone dispersions of the present invention, a method of emulsifying the silicone component, the aqueous solvent, and the emulsifier described above can be employed. A known method can be used for emulsifying these components, and examples thereof include a method in which a silicone prepared in advance, an emulsifier, and other components as necessary are mechanically emulsified in an aqueous medium using a

stirring device such as a homogenizer, an Agi Homo Mixer, or an Ultra Planetary Mixer.

[0070]

In addition, the particle size of the aqueous dispersion can be adjusted by adjusting the size of the stirring blade, the stirring speed, and the stirring time. The average particle diameter of each of the aqueous silicone dispersions of the present invention is preferably 200 nm or less, and more preferably 100 nm or more and 200 nm or less.

[0071]

[Coating layer]

In the present invention, a coating layer (release layer) is formed on at least one surface of a polyester film using the coating composition for release of the present invention. The coating layer (release layer) of the present invention is formed by applying the coating composition for release onto the polyester film, and then drying it.

[0072]

In the present invention, the thickness of the coating layer is preferably 5 nm or more and 70 nm or less in terms of a thickness after drying. When the thickness of the coating layer is less than the lower limit, the release characteristics may be insufficient, and when the

thickness exceeds the upper limit, the peeling strength increases, and it is necessary to increase the concentration of the coating liquid or to increase the coating amount, so that it tends to be difficult to perform coating.

[0073]

When the coating composition for release of the present invention is applied onto a polyester film, an aqueous coating liquid containing the composition is prepared, and the solid concentration of the aqueous coating liquid is preferably 20% by mass or less, more preferably 1% by mass or more and 10% by mass or less based on the mass of the coating liquid. When the solid concentration in the aqueous coating liquid is less than the lower limit, the wettability to the polyester film may be insufficient. When the solid concentration exceeds the upper limit, the stability of the coating liquid and the appearance of the coating layer may be deteriorated. Water is preferably used as the aqueous solvent for adjusting the solid concentration.

[0074]

The aqueous coating liquid can be applied to the polyester film at any stage, but is preferably applied in the process of producing the polyester film, and is preferably applied to the polyester film before oriented

crystallization is completed.

[0075]

Here, the polyester film before oriented crystallization is completed orientation includes an unstretched film, a uniaxially oriented film obtained by orienting an unstretched film in either the machine direction (hereinafter, this direction may be referred to as a continuous film formation direction, a machine direction, or an MD direction) or the transverse direction (hereinafter, this direction may be referred to as a direction orthogonal to the machine direction, a transverse direction, or a TD direction), and a film obtained by subjecting an unstretched film to a low stretch orientation in two directions, namely, the machine direction and the transverse direction (a biaxially stretched film obtained before the film is finally restretched in the machine direction or the transverse direction to complete oriented crystallization). Among them, preferred is so-called in-line coating, in which an aqueous coating liquid of the composition described above is applied to an unstretched film or a uniaxially stretched film oriented in one direction, and stretching in the machine direction and/or stretching in the transverse direction and heat fixation are immediately performed. The coating layer may be dried by the stretching step or the heat setting treatment after

the coating, and a drying step may be further added, as necessary. When the composition is cured using a catalyst to obtain a cured film, the composition may be cured by the stretching step or the heat setting treatment, but a curing step may be further added, as necessary.

[0076]

When the aqueous coating liquid is applied to the polyester film, for example, it is preferable to subject the film surface to a physical treatment, such as a corona surface treatment, a flame treatment, or a plasma treatment, as a preliminary treatment for improving coatability, or to use the above-described emulsifier as a wetting agent together with the composition.

[0077]

As an application method, any known coating method can be applied. For example, a roll coating method, a gravure coating method, a roll brushing method, a spray coating method, an air knife coating method, an impregnation method, a curtain coating method, and the like may be used alone or in combination.

[0078]

<Method for producing silicone release polyester film>

The method for producing a silicone release polyester film is a method for producing a silicone release polyester film, the method comprising a step of forming a coating

layer on at least one surface of a polyester film using a coating composition for release including an aqueous dispersion (1) of one or more silicones (A) containing an alkenyl group and/or a Q unit represented by $\text{SiO}_{4/2}$, an aqueous dispersion (2) of a silicone (B) having a hydrogen atom directly bonded to a Si atom represented by an Si-H group, a crosslinking reaction inhibitor, a platinum-based catalyst, and a nonionic emulsifier,

wherein a number average molecular weight of the silicones (A) is 150000 or more, and

a content of Si atoms contained in the Q unit is in a range of 0.05 mol% or more and 60 mol% or less.

[0079]

The method for producing a silicone release polyester film of the present invention makes it possible to efficiently and easily obtain a silicone release polyester film having the characteristics described above. Note that the producing method described below is an example, and the present invention is not limited thereto.

[0080]

In the producing method, for each configuration, the description regarding the silicone release polyester film and the like in the present specification can be applied appropriately.

[0081]

As the step of forming the coating layer using the coating composition for release of an aqueous dispersion in the producing method, a known method can be appropriately used as long as it is a method of forming the coating layer on the film using the coating composition for release of an aqueous dispersion.

EXAMPLES

[0082]

The present invention will be described specifically by way of Examples, but the present invention is not limited to the following Examples. Physical properties and characteristics in Examples were measured or evaluated by the following methods. The indication with "part" means "part by mass".

[0083]

Each measurement, evaluation, and the like in Examples were performed as follows.

[0084]

(1) Adhesive tape peelability

The adhesive tape peeling strength is a strength obtained by bonding a polyester adhesive tape (No. 31B produced by Nitto Denko Corporation) to the surface of the coating layer (release layer) of the release film, pressure-bonding the resultant with a 5 kg pressure-bonding

roller, leaving the resultant for 30 minutes or more, and then measuring the peeling strength (peeling angle: 180 degrees, peeling rate: 300 mm/min, unit: g/25 mm width) between the release layer and the adhesive tape with a peeling strength tester. The silicone release polyester film of the present invention preferably has a peeling strength of 20 g/25 mm or more and 400 g/25 mm or less. [0085]

(2) Residual adhesion rate

The peeling strength after bonding a polyester adhesive tape (No. 31B produced by Nitto Denko Corporation) to a cold-rolled stainless steel plate (SUS304) specified in JIS G 4305 was measured and taken as the basic adhesive force (f_0). In addition, the polyester adhesive tape was pressure-bonded to the surface of the release layer of the release polyester film with a pressure roller weighing 5 kg and maintained for 30 seconds, the adhesive tape was then peeled off, and the peeling strength after the peeled adhesive tape was attached to the stainless steel plate was measured and taken as the residual adhesive force (f). From the basic adhesive force (f_0) and the residual adhesive force (f) obtained, a residual adhesion rate was determined using the following formula. The peeling angle was 180 degrees, and the peeling rate was 300 mm/min.

$$\text{Residual adhesion rate (\%)} = (f)/(f_0) \times 100$$

The residual adhesion rate is preferably 90% or more, which indicates that the silicone crosslinking density is high. When the residual adhesion rate is less than 90%, this indicates that crosslinking is insufficient.

[0086]

[Examples 1 to 3, Comparative Examples 1 to 4]

Molten polyethylene terephthalate ($[\eta] = 0.64$ dl/g, $T_g = 78^\circ\text{C}$) containing 0.1% by mass of calcium carbonate particles having an average particle diameter of $0.7\ \mu\text{m}$ was extruded from a die, cooled with a cooling drum by a conventional method to form an unstretched film, which was subsequently stretched 3.6 times in the machine direction. Then, an aqueous coating liquid (aqueous dispersion having a solid concentration of 3% by mass) prepared by mixing the components to have the solid content ratio given in Table 1 was uniformly applied to the surface of the film with a roll coater.

[0087]

Subsequently, this coated film was dried at 115°C over about 5 seconds, stretched 4.5 times in the transverse direction at 145°C , and further heat-set at 230°C for about 5 seconds, affording a $25\ \mu\text{m}$ biaxially stretched polyester film having the coating layer shown in Table 1.

[0088]

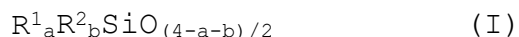
(Aqueous dispersion of silicone (1-a) containing alkenyl

group and Q unit)

An aqueous dispersion of silicone (1-a) having a solid content of 20% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 95% by mass of silicone (1) and 5% by mass of polyoxyethylene tridecyl ether (trade name "NEWKALGEN D-1208" produced by TAKEMOTO OIL & FAT CO., LTD.) as a surfactant using an emulsifier (produced by N.P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. The emulsion particle size was adjusted to an average particle size of 200 nm by adjusting a stirring speed and a stirring time at the time of the emulsification.

[0089]

It is noted that the composition of the silicone (1-a) was composed of: 6.00 mol% of a constitutional unit with, in Formula (I), R^1 being a vinyl group, R^2 being a methyl group, and to a silicon with a vinyl group directly bonded thereto being bonded only one vinyl group; 60.00 mol% of a constitutional unit constituted of a Q unit with $a = b = 0$ in Formula (I); and 34.00 mol% of a constitutional unit with, in Formula (I), R^2 being a methyl group, $a = 0$, and $b = 2$, provided that at both ends, $a = 0$, and $b = 3$, and the silicone (1-a) was adjusted to have a number average molecular weight of 240000 (1-a).



(In the formula (I), R^1 represents an alkenyl group having 2 to 8 carbon atoms, R^2 represents a monovalent saturated hydrocarbon group having 1 to 16 carbon atoms selected from alkyl groups or aryl groups, a represents an integer of 0 to 3, b represents an integer of 0 to 3, provided that $a + b \leq 3$ is satisfied.)

[0090]

(Aqueous dispersion of silicone (1-b) containing alkenyl group but containing no Q unit)

An aqueous dispersion of silicone (1-b) having a solid content of 20% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 95% by mass of silicone (1-b) and 5% by mass of polyoxyethylene tridecyl ether (trade name "NEWKALGEN D-1208" produced by TAKEMOTO OIL & FAT CO., LTD.) as a surfactant using an emulsifier (produced by N.P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. The emulsion particle size was adjusted to an average particle size of 200 nm by adjusting a stirring speed and a stirring time at the time of the emulsification.

[0091]

The composition of the silicone (1-b) is composed of: a constitutional unit in which, in Formula (I), R^1 is a

vinyl group, R² is a methyl group, to silicon with a vinyl group directly bonded thereto is bonded only one vinyl group, the vinyl group is bonded to a terminal silicon atom, and the number of repetition having a silicon atom with a vinyl group bonded thereto is 3; and a constitutional unit of dimethylsiloxane (both terminals are vinyl groups), and the composition was adjusted by the number of repetition of the latter constitutional unit such that the number average molecular weight was 40000.

[0092]

(Aqueous dispersion of silicone (2) having Si-H group)

An aqueous dispersion (2) of Si-H group-containing silicone (2) having a solid content of 10% by mass was obtained by mechanically emulsifying, in an aqueous medium, a raw material composed of 97% by mass of Si-H group-containing silicone (2) and 3% by mass of polyoxyethylene tridecyl ether (trade name "NEWKALGEN D-1208" produced by TAKEMOTO OIL & FAT CO., LTD.) as a surfactant using an emulsifier (produced by N.P. Labo Co., Ltd., device name "Ultra planetary mixer") capable of stirring the whole in a container. The emulsion particle size was adjusted to an average particle size of 160 nm by adjusting a stirring speed and a stirring time at the time of the emulsification.



(In the formula (II), R^3 represents a monovalent saturated hydrocarbon group having 1 to 16 carbon atoms selected from alkyl groups or aryl groups, c represents an integer of 0 to 2, d represents an integer of 1 to 3, provided that $c + d \leq 3$ is satisfied.)

[0093]

The composition of the Si-H group-containing silicone is composed of: a constitutional unit in which, in Formula (II), R^3 is a methyl group, $c = d = 1$, namely, to silicon with a hydrogen group directly bonded thereto is bonded only one hydrogen group, no hydrogen atom is bonded to any terminal silicon atom, and the number of repetition of the constitutional unit having a silicon atom with a hydrogen group directly bonded thereto is 30; and a constitutional unit of dimethylsiloxane (both terminals are methyl groups), and the composition was adjusted by the number of repetition of the latter constitutional unit such that the number average molecular weight was 5000.

[0094]

(Adjustment of silicone coating liquid)

As an aqueous coating composition (coating composition for release), a coating liquid was prepared by mixing a silicone aqueous dispersion in which the aqueous dispersion of the silicone (1-a) or the aqueous dispersion of the silicone (1-b) and the silicone (2) having an Si-H

group had been mixed in a solid blending ratio given in Table 1 with the platinum-based catalyst specified below in an amount of 40 ppm with respect to the total coating liquid mass of the silicone (1-a) and the silicone (2), and the crosslinking reaction inhibitor specified below in an amount of 200 ppm with respect to a coating mass, and then diluting the coating liquid with water such that a dry coating film thickness of 40 nm would be attained.

- Platinum-based catalyst: Platinum-based catalyst emulsion (produced by Shin-Etsu Chemical Co., Ltd., trade name "CAT-PM-10A")

- Crosslinking reaction inhibitor: 1-ethynylcyclohexanol (produced by Alfa Lancaster)

[0095]

The formulation and the results are shown in Table 1. The numerical values of the respective silicones each indicate parts by mass of the solid content.

[0096]

[Table 1]

Table 1

		Number average molecular weight	Example 1	Example 2	Example 3	Compara tive Example 1	Compara tive Example 2	Compara tive Example 3	Compara tive Example 4
Silicone (1-a)		240,000	95	75	65	98	50		
Silicone (1-b)		40,000						95	65
Silicone (2)		5000	5	15	35	2	50	5	35
Adhesive tape	g/25 mm		384	57	32	450	18	7	23

peeling force									
Residual adhesion rate	%		92	93	97	92	87	80	88

[0097]

As can be seen from Table 1, the films of Examples of the present invention were superior in peelability and residual adhesion rate. This is because a film superior in various degrees of peelability and residual adhesive force is obtained by use of a specific configuration including a very high molecular weight silicone. On the other hand, in Comparative Example 1, crosslinking was insufficient, resulting in heavy peeling. In addition, in Comparative Example 2, an increased number of SiH residues remained in the silicone (2), transfer increased, and the residual adhesion rate decreased. In Comparative Example 3, the crosslinking formation was insufficient, the transfer of the main agent increased, and the residual adhesion rate decreased. In addition, in Comparative Example 4, an increased number of SiH residues remained in the silicone (2), transfer increased, and the residual adhesion rate decreased.

CLAIMS

1. A silicone release polyester film having, on at least one surface of the polyester film, a coating layer formed using a coating composition for release including an aqueous dispersion (1) of one or more silicones (A) containing an alkenyl group and/or a Q unit represented by $\text{SiO}_{4/2}$, an aqueous dispersion (2) of a silicone (B) having a hydrogen atom directly bonded to a Si atom represented by an Si-H group, a crosslinking reaction inhibitor, a platinum-based catalyst, and a nonionic emulsifier,

wherein a number average molecular weight of the silicones A is 150000 or more, and

a content of Si atoms contained in the Q unit is 0.05 mol% or more and 60 mol% or less.

2. The silicone release polyester film according to claim 1, wherein a content of the silicone (B) is 3 parts by mass or more and 45 parts by mass or less where a total content of the silicones (A) and the silicone (B) is 100 parts by mass.

3. The silicone release polyester film according to claim 1, wherein the alkenyl group of the silicones (A) is a vinyl group.

4. The silicone release polyester film according to claim 1, wherein a peeling force after being attached to a polyester adhesive tape is 20 g/25 mm width or more and 400 g/25 mm width or less.

5. The silicone release polyester film according to any one of claims 1 to 4, which is to be used for ceramic green sheet forming in production of a stacked ceramic capacitor.

6. A method for producing a silicone release polyester film, the method comprising a step of forming a coating layer on at least one surface of a polyester film using a coating composition for release including an aqueous dispersion (1) of one or more silicones (A) containing an alkenyl group and/or a Q unit represented by $\text{SiO}_{4/2}$, an aqueous dispersion (2) of a silicone (B) having a hydrogen atom directly bonded to a Si atom represented by an Si-H group, a crosslinking reaction inhibitor, a platinum-based catalyst, and a nonionic emulsifier,

wherein a number average molecular weight of the silicones A is 150000 or more, and

a content of Si atoms contained in the Q unit is in a range of 0.05 mol% or more and 60 mol% or less.

7. The method according to claim 6, wherein a content of the silicone (B) is 3 parts by mass or more and 45 parts by mass or less where a total content of the silicones (A) and the silicone (B) is 100 parts by mass.

8. The method according to claim 6 or 7, wherein the alkenyl group of the silicones (A) is a vinyl group.