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(54) **PRIMER COMPOSITION AND LAMINATE**

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(57) **ABSTRACT**

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Imparting superior electrification preventing or reducing properties to a cured silicone product without inhibiting adhesion between a substrate and the cured silicone product when integrating the substrate and the cured silicone product via a primer layer. A condensation reaction curable primer composition comprising a lithium salt (a) and a polyether modified polysiloxane (b); and a laminate obtained by integrating a substrate and a cured silicone product using an electrification preventing or reducing primer layer (cured product of the composition).

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## PRIMER COMPOSITION AND LAMINATE

## FIELD OF THE INVENTION

**[0001]** The present invention relates to a primer composition having electrification preventing or reducing properties; and a laminate including the composition, having electrification preventing or electrification reducing capability. Priority is claimed on Japanese Patent Application No. 2011-017035, filed on Jan. 28, 2011, the content of which is incorporated herein by reference.

## DESCRIPTION OF THE PRIOR ART

**[0002]** Films displaying releaseability (peelability) from various adhesive materials are known as release films (peelable films). Such release films have a structure where, for example, a layer of a cured silicone product having releaseability is formed on a surface of a substrate of plastic film or the like. These release films are manufactured by applying a releasable film-forming silicone composition to the surface of the substrate and then curing.

**[0003]** However, depending on the texture of the substrate, this type of releasable film-forming silicone composition may not bond or adhere to the substrate and, therefore, it is difficult to obtain a release film in which the releasable cured silicone-coated film and the substrate are strongly bonded and integrated.

**[0004]** Japanese Unexamined Patent Application Publication No. H07-003215 and Japanese Unexamined Patent Application Publication No. H09-208923 propose pre-forming a primer layer on a surface of a substrate, applying a releasable film-forming silicone composition thereon, and thermal curing as a solution to the problem described above.

**[0005]** However, silicone has excellent electrical insulating properties and, therefore, when, for example, removing the release film, there is a problem in that the releasable cured silicone film may become electrified and attract fine dust and the like.

**[0006]** Moreover, Japanese Unexamined Patent Application Publication No. 2009-030028 proposes compounding a cured silicone product with an anti-static agent as a solution to the problem described above.

## PRIOR ART DOCUMENTS

## Patent Documents

- [0007]** Patent Document 1: JP07-003215A  
**[0008]** Patent Document 2: JP09-208923A  
**[0009]** Patent Document 3: JP2009-030028A

## SUMMARY OF THE INVENTION

**[0010]** However, it is difficult to integrate the substrate and the cured silicone product well and obtain a laminate having superior electrification preventing or reducing properties.

**[0011]** A first object of the present invention is to impart superior electrification preventing or reducing properties to a cured silicone product without inhibiting the bonding between a substrate and the cured silicone product when integrating the substrate and the cured silicone product via a primer layer. Another object of the present invention is to provide a laminate obtained by integrating a substrate and a cured silicone product using an electrification preventing or reducing primer layer.

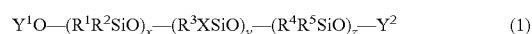
## Means to Resolve the Problems

**[0012]** The first object of the present invention is achieved by a condensation reaction curable primer composition comprising: a lithium salt (a) and a polyether modified polysiloxane (b), and preferably further comprising an isocyanate group-containing compound (c). The other object of the present invention is achieved by a laminate obtained by integrating a substrate and a cured silicone product using an electrification preventing or reducing primer layer, which is a cured product of the condensation reaction curable primer composition described above.

**[0013]** The lithium salt (a) is one or two or more selected from the group consisting of  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiSO}_3\text{CF}_3$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiSO}_3\text{C}_4\text{F}_9$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ , and  $\text{LiB}(\text{C}_6\text{H}_5)_4$ .

**[0014]** The polyether modified polysiloxane (b) is preferably a polyether modified polysiloxane having a hydroxyl group.

**[0015]** The polyether modified polysiloxane (b) is preferably a polyether modified polysiloxane having a terminal hydroxyl group represented by general formula (1) below:



**[0016]** In this formula,  $\text{R}^1\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ , and  $\text{R}^5$  each independently represent a hydrogen atom, a hydroxyl group, or

**[0017]** a monovalent hydrocarbon group. "X" represents  $-\text{R}^6-(\text{OR}^7)_a-(\text{OR}^8)_b-\text{OH}$  (wherein  $\text{R}^6$ ,  $\text{R}^7$ , and  $\text{R}^8$  each independently represent a divalent hydrocarbon group; and "a" and "b" are integers that satisfy  $a \geq 0$  and  $b \geq 0$ ).

**[0018]**  $\text{Y}^1$  and  $\text{Y}^2$  each independently represent "X", a hydrogen atom, or a monovalent hydrocarbon group.

**[0019]** "x", "y", and "z" are integers that satisfy  $x \geq 0$ ,  $y \geq 0$ ,  $z \geq 0$ , and  $x+y+z \geq 1$ .

**[0020]** However, when  $y=0$ , at least one of  $\text{Y}^1$  and  $\text{Y}^2$  is "X".

**[0021]** The condensation reaction curable primer composition of the present invention preferably further includes an isocyanate group-containing compound (c), and more preferably includes an isocyanate group-containing compound (c) that is a hexamethylene diisocyanate isocyanurate.

**[0022]** The condensation reaction curable primer composition of the present invention preferably includes one or two or more silane compounds (d) having a reactive functional group; and one or two or more compounds (e) selected from the group consisting of an organic aluminum compound, an organic titanate ester compound, and a platinum-based compound.

**[0023]** The silane compound (d) having a reactive functional group is preferably a silane compound represented by general formula (2) below:



**[0024]** In this formula,

**[0025]**  $\text{R}^9$  independently represents a reactive functional group,

**[0026]**  $\text{R}^{10}$  independently represents a monovalent hydrocarbon group, and

**[0027]** "c" is an integer from 1 to 3.

**[0028]** The present invention also relates to a cured product of the condensation reaction curable primer composition described above.

**[0029]** One aspect of a laminate of the present invention comprises a substrate and the cured product of the condensation reaction curable primer composition.

**[0030]** Another aspect of the laminate of the present invention comprises a substrate, a primer layer of the cured product of the condensation reaction curable primer composition, and a cured silicone layer. In this aspect, the primer layer is provided on the substrate and the cured silicone layer is provided on the primer layer.

**[0031]** The cured silicone layer is preferably a cured product of an addition reaction curable silicone.

**[0032]** The substrate is preferably made from resin.

**[0033]** The present invention also relates to a releasable or adhesive film or sheet, and a releasable or adhesive roll or roller including the laminate described above.

**[0034]** The present invention also relates to a method of preventing or reducing electrification of a laminate comprising the substrate and the cured silicone layer, wherein a primer layer of the cured product of the condensation reaction curable primer composition described above is provided between the substrate and the cured silicone layer.

#### Effects of the Invention

**[0035]** The primer composition or the primer layer formed from said composition of the present invention can increase bonding or adhesion between a substrate and a cured silicone product and, therefore, the substrate and the cured silicone product can be integrated via the primer layer well. Moreover, the primer composition or the primer layer formed from said composition of the present invention can impart superior electrification preventing or reducing properties to a layer of the cured silicone product, without inhibiting bonding between the substrate and the cured silicone product.

**[0036]** With the present invention, the primer composition or the primer layer formed from said composition of the present invention, regardless of including the lithium salt (a) and the polyether modified polysiloxane (b) as anti-static agents, can impart superior electrification preventing or reducing properties to the cured silicone product (silicone cured layer) formed on the primer layer.

**[0037]** The primer composition or the primer layer formed from said composition of the present invention does not negatively affect the curability of the cured silicone product. Therefore, the cured silicone product in the laminate of the present invention is integrated strongly with the substrate without impairing the curability or the releaseability or other beneficial surface properties thereof.

**[0038]** The cured silicone product of the laminate of the present invention has superior electrification preventing or reducing properties. For example, the laminate of the present invention is substantially free of properties that cause static electricity, which attracts fine dust and dirt. Therefore, the laminate of the present invention is suitable for use in applications where electrification is not preferable.

**[0039]** With the method of preventing or reducing electrification of the present invention, excellent electrification preventing or reducing properties can be imparted to a laminate including a substrate and a cured silicone product. Also, with the method of preventing or reducing electrification of the present invention, the cured silicone product and the substrate can be strongly integrated.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0040]** The present invention is characterized by the use of a condensation reaction curable primer composition includ-

ing a lithium salt (a) and a polyether modified polysiloxane (b). A detailed description thereof is given hereinafter.

**[0041]** In the present invention, the lithium salt (a) is a salt in which a positive ion of lithium and an arbitrary negative ion are ionically bonded. The type of lithium salt is not particularly limited, and examples thereof include  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiSO}_3\text{CF}_3$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiSO}_3\text{C}_4\text{F}_9$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ ,  $\text{LiB}(\text{C}_6\text{H}_5)_4$ , and the like. A single type of lithium salt may be used or two or more types may be combined.

**[0042]** The lithium salt may take the form of a solution, being dissolved in an organic solvent or a liquid organic polymer.

**[0043]** The organic solvent in which the lithium salt is dissolved is preferably a polar solvent, in which lithium salts are highly soluble. Examples thereof include methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, tert-butyl alcohol, amyl alcohol, hexyl alcohol, and similar alcohol systems; acetone, methyl ethyl ketone, methyl isobutyl ketone, 1-butanone, cyclohexanone, and similar ketone systems; diethylether, dibutylether, tetrahydrofuran, 1,4-dioxane, and similar ether systems; diethyl carbonate, dipropyl carbonate, ethylene carbonate, propylene carbonate, and similar carbonate systems; and the like. Preferable ester systems include ethyl acetate, n-propyl acetate, isobutyl acetate, and similar acetic esters; malonic esters; succinic esters; glutaric esters; adipate esters; phthalate esters; and the like. Systems having an alkylene oxide group and preferably an ethylene oxide group ( $-\text{CH}_2\text{CH}_2\text{O}-$ ) as a substituent of the organic solvent are particularly preferable because polarity is comparatively high and solubility of the lithium salt is high.

**[0044]** On the other hand, provided that a molecular weight thereof is comparatively low and the organic polymer itself is a liquid, a liquid organic polymer may be used as-is, or a solution in which a liquid or solid organic polymer is dissolved in a monomer or organic solvent constituting the organic polymer may be used as the liquid organic polymer in which the lithium salt is dissolved.

**[0045]** Examples of the organic polymer described above are not particularly limited provided that they are products of polymerizing, condensing, or condensation polymerizing a monomer, and examples thereof include polyesters, polyethers, polyurethanes, polycarbonates, polyamides, polyimides, poly(meth)acrylates, polyphosphazenes, polyvinylalcohols, and similar organic polymers.

**[0046]** Examples of the organic solvent for dissolving the organic polymer include toluene, xylene, and similar aromatic hydrocarbon system solvents; n-hexane, ligroin, kerosene, mineral spirits, and similar aliphatic hydrocarbon system solvents; cyclohexane, decahydronaphthalene, and similar cycloaliphatic hydrocarbon system solvents; methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, tert-butyl alcohol, amyl alcohol, hexyl alcohol, and similar alcohol system solvents; acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, and similar ketone system solvents; diethylether, dibutylether, tetrahydrofuran, 1,4-dioxane, and similar ether system solvents; diethyl carbonate, dipropyl carbonate, ethylene carbonate, propylene carbonate, and other carbonate system solvents; ethyl acetate, n-propyl acetate, isobutyl acetate, and other acetic esters; and malonic esters, succinic esters, glutaric esters, adipate esters, phthalate esters, and other ester system solvents.

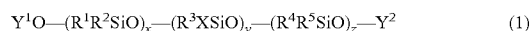
**[0047]** On the other hand, when dissolving the organic polymer in a monomer constituting the organic polymer, preferably the monomer constituting the polymer being dissolved is used, and examples thereof include ethylene glycol, diethyleneglycol, 1,4-butanediol, 1,6-hexanediol, catechol, and similar alcohols; ethylenediamine, hexamethylenediamine, isophoronediamine, and similar amines; adipic acid, phthalic acid, and similar carboxylic acids; hexamethylene diisocyanate, isophoronediiisocyanate, and similar isocyanates; ethylene oxide, propylene oxide, tetrahydrofuran, and similar alkylene oxides; ethylene carbonate, propylene carbonate, and similar alkylene carbonates; methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, 2-hydroxyethyl(meth)acrylate, and similar(meth)acrylates; N-vinylpyrrolidone;  $\gamma$ -caprolactone;  $\epsilon$ -caprolactam; vinyl acetate; and the like.

**[0048]** In order to increase the solubility of the lithium salt, the liquid organic polymer preferably contains any or all of the organic polymer, the organic solvent, and the monomer constituting the liquid organic polymer, and also has an alkylene oxide group, preferably the ethylene oxide group ( $-\text{CH}_2\text{CH}_2\text{O}-$ ), as a substituent.

**[0049]** A content of the lithium salt (a) is not particularly limited, but can be in a range of 0.05 to 200 parts by weight (mass), preferably 0.1 to 100 parts by weight (mass), and more preferably 0.3 to 60 parts by weight (mass) per 100 parts by weight (mass) of the solid content of the condensation reaction curable primer composition. If the content is less than 0.1 parts by weight (mass), the lithium ion concentration will be excessively low, leading to the possibility that the antistatic properties may be insufficient. If the content exceeds 200 parts by weight (mass), the lithium salt will absorb the moisture in the air and deliquesce, leading to the possibility that the antistatic properties may be insufficient. Unless noted otherwise, "the solid content of the condensation reaction curable primer composition" refers to a total of the component (a) and components (b) to (e) (described hereinafter) that form the solid primer layer obtained via condensation reaction and any non-volatile optional ingredients. Note that a solvent (f) that does not form solid content is not included therein.

**[0050]** The condensation reaction curing primer composition of present invention is imparted with superior electrification preventing or reducing properties by using the polyether modified polysiloxane (b) in combination with the lithium salt (a) and, moreover, bonding with the cured silicone product and curability of the composition is not negatively affected. The type of polyether modified polysiloxane (b) is not particularly limited, but a polyether modified polysiloxane having a hydroxyl group is preferable and a polyether modified polysiloxane having a terminal hydroxyl group is more preferable.

**[0051]** The polyether modified polysiloxane (b) is preferably a polyether modified polysiloxane having a terminal hydroxyl group represented by general formula (1) below:



**[0052]** In this formula,  $\text{R}^1\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ , and  $\text{R}^5$  each independently represent a hydrogen atom, a hydroxyl group, or a monovalent hydrocarbon group. "X" represents  $-\text{R}^6-(\text{OR}^7)_a-(\text{OR}^8)_b-\text{OH}$  (wherein,  $\text{R}^6$ ,  $\text{R}^7$ , and  $\text{R}^8$  each independently represent a divalent hydrocarbon group; and "a" and "b" are integers that satisfy  $a \geq 0$  and  $b \geq 0$ ).

**[0053]**  $\text{Y}^1$  and  $\text{Y}^2$  each independently represent "X", a hydrogen atom, or a monovalent hydrocarbon group.

**[0054]** "x", "y", and "z" are integers that satisfy  $x \geq 0$ ,  $y \geq 0$ ,  $z \geq 0$ , and  $x+y+z \geq 1$ .

**[0055]** However, when  $y=0$ , at least one of  $\text{Y}^1$  and  $\text{Y}^2$  is "X".

**[0056]** For example, "a" and "b" can each independently be an integer from 0 to 1,000, and are each preferably an integer from 0 to 100, and more preferably from 0 to 50.

**[0057]** For example, "x" and "z" can each independently be an integer from 1 to 100,000, and are each preferably an integer from 1 to 10,000, and more preferably from 1 to 1,000. On the other hand, "y" can be an integer from 0 to 100,000, and is preferably an integer from 0 to 10,000, and more preferably from 0 to 1,000. However, when  $y=0$ , at least one of  $\text{Y}^1$  and  $\text{Y}^2$  is "X".

**[0058]** The monovalent hydrocarbon group is preferably a substituted or unsubstituted straight or branched monovalent hydrocarbon group having from 1 to 30 carbons, and examples thereof include methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, heptyl groups, octyl groups, and similar straight or branched alkyl groups having from 1 to 30 carbons; cyclopentyl groups, cyclohexyl groups, and similar cycloalkyl groups having from 3 to 30 carbons; vinyl groups, allyl groups, butenyl groups, and similar alkenyl groups having from 2 to 30 carbons; phenyl groups, tolyl groups, and similar aryl groups having from 6 to 30 carbons; benzyl groups and similar aralkyl groups having from 7 to 30 carbons; and groups wherein the hydrogen atoms bonded to the carbon atoms of these groups are substituted at least partially by fluorine or a similar halogen atom, or an organic group having a hydroxyl group, an epoxy group, a glycidyl group, an acyl group, a carboxyl group, an ester group, an amino group, an amide group, a (meth)acryl group, a mercapto group, an isocyanate group, or the like (however, the total number of carbons is from 1 to 30). A straight alkyl group having from 1 to 6 carbons or phenyl group is preferable and a methyl group, ethyl group, or phenyl group is more preferable.

**[0059]** Examples of the divalent hydrocarbon group include substituted or unsubstituted straight or branched divalent hydrocarbon groups. Specific examples thereof include methylene groups, dimethylene groups, trimethylene groups, tetramethylene groups, pentamethylene groups, hexamethylene groups, heptamethylene groups, octamethylene groups, and similar straight or branched alkylene groups; vinylene groups, arylene groups, butenylene groups, hexenylene groups, octenylene groups, and similar alkenylene groups; phenylene groups, diphenylene groups, and similar arylene groups; dimethylenephenylene groups and similar alkylene-arylene groups; and groups wherein the hydrogen atoms bonded to the carbon atoms of these groups are substituted at least partially by fluorine or a similar halogen atom, or an organic group having a hydroxyl group, an epoxy group, a glycidyl group, an acyl group, a carboxyl group, an ester group, an amino group, an amide group, a (meth)acryl group, a mercapto group, an isocyanate group, or the like.

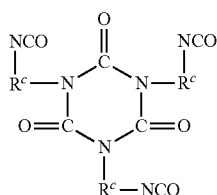
**[0060]** The number of carbons of the divalent hydrocarbon group is not particularly limited, but is preferably from 1 to 30, more preferably from 1 to 20, and even more preferably from 1 to 10.  $\text{R}^6$  and  $\text{R}^7$  are preferably straight or branched alkylene groups, and more preferably are ethylene groups, propylene groups, or butylene groups.  $\text{R}^7$  and  $\text{R}^8$  are preferably different types of divalent hydrocarbon groups.

**[0061]** A content of the polyether modified polysiloxane (b) is not particularly limited, but can be in a range of 0.05 to 200 parts by weight (mass), preferably 0.1 to 100 parts by weight (mass), and more preferably 0.3 to 60 parts by weight (mass) per 100 parts by weight (mass) of the solid content of the condensation reaction curable primer composition. If the content is less than 0.1 parts by weight (mass) or exceeds 200 parts by weight (mass), antistatic properties may be insufficient.

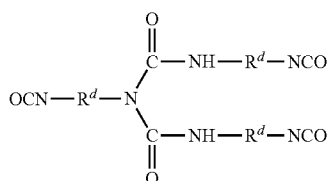
**[0062]** The condensation reaction curable primer composition of the present invention preferably further includes the isocyanate group-containing compound (c) and, as a result, primer effectiveness with respect to the cured silicone product and the curability of the primer layer can be enhanced. The isocyanate group-containing compound (c) is not particularly limited provided that it is a compound having at least one isocyanate group in the molecule, and examples thereof include 2,4-tolylene diisocyanate, diphenylmethane-4,4'-diisocyanate, xylylene diisocyanate, isophorone diisocyanate, lysine methyl ester diisocyanate, methylcyclohexyl diisocyanate, trimethylhexamethylene diisocyanate, hexamethylene diisocyanate, methylene bis(cyclohexyl isocyanate), bis(isocyanate methyl)cyclohexane, 1,6,11-undecane triisocyanate, n-pentane-1,4-diisocyanate, trimers thereof, isocyanurates or biurets thereof, polymers thereof having two or more isocyanate groups, blocked isocyanates, and the like.

**[0063]** The isocyanate group-containing compound (c) is preferably an isocyanurate or biuret represented by general formula (3) or (4) below.

Formula 1



General formula (3)



General formula (4)

**[0064]** In these formulae,  $R^c$  and  $R^d$  each independently represent a divalent hydrocarbon group. Note that the definition of divalent hydrocarbon group and examples thereof are the same as those described above.

**[0065]** The isocyanate group-containing compound (c) is more preferably a hexamethylene diisocyanate isocyanurate.

**[0066]** A content of the isocyanate group-containing compound (c) is not particularly limited, but can be in a range of 0.01 to 70 parts by weight (mass), preferably 0.03 to 40 parts by weight (mass), and more preferably 0.10 to 20 parts by weight (mass) per 100 parts by weight (mass) of the solid content of the condensation reaction curable primer composition. If the content is less than 0.03 parts by weight (mass) or exceeds 70 parts by weight (mass), curability of the primer

layer, antistatic properties, and primer effectiveness with respect to the cured silicone product may not be sufficiently improved.

**[0067]** The primer composition of the present invention is a condensation reaction curable composition and, when including the lithium salt (a) and the polyether modified polysiloxane (b), the cured silicone product and the substrate can be integrated well via a cured primer layer (formed from the primer composition) and superior electrification preventing or reducing effects can be imparted to the cured silicone product without impairing the curability and bonding with the cured silicone product formed on the primer layer. Provided that the primer composition of the present invention is a condensation reaction curable primer composition, the primer composition may be either silicone-based or non-silicone-based. From the perspective of enhancing compatibility with the component (b) and bonding with the cured silicone product, the primer composition is preferably a condensation reaction curable silicone-based primer composition.

**[0068]** The condensation reaction curable silicone-based primer composition preferably includes one or two or more silane compounds (d) having a reactive functional group; and one or two or more compounds (e) selected from the group consisting of an organic aluminum compound, an organic titanate ester compound, and a platinum-based compound. With the primer layer formed by condensation curing these components, particularly superior bonding with the cured silicone product can be obtained, the lithium salt (a) and the polyether modified polysiloxane (b) can display uniform compatibility in the primer layer, and particularly superior curability and electrification preventing or reducing effects can be obtained.

**[0069]** The silane compound (d) having the reactive functional group is a base compound of the condensation reaction curable silicone-based primer composition, and is not particularly limited provided that it has at least one reactive functional group in the molecule, but preferably is a compound represented by general formula (2) below.



**[0070]** In this formula,

**[0071]**  $R^9$  independently represents a reactive functional group,

**[0072]**  $R^{10}$  independently represents a monovalent hydrocarbon group, and

**[0073]** “c” is an integer from 1 to 3.

**[0074]** In the present invention, the reactive functional group ( $R^9$ ) is defined as a vinyl group, an allyl group, a butenyl group, or a similar alkenyl group; or a hydroxyl group, an epoxy group, a glycidyl group, an acyl group, a carboxyl group, an ester group, an amino group, an amide group, a (meth)acryl group, a hydroxyl group, a mercapto group, an isocyanate group, or similar reactable functional group or a monovalent organic group having said functional group. One or a plurality of functional groups may exist in the monovalent organic group.  $R^9$  is preferably a monosaturated or aromatic hydrocarbon group having at least one of the functional groups described above. Specific examples of the reactive functional group include 3-hydroxypropyl groups, 3-(2-hydroxyethoxy)propyl groups, 3-mercaptopropyl groups, 2,3-epoxypropyl groups, 3,4-epoxybutyl groups, 4,5-epoxypentyl groups, 2-glycidoxyethyl groups, 3-glycidoxypropyl groups, 4-glycidoxybutyl groups, 2-(3,4-epoxycy-

clohexyl)ethyl groups, 3-(3,4-epoxycyclohexyl)propyl groups, aminopropyl groups, N-methylaminopropyl groups, N-butylaminopropyl groups, N,N-dibutylaminopropyl groups, 3-(2-aminoethoxy)propyl groups, 3-(2-aminoethylamino)propyl groups, 3-carboxypropyl groups, 10-carboxydecyl groups, 3-isocyanate propyl groups, and the like.

**[0075]** R<sup>10</sup> preferably is a monovalent hydrocarbon group, does not have the reactive functional group described above, and is a substituted or unsubstituted straight or branched monovalent hydrocarbon group having from 1 to 30 carbons. Examples thereof include methyl groups, ethyl groups, propyl groups, butyl groups, pentyl groups, hexyl groups, heptyl groups, octyl groups, and similar straight or branched alkyl groups having from 1 to 30 carbons; cyclopentyl groups, cyclohexyl groups, and similar cycloalkyl groups having from 3 to 30 carbons; phenyl groups, tolyl groups, and similar aryl groups having from 6 to 30 carbons; benzyl groups and similar aralkyl groups having from 7 to 30 carbons; and groups wherein the hydrogen atoms bonded to the carbon atoms of these groups are substituted at least partially by fluorine or a similar halogen atom (however, the total number of carbons is from 1 to 30). A straight alkyl group having from 1 to 6 carbons or phenyl group is preferable and a methyl group, ethyl group, or phenyl group is more preferable. Particularly, the group represented by (OR<sup>10</sup>) is preferably an alkoxy group having from 1 to 12 carbons, and examples thereof include methoxy groups, ethoxy groups, propoxy groups, and similar alkoxy groups.

**[0076]** Examples of the silane compound represented by general formula (2) include alkenyl trialkoxysilanes. Examples of the alkenyl trialkoxysilanes include allyltrimethoxysilane, allyltriethoxysilane, allyltri(ethoxymethoxy)silane, butenyltrimethoxysilane, hexenyltrimethoxysilane, hexenyltriethoxysilane, and one or two or more partially hydrolyzed condensates of organoalkoxysilanes thereof. Of these, allyltrimethoxysilane is preferable.

**[0077]** On the other hand, examples of the silane compound represented by general formula (2) include  $\gamma$ -methacryloxy group-containing organoalkoxysilanes, epoxy group-containing organoalkoxysilanes, vinyl group-containing organoalkoxysilanes, vinyl group-containing acetoxysilanes, and the like. Of these, examples of the  $\gamma$ -methacryloxy group-containing organoalkoxysilanes include  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -methacryloxypropyltriethoxysilane, and  $\gamma$ -methacryloxypropylmethyldimethoxysilane; examples of the epoxy group-containing organoalkoxysilanes include  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane, and  $\beta$ -(3,4-epoxycyclohexyl)ethyl trimethoxysilane; and examples of the vinyl group-containing organoalkoxysilanes include vinyl trimethoxysilane, vinyl triethoxysilane, and vinyl methyl dimethoxysilane.

**[0078]** The one or two or more compounds (e) selected from the group consisting of an organic aluminum compound, an organic titanate ester compound, and a platinum-based compound are components that function as a condensation reaction catalyst of the component (d) and that enhance bonding with the cured silicone product.

**[0079]** Examples of the organic aluminum compound include (CH<sub>3</sub>O)<sub>3</sub>Al, (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>Al, (n-C<sub>6</sub>H<sub>7</sub>)<sub>3</sub>Al, and similar aluminum alcoholates; naphthenic acid, stearic acid, oleylic acid, benzoic acid, and similar aluminum salts; aluminum chelates obtained by reacting an aluminum alcoholate with an acetoacetic acid ester or a dialkyl malonate; organic acid salts

of aluminum oxide; aluminum acetyl acetonate; and the like. Of these, aluminum chelates are preferable, and specific examples thereof include aluminum tris(acetyl acetonate), aluminum monoacetyl acetonate bis(ethylacetoacetate), aluminum bisethylacetoacetate monoacetyl acetonate, and the like.

**[0080]** A single aluminum chelate may be used or a combination of two or more may be used.

**[0081]** Examples of the organic titanate ester include organic titanate acid esters, chelate compounds of titanium, chelate compounds of a silicic acid ester of titanium, and partially hydrolyzed condensates thereof. Specific examples of such compounds include tetraisopropyl titanate, tetra-n-butyl titanate, butyl titanate dimer, tetra(2-ethylhexyl)titanate, diethoxytitanium bis(acetyl acetonate), titanium diacetylacetonate, titanium diacetylacetate, titanium octylglycolate, titanium lactate, titanium lactate ethyl ester, titanium triethanolamine, and partially hydrolyzed condensates thereof. A single aluminum chelate may be used or a combination of two or more may be used.

**[0082]** Examples of the platinum-based compound include chloroplatinic acid, alcohol-modified chloroplatinic acid, complexes of platinum and a diketone, platinum-olefin complexes, complexes of chloroplatinic acid and an alkenylsiloxane, and the like. Of these, for use in hydrosilylation reactions, the platinum-olefin complexes and the complexes of chloroplatinic acid and an alkenylsiloxane (e.g. divinyltetramethyl disiloxane) are preferable, and a complex compound of chloroplatinic acid and a divinyltetramethyl disiloxane is more preferable.

**[0083]** Contents of the components (d) and (e) are not particularly limited, but the content of the component (e) is preferably from 1 to 1,000 parts by weight (mass), more preferably from 5 to 500 parts by weight (mass), and even more preferably from 10 to 200 parts by weight (mass) per 100 parts by weight (mass) of the component (d).

**[0084]** The primer composition of the present invention may include a solvent (f). The solvent (f) is used to adjust the viscosity of the primer composition of the present invention to a viscosity that is suitable for the work of applying the primer, and is not particularly limited provided that it can dissolve the component (a) and the component (b), the component (a) to the component (c) or, alternately, the component (a) to the component (e), described respectively above. Examples of the solvent include toluene, xylene, and similar aromatic hydrocarbon solvents; pentane, hexane, heptane, and similar aliphatic hydrocarbon solvents; trichloroethylene, perchloroethylene, trifluoromethylbenzene, 1,3-bis(trifluoromethyl)benzene, methylpentafluorobenzene, and similar halogenated hydrocarbon solvents; ethyl acetate, methyl ethyl ketone, methyl isobutyl ketone, and similar non-silicone-based solvents; hexamethyl cyclotrisiloxane, octamethyl cyclotetrasiloxane, decamethyl cyclopentasiloxane, and similar silicone-based solvents. The content of the solvent (f) can be determined as desired, but is preferably from 10 to 99.9 wt. % (mass %) of the primer composition.

**[0085]** The primer composition of the present invention can include various additives in addition to the components described above for the purpose of enhancing the performance of the primer composition. Examples of the additives include an organohydrogenpolysiloxane represented by the average unit formula:



(in the formula,

[0086] R<sup>11</sup> represents a monovalent hydrocarbon group;

[0087] “d” is, on average 0 ≤ d ≤ 3; and “e” is, on average, 1 ≤ e ≤ 3; however, 1 ≤ d + e ≤ 3) having a viscosity at 25° C. of from 1 to 10,000 centistokes;

[0088] 2,5-dimethyl-2,5 di-(t-butylperoxy)hexane, di-t-butyl peroxide, benzoyl peroxide, vinyl tris(t-butylperoxy)silane, trimethyl(t-butylperoxy)silane, and similar organic peroxides;

[0089] a diorganopolysiloxane represented by the average unit formula:

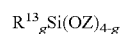


(in the formula,

[0090] R<sup>12</sup> represents a monovalent hydrocarbon group; however at least 0.2 mol % of R<sup>12</sup> is comprised of alkenyl groups; and

[0091] “P” is a number from 1.9 to 2.3) having a viscosity at 25° C. of not less than 5,000 centistokes;

[0092] a diorganopolysiloxane represented by the average unit formula:



(in the formula,

[0093] R<sup>13</sup> each independently represent a monovalent hydrocarbon group having from 1 to 8 carbons;

[0094] “Z” each independently represent a hydrogen atom, an alkyl group, an aryl group, an aralkyl group, or a —R<sup>n</sup>—OR<sup>13</sup> group (where R<sup>n</sup> is an alkylene group); and “g” represents a value from 0 to 3);

[0095] powdered silica or a similar inorganic filler;

[0096] a fatty acid salt of cerium, a fatty acid salt of iron, titanium oxide, carbon black, or similar heat resistance enhancers or pigments; or the like. Note that the definition of the monovalent hydrocarbon group and examples thereof are the same as those described above. Of the silanes described above, compounding alkyltrialkoxysilanes, dialkyl dialkoxysilanes, trialkyl alkoxysilanes, and similar hydrolysable silanes other than the component (d) in the condensation reaction curable primer composition of the present invention as necessary is included in the scope of the preferred embodiment of the present invention.

[0097] The condensation reaction curable primer composition of the present invention can be manufactured by uniformly mixing the components described above using a mixer or similar mechanical force.

[0098] With the condensation reaction curable primer composition of the present invention, various substrates and cured silicone products can be integrated by curing. The present invention also relates to a laminate including a substrate and a cured product of the primer composition described above; and a laminate including a substrate and a primer layer of the cured product of the primer composition described above, and a cured silicone layer, where the primer layer is provided on the substrate and the cured silicone layer is provided on the primer layer.

[0099] The laminate can be manufactured by: forming the primer layer by applying the condensation reaction curable primer composition of the present invention to the substrate and then air-drying for not less than 30 minutes or, alternately, heat treating at a temperature from, for example, 50° C. to 110° C.; and, thereafter, forming the cured silicone layer by applying the curable silicone composition and heating, or the

like. The method of applying is not particularly limited, and spray, brush, immersion, and similar known techniques can be used.

[0100] The cure system used as the curable silicone composition is not particularly limited, and examples thereof include addition reaction cure systems, radical reaction cure systems including an organic peroxide, high energy beam cure systems, condensation reaction cure systems, and similar curable silicone compositions. Particularly, a radical reaction curable silicone composition including diorganopolysiloxane raw rubber and an organic peroxide, or an addition reaction curable silicone composition including an alkenyl group-containing diorganopolysiloxane, an organohydrogenopolysiloxane, and a platinum-based catalyst is preferable. Moreover, the releasable (peelable) silicone cured layer formed on the primer layer of the present invention is preferably a cured product of an addition reaction curable silicone composition that is cured using a platinum-based catalyst.

[0101] The addition reaction curable silicone composition includes, for example:

[0102] (A) an organopolysiloxane having at least two alkenyl groups bonded to a silicon atom in the molecule, (B) an organohydrogenopolysiloxane having at least two hydrogen atoms bonded to a silicon atom in the molecule, and (C) a hydrosilylation reaction platinum-based catalyst.

[0103] Generally, the component (A) has a straight molecular structure, but may also have a branched structure. The silicon-bonded alkenyl groups of the component (A) are preferably alkenyl groups having from 2 to 10 carbons, and examples thereof include vinyl groups, allyl groups, butenyl groups, pentenyl groups, hexenyl groups, heptenyl groups, octenyl groups, nonenyl groups, and decenyl groups. Of these, vinyl groups are preferable, but allyl groups and hexenyl groups are also preferable. The content of the alkenyl groups in the molecule is preferably from 0.003 to 20.0 mol %, and more preferably from 0.005 to 10.0 mol % of all the organic groups bonded to the silicon atom in a molecule. An even more preferable range of the content is from 0.01 to 5.0 mol %. If the content of the alkenyl groups is less than the lower limit described above, a curing rate sufficient for practical use may not be obtained. If the content exceeds the upper limit described above, peel force of the cured layer may increase excessively. The alkenyl groups can be bonded to a silicon atom at the end of the molecular chain, to a silicon atom in a sidechain, or to both a silicon atom at the end of the molecular chain and a silicon atom in a sidechain.

[0104] Examples of organic groups, other than the alkenyl groups bonded to the silicon atom, in the component (A) include methyl groups, ethyl groups, propyl groups, butyl groups, hexyl groups, heptyl groups, octyl groups, nonyl groups, decyl groups, and similar alkyl groups; phenyl groups, tolyl groups, xylyl groups, and similar aryl groups; benzyl groups, phenethyl groups, and similar aralkyl groups; 3-chloropropyl groups, perfluoroalkyl groups represented by the formula: C<sub>m</sub>F<sub>2m+1</sub>CH<sub>2</sub>CH<sub>2</sub>— (where “m” is an integer from 1 to 10; e.g. 3,3,3-trifluoropropyl groups and pentafluorobutyl groups), and similar halogenated alkyl groups; etherified perfluoroalkyl groups represented by the formulae: F[CF(CF<sub>3</sub>)CF<sub>2</sub>O]<sub>n</sub>CF(CF<sub>3</sub>)CF<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—, F[CF(CF<sub>3</sub>)CF<sub>2</sub>O]<sub>n</sub>CF(CF<sub>3</sub>)CF<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—, F[CF(CF<sub>3</sub>)CF<sub>2</sub>O]<sub>n</sub>CF(CF<sub>3</sub>)CF<sub>2</sub>CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>—, F[CF(CF<sub>3</sub>)CF<sub>2</sub>O]<sub>n</sub>CF(CF<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>—, C<sub>m</sub>F<sub>2m+1</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—, and C<sub>m</sub>F<sub>2m+1</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH— (where “n” is an integer from 1 to 5, and “m” is an integer from 3 to 10); and cyanoethyl

groups. Of these, from the perspectives of ease of synthesis and properties of the cured layer, alkyl groups, phenyl groups, or perfluoroalkyl groups (however, having not less than 50 mol % methyl groups) are preferable. More preferably, all of the organic groups other than the alkenyl groups are methyl groups.

**[0105]** Specific examples of the component (A) include dimethylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups, dimethylsiloxane-methylvinylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, dimethylsiloxane-methylvinylsiloxane copolymers capped at both molecular terminals with dimethylvinylsiloxy groups, dimethylsiloxane-methylvinylsiloxane copolymers capped at both molecular terminals with dimethylethoxysiloxy groups, dimethylsiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with dimethylvinylsiloxy groups, and dimethylsiloxane-methyl (3,3,3-trifluoropropyl)siloxane copolymers capped at both molecular terminals with dimethylvinylsiloxy groups.

**[0106]** The component (A) may be a liquid or in a raw rubber state at room temperature, but, when used in a solvent-free composition, is preferably a liquid having a viscosity of preferably from 50 to 50,000 mPa·s and more preferably from 50 to 20,000 mPa·s. When the component (A) is in a raw rubber state at room temperature, as described hereinafter, the component (A) is preferably dissolved in xylene, toluene, or a similar organic solvent.

**[0107]** The component (A) is a base compound of the addition reaction curable silicone composition, and a content thereof can, for example, be from 60.0 to 99.5 wt. % (mass %), and preferably is from 70.0 to 99.0 wt. % (mass %) of the entire solid content of the composition. A component (B) is a crosslinking agent that crosslinks the component (A) via a hydrosilylation reaction, and a content thereof can, for example, be from 0.5 to 40.0 wt. % (mass %) of the entire composition. "Of the entire solid content of the composition" refers to a compounded amount shown as the contents (in wt. % (mass %)) of each of the components when an entire weight (mass), excluding the organic solvent, of a sum of the component (A), the component (B), and the non-volatile optional components that form the cured product of the addition reaction curable silicone composition is set to 100 wt. % (mass %).

**[0108]** The component (B) is preferably an organohydrogenpolysiloxane that is an alkyl group or phenyl group having a viscosity at 25° C. from 1 to 1,000 mPa·s, at least two silicon-bonded hydrogen atoms per molecule, and in which silicon-bonded organic groups have from 1 to 8 carbons. It is necessary for the component (B) to have two or more silicon-bonded hydrogen atoms in the molecule in order to crosslink the component (A) and, preferably, the component (B) has three or more silicon-bonded hydrogen atoms per molecule.

**[0109]** The bonding sites of the silicon-bonded hydrogen atoms in the component (B) are not particularly limited, and examples thereof include molecular terminals and/or sidechains. The content of the silicon-bonded hydrogen atoms is preferably from 0.001 to 1.7 wt. % (mass %) and more preferably from 0.005 to 1.7 wt. % (mass %).

**[0110]** Examples of the silicon-bonded organic groups of the component (B) include methyl groups, ethyl groups, propyl groups, butyl groups, octyl groups, and similar alkyl groups having from 1 to 8 carbons and phenyl groups, and not less than 50% of a total thereof is preferably alkyl groups

having from 1 to 8 carbons. Of these alkyl groups, from the perspectives of cured layer properties and ease of manufacture, methyl groups are preferable. The component (B) may have a straight, branched, networked, or cyclic molecular structure.

**[0111]** A viscosity at 25° C. of the component (B) is preferably from 1 to 1,000 mPa·s and more preferably from 5 to 500 mPa·s. It is not preferable that the viscosity at 25° C. is less than the lower limit described above because the component (B) will be prone to volatilizing in the silicone composition. Additionally it is not preferable that the viscosity at 25° C. exceed the upper limit described above because curing time of the silicone composition may lengthen and the overall viscosity of the addition reaction curable silicone composition will be high.

**[0112]** Specific examples of the component (B) include methylhydrogenpolysiloxanes capped at both molecular terminals with trimethylsiloxy groups, dimethylsiloxane-methyl hydrogen siloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, dimethylsiloxane-methyl hydrogen siloxane copolymers capped at both molecular terminals with dimethylhydrogensiloxy groups, cyclic methylhydrogenpolysiloxane, cyclic methylhydrogensiloxane-dimethylsiloxane copolymers, tris(dimethylhydrogensiloxy) methylsilanes, and tetra(dimethylhydrogensiloxy)silanes.

**[0113]** A compounding ratio of the component (A) to the component (B) is preferably such that a molar ratio of the amount of silicon-bonded hydrogen atoms in the component (B) to the amount of alkenyl groups in the component (A) is from 0.3 to 10.0. If this molar ratio is less than 0.3, the cured layer may be weak. If this molar ratio exceeds 10.0, releasability from adhesive matter may decline, and blocking may easily occur between cured layers. Additionally, change over time of peel force may increase and practical usability may be impaired. From these perspectives, amounts such that the molar ratio is from 0.7 to 5.0 are preferable.

**[0114]** A component (C) promotes the hydrosilylation reaction crosslinking of the component (A) and the component (B) and also promotes curing. Specific examples of the component (C) include chloroplatinic acid, an alcohol solution of chloroplatinic acid, an aldehyde solution of chloroplatinic acid, an olefin complex of chloroplatinic acid, and a complex of chloroplatinic acid and a diketone; a complex of chloroplatinic acid and a divinyltetramethyl disiloxane, a complex of chloroplatinic acid and a tetramethyltetravinylcyclotetrasiloxane, a platinum-divinyltetramethyl disiloxane complex, a platinum-tetramethyltetravinylcyclotetrasiloxane complex, and similar platinum-alkenylsiloxane complexes; compounds where platinum tetrachloride, platinum fine particles, alumina fine particles, or silica fine particles carry fine particles of platinum, platinum black, olefin complexes of platinum, diketone complexes of platinum, and carbonyl complexes of platinum.

**[0115]** From the perspectives of compatibility with the component (A) and the component (B), solubility in organic solvents, and curing reaction promotion capability, the component (C) is preferably chloroplatinic acid, a complex of chloroplatinic acid and a divinyltetramethyl disiloxane, a complex of chloroplatinic acid and a tetramethyltetravinylcyclotetrasiloxane, a platinum-divinyltetramethyl disiloxane complex, a platinum-tetramethyltetravinylcyclotetrasiloxane complex, or a similar platinum-alkenylsiloxane complex.

**[0116]** A compounded amount of the component (C) is a catalytic amount or, in other words, an amount sufficient to



cure the silicone composition. From the perspectives of curability of the composition, bonding to the substrate, and cost effectiveness, the compounded amount is, in terms of the amount of platinum metal, preferably in a range from 5 to 1,000 ppm and more preferably in a range from 10 to 500 ppm per 100 parts by weight (mass) of a total of the component (A) and the component (B).

[0117] In addition to the components described above, the addition reaction curable silicone composition preferably includes a hydrosilylation reaction suppressing agent in order to suppress gelling and curing at room temperature, enhance storage stability, and impart heat curability properties to the composition. Examples of the hydrosilylation reaction suppressing agent include acetylene-based compounds, ene-yne compounds, organic nitrogen compounds, organic phosphorus compounds, and oxime compounds. Specific examples thereof include 3-methyl-1-butyne-3-ol (methylbutynol), 3,5-dimethyl-1-hexyne-3-ol, 3-methyl-1-pentene-3-ol, phenylbutynol, and similar alkynyl alcohols; 3-methyl-3-pentene-1-yne, 3,5-dimethyl-1-hexyne-3-yne, 1-ethynyl-1-cyclohexanol, benzotriazole, methylvinylcyclosiloxane, and the like. A compounded amount of the hydrosilylation reaction suppressing agent, with the total amount of the components (A) to (C) described above being 100 parts by weight (mass), is generally in a range from 0.001 to 5 parts by weight (mass), but may be selected appropriately depending on the type of each component used, performance and amount of the hydrosilylation reaction platinum-based catalyst, the amount of alkenyl groups in the component (A), and the amount of silicon-bonded hydrogen atoms in the component (B).

[0118] The curable silicone composition can, as necessary, include an organic solvent. Specific examples of the organic solvent include toluene, xylene, and similar aromatic hydrocarbons; pentane, hexane, heptane, and similar aliphatic hydrocarbons; trichloroethylene, perchloroethylene, trifluoromethylbenzene, 1,3-bis(trifluoromethyl)benzene, methyl-pentafluorobenzene, and similar halogenated hydrocarbons; ethyl acetate; methyl ethyl ketone; and methyl isobutyl ketone. Of these, from the perspectives of solubility, safety, and cost performance, toluene, xylene, and n-hexane are preferable.

[0119] As necessary, other optional components can be added to the curable silicone composition. For example, stabilizers, heat-resistance enhancers, fillers, pigments, leveling agents, release control agents (heavy peeling additives or light peeling additives), mist suppressants, agents for enhancing adhesion to the substrate, anti-static agents, anti-foaming agents, non-reactive organopolysiloxanes, and the like may be added. Additionally, depending on the method by which the composition is applied in the manufacturing process, a silica fine particle or similar known thickening agent can be compounded in order to obtain a desired thickness of the coating. Furthermore, optionally, the lithium salt (a) and the polyether modified polysiloxane (b) can be added to the curable silicone composition and to the primer layer. Moreover, optionally, in addition to the component (A) and the component (B), an isocyanate group-containing compound (c) can be added to the curable silicone composition. In other words, in addition to the primer layer formed on the substrate, the cured silicone layer formed from the curable silicone composition can also include the lithium salt (a) and the polyether modified polysiloxane (b).

[0120] From the perspective of coatability on the substrate, an overall viscosity of the curable silicone composition at 25°

C. when the composition is solvent-free is preferably in a range from 50 to 5,000 mPa·s and, when the composition includes a solvent, is preferably in a range from 0.5 to 50,000 mPa·s.

[0121] The curable silicone composition can be easily manufactured by uniformly mixing the components described above. The order in which the components are compounded is not particularly limited, but, for example, in cases where the composition is not used immediately following mixing, the component (A), the component (B), and the component (C) are preferably each stored separately and mixed in immediately prior to use.

[0122] A suitable curing temperature of the curable silicone composition on the primer layer is generally from 50 to 200° C., but, provided that the heat resistance of the sheet-like substrate is excellent, may be 200° C. or higher. The method of heating is not particularly limited, and examples thereof include heating in a hot-air circulation oven, passing through a long heating furnace, and heat ray radiation by an infrared or halogen lamp. The curable silicone composition on the primer layer may also be cured using a combination of heating and UV light irradiation. Curing of the silicone composition is preferably carried out from 50 to 200° C. and, in this case, heating time can be set to be from 1 second to 5 minutes.

[0123] The primer composition of the present invention can be used to strongly adhere a cured silicone product to a substrate of iron, stainless steel, aluminum, nickel, zinc, copper, and various other metals; acrylic resins, phenolic resins, epoxy resins, polycarbonate resins, polybutylene terephthalate resins, alkali-treated fluoro resins, and various other resins; glass; ceramics; and other various inorganic materials. Hencefore, it has been difficult to strongly adhere a cured silicone product to a substrate having low surface activity such as, for example, stainless steel, nickel, polycarbonate, polybutylene terephthalate, alkali-treated fluoro resin, and similar substrates. However, when the primer composition of the present invention is applied, such a substrate and a cured silicone product can be strongly adhered and integrated.

[0124] Taking advantage of these properties, the primer composition of the present invention is useful in the manufacture of a product (the laminate) provided with a silicone release layer (peeling layer) such as a release film, a release paper, a release sheet, adhesive tape, adhesive film, packaging for adhesive products, and the like. In addition, the primer composition of the present invention can be effectively used as a primer layer for strongly adhering the core metal of a copying machine roll to a cured silicone layer, adhering the housing of an oil seal to a cured silicone layer, or adhering other metal or resin substrates and cured silicone layers.

[0125] In the present invention, due to the effects of the lithium salt in the primer layer, electrification of the surface of the cured silicone product can be prevented or reduced without compounding an anti-static agent in the cured silicone layer.

[0126] Therefore the present invention has an aspect as a method of preventing or reducing electrification of a laminate including a substrate and a cured silicone layer, wherein a primer layer is the cured product of the primer composition of the present invention is provided between the substrate and the cured silicone layer. Moreover, with the method described above, adhesion between the substrate and the cured silicone product layer is not inhibited.

## INDUSTRIAL APPLICABILITY

[0127] The primer composition of the present invention can be used as a base coat for imparting electrification preventing or reducing properties to a cured silicone product in addition to being used to strongly adhere a substrate and the cured silicone product regardless of the texture of the substrate.

[0128] The laminate of the present invention can be used as a releasable film or sheet (release paper, release tape, or the like) in cases where the cured silicone layer has releasability or, alternately, can be used as a member of a roll or roller (transport roll, toner anchoring rubber roll, or the like). On the other hand, in cases where the cured silicone layer has adhesive properties, the laminate of the present invention can be used as an adhesive film or sheet (adhesive tape or the like) or, alternately as a member of a roll or roller (cleaning roll or the like).

[0129] Static electricity electrification in the laminate of the present invention is reduced and, as a result, attraction of dust and dirt caused by static electricity is suppressed. Therefore, the laminate of the present invention can be suitably used in fields requiring clean environments such as the semiconductor, display, touch panel, copying machine, printer, and similar fields.

## EXAMPLES

[0130] Hereinafter, examples will be used to describe the present invention in more detail, but the present invention is not limited to these examples. Note that in the descriptions given below "parts" refer to parts by weight (mass).

## Practical Example 1

[0131] A primer composition I was prepared by mixing 10.0 parts of a glycidoxypropyltrimethoxysilane (d1); 10.0 parts of a  $\gamma$ -methacryloxypropyltrimethoxysilane (d2); 5.0 parts of an aluminum bis-ethylacetoacetate-mono-acetylacetonate (e1); 10.0 parts of a mixture (Denon RH-10, manufactured by Marubishi Oil Chemical Co., Ltd.) including polyether-modified silicone capped by terminal hydroxyl groups (b 1), a lithium salt (a1), and a methyl ethyl ketone (f1); 3.0 parts of a hexamethylene diisocyanate isocyanurate (Coronate HX, manufactured by Nippon Polyurethane Industry Co., Ltd.) (c1); 750 parts of the methyl ethyl ketone (f1); and 750 parts of toluene (f2). The mixture was applied on a polyethylene terephthalate (PET) film having a thickness of 38 microns so that a coated amount after drying would be 0.08 g/m<sup>2</sup>, and then dried for 10 seconds in a hot-air circulation oven preheated to 100° C. Thus, a primer-coated film I was obtained.

[0132] Thereafter, a coating bath was prepared including 100 parts of an addition curable silicone release agent (SD7226, manufactured by Dow Corning Toray Co., Ltd.); 450 parts of a methyl ethyl ketone; 450 parts of toluene; and 1.5 parts of an addition reaction platinum catalyst (SRX212, manufactured by Dow Corning Toray Co., Ltd.), said coating bath was coated on the primer-coated film I so that a coated amount after drying would be about 0.15 g/m<sup>2</sup>, and then the coated product was dried for 30 seconds in a hot-air circulation oven preheated to 130° C. Thus, a laminate I having a silicone cured layer on a surface of a plastic film was obtained.

## Comparative Example 1

[0133] Aside from not including the Denon RH-10 and the Coronate HX, a laminate II was obtained the same as the laminate of Practical Example 1.

## Practical Example 2

[0134] A primer composition II was prepared by mixing 330 parts of n-heptane (f3); 15.0 parts of an allyltrimethoxysilane (d3); 5.0 parts of tetra(n-butyl)titanate (e2); 2.0 parts of a complex of chloroplatinic acid and divinyltetramethyl disiloxane; 7.0 parts of a mixture (Denon RH-10, manufactured by Marubishi Oil Chemical Co., Ltd.) including a polyether-modified silicone capped by terminal hydroxyl groups (b1), a lithium salt (a1), and a methyl ethyl ketone (f1); 2.0 parts of a hexamethylene diisocyanate isocyanurate (Coronate HX, manufactured by Nippon Polyurethane Industry Co., Ltd.) (c1); and 1,000 parts of a methyl ethyl ketone (f1). The mixture was applied on a polyethylene terephthalate (PET) film having a thickness of 38 microns so that a coated amount after drying would be 0.08 g/m<sup>2</sup>, and then dried for 10 seconds in a hot-air circulation oven preheated to 100° C. Thus, a primer-coated film II was obtained.

[0135] Thereafter, a coating bath was prepared including 100 parts of an addition curable silicone release agent (SD7226, manufactured by Dow Corning Toray Co., Ltd.); 450 parts of a methyl ethyl ketone; 450 parts of toluene; and 1.5 parts of an addition reaction platinum catalyst (SRX212, manufactured by Dow Corning Toray Co., Ltd.), said coating bath was coated on the primer-coated film II so that a coated amount after drying would be about 0.15 g/m<sup>2</sup>, and then the coated product was dried for 30 seconds in a hot-air circulation oven preheated to 130° C. Thus, a laminate III having a silicone cured layer on a surface of a plastic film was obtained.

## Comparative Example 2

[0136] Aside from not including the Denon RH-10 and the Coronate HX, a laminate IV was obtained the same as the laminate of Practical Example 2.

## Comparative Example 3

[0137] Aside from using 6.0 parts of a polyoxyalkylene alkenyl ether sulfate (Electrostriper ME-5, manufactured by Kao Corp.) and 6.0 parts of a polyether-modified silicone (SH193, manufactured by Dow Corning Toray Co., Ltd.) in place of the 10 parts of Denon RH-10 as an anti-static agent, a laminate V was obtained the same as the laminate of Practical Example 1.

## Comparative Example 4

[0138] A release agent composition I was prepared including 100 parts of an addition reaction curable silicone release agent (SD7226, manufactured by Dow Corning Toray Co., Ltd.); 450 parts of a methyl ethyl ketone; 450 parts of toluene; 1.5 parts of an addition reaction platinum catalyst (SRX212, manufactured by Dow Corning Toray Co., Ltd.); 5.0 parts of a mixture (Denon RH-10, manufactured by Marubishi Oil Chemical Co., Ltd.) of a polyether-modified silicone capped by terminal hydroxyl groups, a lithium salt, and a methyl ethyl ketone; and 1.5 parts of a hexamethylene diisocyanate isocyanurate (Coronate HX, manufactured by Nippon Polyurethane Industry Co., Ltd.). Without applying a primer, the

release agent composition I was applied on a polyethylene terephthalate (PET) film having a thickness of 38 microns so that a coated amount after drying would be about 0.15 g/m<sup>2</sup>, and then the coated product was dried for 30 seconds in a hot-air circulation oven preheated to 130° C. Thus, a laminate VI having a silicone cured layer on a surface of a plastic film was obtained.

[0139] The formulations of the primer compositions used in Practical Examples 1 and 2 and Comparative Examples 1 to 3 are shown below.

[0140] Note that when obtaining the laminates I to VI, the same addition reaction curable silicone release agent SD7226 (manufactured by Dow Corning Toray Co., Ltd.) was used when forming the silicone cured layer on the primer layer.

TABLE 1

Primer compositions of Practical Example 1 and Comparative Example 1 (unit: parts)		
	Practical Example 1	Comparative Example 1
Glycidoxypropyltrimethoxysilane	10.0	10.0
γ-methacryloxypropyltrimethoxysilane	10.0	10.0
Aluminum bis-ethylacetoacetate-mono-acetylacetonate	5.0	5.0
Denon RH-10 (manufactured by Marubishi Oil Chemical Co., Ltd.)	10.0	—
Coronate HX (manufactured by Nippon Polyurethane Industry Co., Ltd.)	3.0	—
Methyl ethyl ketone	750	750
Toluene	750	750

TABLE 2

Primer compositions of Practical Example 2 and Comparative Example 2 (unit: parts)		
	Practical Example 2	Comparative Example 2
n-heptane	330	330
Allyltrimethoxysilane	15.0	15.0
Tetra (n-butyl) titanate	5.0	5.0
Complex of chloroplatinic acid and divinyltetramethyl disiloxane	2.0	2.0
Denon RH-10 (manufactured by Marubishi Oil Chemical Co., Ltd.)	7.0	—
Coronate HX (manufactured by Nippon Polyurethane Industry Co., Ltd.)	2.0	—
Methyl ethyl ketone	1000	1000

TABLE 3

Primer composition of Comparative Example 3 (unit: parts)	
	Comparative Example 3
Glycidoxypropyltrimethoxysilane	10.0
γ-methacryloxypropyltrimethoxysilane	10.0
Aluminum bis-ethylacetoacetate-mono-acetylacetonate	5.0
Polyoxyalkylene alkenyl ether sulfate SH193 (manufactured by Dow Corning Toray Co., Ltd.)	6.0
Coronate HX (manufactured by Nippon Polyurethane Industry Co., Ltd.)	3.0
Methyl ethyl ketone	750
Toluene	750

[0141] The adhesion, release resistance, residual adhesion ratio, surface resistance, and the half-life of charge decay of the laminates I to VI obtained in Practical Examples 1 and 2 and Comparative Examples 1 to 4 were measured and evaluated as follows. The results are shown in Table 4.

## (a) Adhesion

[0142] The laminates were aged for seven days in an oven at a humidity of 90% and a temperature of 40° C. Thereafter, the coated surface was rubbed with a finger. A quality of adhesion was evaluated by an observation of whether or not the coating layer fell off by the unaided eye.

## (b) Release Resistance

[0143] The laminates were aged for one day in an oven at a temperature of 70° C. Thereafter, an acrylic-based solvent adhesive (Olivine BPS-5127, manufactured by Toyo Ink Manufacturing Co., Ltd.) was applied to an application surface and was dried for 120 seconds in a hot-air circulation oven preheated to 70° C. Next, a polyethylene terephthalate (PET) film having a thickness of 25 microns was adhered to this treated surface and was aged for one day at a temperature of 25° C. under a load of 20 g/cm<sup>2</sup>. Samples were fabricated by cutting this aged product at a width of 5 cm. Using a tensile tester, the adhered PET film was peeled from the samples at an angle of 180° and a peel rate of 0.3 m/minute and the force (g) needed to perform the peeling was measured.

## (c) Residual Adhesion Ratio

[0144] Polyester adhesive tape (Nitto Polyester Tape 31B, manufactured by Nitto Denko Corporation) was adhered to the laminate and was aged for 20 hours at a temperature of 70° C. and under a load of 20 g/cm<sup>2</sup>. Thereafter, the adhered polyester adhesive tape was peeled off and that tape was adhered to a stainless steel plate using a 2 kg rubber roller. After aging for 30 minutes at 25° C., the adhered adhesive tape was peeled from the stainless steel plate at an angle of 180° and a peel rate of 0.3 m/minute using a tensile tester, and the adhesive strength (g) thereof was measured. This measured value was taken as “residual adhesive strength”. On the other hand, an unused polyester adhesive tape was adhered to the surface of the stainless steel plate using a 2 kg rubber roller, and the adhesive strength (g) thereof was measured in the same manner as described above. This measured value was taken as “base adhesive strength”. These adhesive strength values were used to calculate the residual adhesion ratio according to the following formula.

$$\text{Residual adhesion ratio(\%)} = \frac{\text{Residual adhesive strength}}{\text{Residual adhesive strength} + \text{Base adhesive strength}} \times 100$$

## (d) Surface Resistance

[0145] Surface resistance was measured using a STACK TR-2 type surface resistance meter (manufactured by Tokyo Electronics Co., Ltd.).

## (e) Measurement of Half-Life of Charge Decay

[0146] The half-life of charge decay was measured in accordance with the method described in JIS L1094 using a HONESTMETER H-110 (manufactured by Shishido Electrostatic Ltd.).

TABLE 4

	Practical Examples		Comparative Examples			
	Practical Example 1	Practical Example 2	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Adhesion	Good	Good	Good	Good	Poor	Poor
Release resistance (g)	18	22	20	19	Not measurable*	
Residual adhesion ratio (%)	93	93	94	93	Not measurable*	
Surface resistance ( $\Omega$ )	$1 \times 10^{10}$	$1 \times 10^{10}$	$5 \times 10^{11}$ or greater	$5 \times 10^{11}$ or greater	$5 \times 10^{11}$ or greater	$4 \times 10^9$
Half-life of charge decay (seconds)	5	3	120 or longer	120 or longer	85	1

\*With the laminates of Comparative Examples 3 and 4, the release resistance and residual adhesion ratio could not be measured because the adhesion of the Silicone cured layer was poor.

**[0147]** It is clear from Table 4 that with Practical Examples 1 and 2 that correspond to the present invention, adhesion between the silicone cured layer and the substrate is excellent, insulating properties are superior, and that electrification on the silicone cured layer can be prevented or reduced.

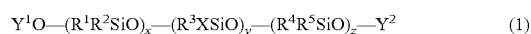
**[0148]** On the other hand, with Comparative Examples 1 and 2, in which primer compositions were used that lacked the component (A) (lithium salt), the polyether modified polysiloxane (b), and the isocyanate group-containing compound (c) of the present invention, the half-life of charge decay was long, and electrification on the silicone cured layer could not be effectively reduced. As shown in Comparative Example 3, when an anti-static agent other than a lithium salt is used, not only does the half-life of charge decay lengthen and it become impossible to effectively reduce electrification on the silicone cured layer, the adhesion between the silicone cured layer and the substrate on which said primer layer is used decreases significantly and both the primer effectiveness and the electrification preventing properties are insufficient. Moreover, as shown in Comparative Example 4, adhesion between the silicone cured layer and the substrate decreases significantly when a primer is not used.

1. A condensation reaction curable primer composition comprising: a lithium salt (a), and a polyether modified polysiloxane (b).

2. The condensation reaction curable primer composition of claim 1, wherein the lithium salt (a) is one or two or more selected from the group consisting of  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiSO}_3\text{CF}_3$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ,  $\text{LiSO}_3\text{C}_4\text{F}_9$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ , and  $\text{LiB}(\text{C}_6\text{H}_5)_4$ .

3. The condensation reaction curable primer composition of claim 1, wherein the polyether modified polysiloxane (b) is a polyether modified polysiloxane having a hydroxyl group.

4. The condensation reaction curable primer composition of claim 1, wherein the polyether modified polysiloxane (b) is a polyether modified polysiloxane having a terminal hydroxyl group represented by general formula (1) below:



wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ , and  $\text{R}^5$  each independently represent a hydrogen atom, a hydroxyl group, or a monovalent hydrocarbon group; X represents  $-\text{R}^6-(\text{OR}^7)_a-(\text{OR}^8)_b-\text{OH}$  wherein  $\text{R}^6$ ,  $\text{R}^7$ , and  $\text{R}^8$  each independently represent a divalent hydrocarbon group;

and a and b are integers that satisfy  $a \geq 0$  and  $b \geq 0$ ;  $\text{Y}^1$  and  $\text{Y}^2$  each independently represent X, a hydrogen atom, or a monovalent hydrocarbon group; and x, y, and z are integers that satisfy  $x \geq 0$ ,  $y \geq 0$ ,  $z \geq 0$ , and  $x+y+z \geq 1$ ; however, when  $y=0$ , at least one of  $\text{Y}^1$  and  $\text{Y}^2$  is X.

5. The condensation reaction curable primer composition of claim 1, further comprising an isocyanate group-containing compound (c).

6. The condensation reaction curable primer composition of claim 5, wherein the isocyanate group-containing compound (c) is a hexamethylene diisocyanate isocyanurate.

7. The condensation reaction curable primer composition of claim 1, further comprising: one or two or more silane compounds (d) having a reactive functional group; and

one or two or more compounds (e) selected from the group consisting of an organic aluminum compound, an organic titanate ester compound, and a platinum-based compound.

8. The condensation reaction curable primer composition of claim 7, wherein the silane compound (d) having a reactive functional group is represented by general formula (2) below:



wherein  $\text{R}^9$  independently represents a reactive functional group;  $\text{R}^{10}$  independently represents a monovalent hydrocarbon group; and c is an integer from 1 to 3.

9. A cured product of the condensation reaction curable primer composition according to claim 1.

10. A laminate comprising a substrate and the cured product according to claim 9.

11. A laminate comprising a substrate, a primer layer of the cured product according to claim 9, and a cured silicone layer, wherein the primer layer is provided on the substrate, and the cured silicone layer is provided on the primer layer.

12. The laminate of claim 11, wherein the cured silicone layer is a cured product of an addition reaction curable silicone composition.

13. The laminate of claim 10, wherein the substrate is made from resin.

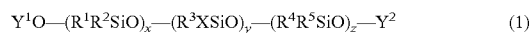
14. A releasable or adhesive film or sheet comprising the laminate according to claim 10.

15. A releasable or adhesive roll or roller comprising the laminate according to claim 10.

**16.** A method of preventing or reducing electrification of a laminate comprising a substrate and a cured silicone layer, wherein a primer layer of the cured product according to claim 9 is provided between the substrate and the cured silicone layer.

**17.** The condensation reaction curable primer composition of claim 2, wherein the polyether modified polysiloxane (b) is a polyether modified polysiloxane having a hydroxyl group.

**18.** The condensation reaction curable primer composition of claim 2, wherein the polyether modified polysiloxane (b) is a polyether modified polysiloxane having a terminal hydroxyl group represented by general formula (1) below:



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and  $R^5$  each independently represent a hydrogen atom, a hydroxyl group, or a monovalent hydrocarbon group; X represents  $-R^6-(OR^7)_a-(OR^8)_b-OH$  wherein  $R^6$ ,  $R^7$ , and  $R^8$  each independently represent a divalent hydrocarbon group; and a and b are integers that satisfy  $a \geq 0$  and  $b \geq 0$ ;  $Y^1$  and  $Y^2$  each independently represent X, a hydrogen atom, or a monovalent hydrocarbon group; and x, y, and z are integers that satisfy  $x \geq 0$ ,  $y \geq 0$ ,  $z \geq 0$ , and  $x+y+z \geq 1$ ; however, when  $y=0$ , at least one of  $Y^1$  and  $Y^2$  is X.

\* \* \* \* \*