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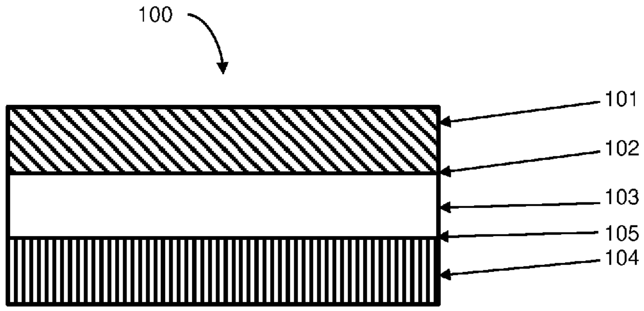

Figure 1

(57) Abstract: Provided is a polyorganosiloxane release coating composition, including: (A) an aryl-functional polydiorganosiloxane having a content of aliphatically unsaturated groups, (B) a polyorganosilicate resin having silicon bonded alkenyl groups, (C) a polyalkylhydrogensiloxane, having at least two silicon-bonded hydrogen atoms per a molecule, (D) a hydrosilylation reaction catalyst in a catalytic amount, (E) a hydrosilylation reaction inhibitor, (F) an anchorage additive, and optionally (G) a solvent; where the composition is free of polydiorganosiloxanes that do not have silicon bonded aryl groups, other than starting material (A). Also provided are a method for preparing a release liner(100) with a release coating(101) and the prepared release liner(100).

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POLYORGANOSILOXANE RELEASE COATING COMPOSITION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] None.

TECHNICAL FIELD

[0002] A polyorganosiloxane release coating composition and method for its preparation are disclosed. The polyorganosiloxane release coating composition can be cured on a substrate to form a release liner useful for protecting a pressure sensitive adhesive.

BACKGROUND

[0003] The use and market size of tight release liner applications is expanding in Asian markets. One proposed method to increase release force of a polyorganosiloxane release coating is to add a high release additive (generally a siloxane resin) to a diluted or solvent based release coating composition. However, including such an additive may be inefficient.

PROBLEM TO BE SOLVED

[0004] A polyorganosiloxane release coating composition, which can be applied onto the surface of a substrate such as a polymer film or paper to provide tight release force with low migration (as indicated by high sustained adhesion strength) is desired by customers, particularly in the electronics industry to avoid contamination of electronic components with polyorganosiloxane while still providing the desired release force.

SUMMARY

[0005] A polyorganosiloxane release coating composition comprises:

(A) a polydiorganosiloxane of unit formula:

$(R^1{}_2R^2SiO_{1/2})_a(R^1{}_2SiO_{2/2})_b(R^1R^3SiO_{2/2})_c(R^3{}_2SiO_{2/2})_d$, where each R^1 is an independently selected alkyl group of 1 to 18 carbon atoms, each R^2 is an independently selected alkenyl group of 2 to 18 carbon atoms, each R^3 is an independently selected aryl group of 5 to 20 carbon atoms, subscript a has an average value of 2, subscript b > 0, subscript c ≥ 0, subscript d ≥ 0 with the proviso that a quantity (c + d) > 0;

(B) a polyorganosilicate resin having silicon bonded alkenyl groups,

(C) a polyalkylhydrogensiloxane, having at least two silicon-bonded hydrogen atoms per a molecule;

(D) a hydrosilylation reaction catalyst in a catalytic amount;

(E) a hydrosilylation reaction inhibitor

(F) an anchorage additive; and

optionally (G) a solvent;

where the composition is free of polydiorganosiloxanes that do not have silicon bonded aryl groups.

[0006] A method for preparing a release liner comprises:

1) coating the polyorganosiloxane release coating composition described above on a surface of a substrate, and

2) curing the composition to form a release coating on the surface of the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 shows a partial cross section of a release liner 100. The release liner comprises a polyorganosiloxane release coating 101 prepared by curing the polyorganosiloxane release coating composition described herein on a first surface 102 of a film substrate 103. The release liner 100 further includes a carrier 104 mounted to an opposing surface 105 of the film substrate 103.

DETAILED DESCRIPTION

[0008] A polyorganosiloxane release coating composition comprises:

(A) a polydiorganosiloxane of unit formula:

$(R^1{}_2R^2SiO_{1/2})_a(R^1{}_2SiO_{2/2})_b(R^1R^3SiO_{2/2})_c(R^3{}_2SiO_{2/2})_d$, where each R^1 is an independently selected alkyl group of 1 to 18 carbon atoms, each R^2 is an independently selected alkenyl group of 2 to 18 carbon atoms, each R^3 is an independently selected aryl group of 5 to 20 carbon atoms, subscript a has an average value of 2, subscript b > 0, subscript c ≥ 0, subscript d ≥ 0 with the proviso that a quantity (c + d) > 0;

(B) a polyorganosilicate resin having silicon bonded alkenyl groups,

(C) a polyalkylhydrogensiloxane, having at least two silicon-bonded hydrogen atoms per a molecule, where the polyalkylhydrogensiloxane is present in an amount sufficient to provide 0.8 mole to 5 moles of silicon-bonded hydrogen atoms per mole of alkenyl groups in starting materials (A) and (B);

(D) a hydrosilylation reaction catalyst in a catalytic amount;

(E) a hydrosilylation reaction inhibitor, in an amount of 0.001 part by weight to 2 parts by weight, per 100 parts by weight of starting materials (A) and (B);

(F) an anchorage additive, in an amount of 0.01 part by weight to 10 parts by weight per 100 parts by weight of starting materials (A)and (B); and

optionally (G) a solvent;

where the composition is free of polydiorganosiloxanes that do not have silicon bonded aryl groups.

(A) Polydiorganosiloxane

[0009] The polyorganosiloxane release coating composition herein comprises starting material (A), a polydiorganosiloxane having both a silicon bonded alkenyl group and a silicon bonded aryl group. This polydiorganosiloxane may be a bis-alkenyl-terminated polydiorganosiloxane with pendant aryl groups. Starting material (A) the polydiorganosiloxane may have unit formula: $(R^1{}_2R^2SiO_{1/2})_a(R^1{}_2SiO_{2/2})_b(R^1R^3SiO_{2/2})_c(R^3{}_2SiO_{2/2})_d$, where each R^1 is an independently selected alkyl group of 1 to 18 carbon atoms, each R^2 is an independently selected alkenyl group of 2 to 18 carbon atoms, each R^3 is an independently selected aryl group of 5 to 20 carbon atoms, subscript a has an average value of 2, subscript b > 0, subscript c ≥ 0, subscript d ≥ 0 with the proviso that a quantity (c + d) > 0.

[0010] The alkyl group for R^1 has 1 to 18 carbon atoms, alternatively 1 to 12 carbon atoms, alternatively 1 to 6 carbon atoms, and alternatively 1 to 4 carbon atoms. Suitable alkyl groups for R^1 are exemplified by, but not limited to, methyl, ethyl, propyl (*e.g.*, iso-propyl and/or n-propyl), butyl (*e.g.*, isobutyl, n-butyl, tert-butyl, and/or sec-butyl), pentyl (*e.g.*, isopentyl, neopentyl, and/or tert-pentyl), hexyl, as well as branched saturated hydrocarbon groups of 6 carbon atoms. Alternatively, each R^1 is independently selected from the group consisting of methyl, ethyl, and propyl. Each instance of R^1 may be the same or different. Alternatively, each R^1 is a methyl group.

[0011] The alkenyl group for R^2 is capable of undergoing hydrosilylation reaction. Suitable alkenyl groups include as vinyl, allyl, butenyl, and hexenyl. Alternatively, each R^2 may be vinyl, allyl or hexenyl; and alternatively vinyl or hexenyl. Each instance of R^2 may be the same or different. Alternatively, each R^2 is a vinyl group.

[0012] The aryl group for R^3 has 5 to 20 carbon atoms, alternatively 6 to 10 carbon atoms. Suitable aryl groups are exemplified by, but not limited to, phenyl, tolyl, xylyl, naphthyl, benzyl, and dimethyl phenyl. Each instance of R^3 may be the same or different. Alternatively, each R^3 may be phenyl.

[0013] The subscripts a, b, c, and d in the unit formula above are sufficient to provide the polydiorganosiloxane with a Mn of at least 3,000 g/mol, alternatively 3,000 g/mol to 500,000 g/mol, and alternatively 15,000 g/mol to 400,000 g/mol. The polydiorganosiloxane may have an alkenyl group content of 0.01% to 5% by weight. The polydiorganosiloxane may have an aryl group content of 1% to 50% by weight.

[0014] Examples of aryl-functional polydiorganosiloxanes include dimethylvinyl-siloxy-terminated poly(dimethyl/methylphenyl)siloxane copolymers, dimethylvinyl-siloxy-terminated poly(dimethyl/diphenyl)siloxane copolymers, dimethylhexenyl-siloxy-terminated poly(dimethyl/methylphenyl)siloxane copolymers, dimethylhexenyl-siloxy-terminated poly(dimethyl/diphenyl)siloxane copolymers, and combinations of two or more thereof. the Aryl-functional polydiorganosiloxanes may be synthesized by equilibration processes known in the art, such as that described in U.S. Patent 6,956,087 and U.S. Patent 5,169,920.

(B) Polyorganosilicate Resin

[0015] The polyorganosiloxane release coating composition described herein further comprises starting material (B), a polyorganosilicate resin having silicon bonded alkenyl groups. The polyorganosilicate resin comprises monofunctional units ("M" units) of formula $R^M{}_3SiO_{1/2}$ and tetrafunctional units ("Q" units) of formula $SiO_{4/2}$, where each R^M is an independently selected monovalent hydrocarbyl group. Suitable monovalent hydrocarbyl groups for R^M may have 1 to 20 carbon atoms, alternatively 1 to 12 carbon atoms, alternatively 1 to 8 carbon atoms, alternatively 1 to 4 carbon atoms, and alternatively 1 to 2 carbon atoms. Alternatively, the hydrocarbyl groups for R^M may be selected from the group consisting of alkyl groups, alkenyl groups and aryl groups; alternatively alkyl and aryl; alternatively alkyl and alkenyl; and alternatively alkyl. The alkyl groups are exemplified by methyl, ethyl, propyl (*e.g.*, iso-propyl and/or n-propyl), butyl (*e.g.*, isobutyl, n-butyl, tert-butyl, and/or sec-butyl), pentyl (*e.g.*, isopentyl, neopentyl, and/or tert-pentyl), hexyl, heptyl, octyl, nonyl, and decyl, as well as branched saturated monovalent hydrocarbyl groups of 6 or more carbon atoms including cycloalkyl groups such as cyclopentyl and cyclohexyl. The aryl groups are exemplified by cyclopentadienyl, phenyl, tolyl, xylyl, anthracenyl, benzyl, 1-phenylethyl, 2-phenylethyl, and naphthyl. Monocyclic aryl groups may have 5 to 9 carbon atoms, alternatively 6 to 7 carbon atoms, and alternatively 5 to 6 carbon atoms. Polycyclic aryl groups may have 10 to 17 carbon atoms, alternatively 10 to 14 carbon atoms, and alternatively 12 to 14 carbon atoms. Alternatively, in the polyorganosilicate resin, each R^M may be independently selected from the group consisting of alkyl, alkenyl, and aryl. Alternatively, each R^M may be selected from methyl, vinyl and phenyl. Alternatively, at least one-third, alternatively at least two thirds of the R^M groups are methyl groups. Alternatively, the M units may be exemplified by $(Me_3SiO_{1/2})$, $(Me_2PhSiO_{1/2})$, and ($Me_2ViSiO_{1/2}$). The polyorganosilicate resin is soluble in solvents such as those described herein, exemplified by liquid hydrocarbons, such as benzene, toluene, xylene, and heptane, or in liquid organosilicon compounds such as low viscosity linear and cyclic polydiorganosiloxanes.

[0016] When prepared, the polyorganosilicate resin comprises the M and Q units described above, and the polyorganosilicate resin further comprises units with silanol (silicon bonded hydroxyl) groups and may comprise neopentamer of formula $Si(OSiR^M{}_3)_4$, where R^M is as described above. Si^{29} Nuclear Magnetic Resonance (NMR) spectroscopy, as described in U.S. Patent 9,509,209 at col. 32, Reference Example 2, may be used to measure molar ratio of M and Q units, where said ratio is expressed as {M(resin)+(M(neopentamer)}/{Q(resin)+Q(neopentamer)} and represents the molar ratio of the total number of triorganosiloxy groups (M units) of the resinous and neopentamer portions of the polyorganosilicate resin to the total number of silicate groups (Q units) in the resinous and neopentamer portions (M:Q ratio). M:Q ratio may be 0.5:1 to 1.5:1, alternatively 0.6:1 to 0.9:1.

[0017] The Mn of the polyorganosilicate resin depends on various factors including the types of hydrocarbyl groups represented by R^M that are present. The Mn of the polyorganosilicate resin refers to the number average molecular weight measured using GPC according to the procedure in U.S. Patent 9,593,209 at col. 31, Reference Example 1. The Mn of the polyorganosilicate resin may be greater than 1,000 g/mol, alternatively 1,000 g/mol to 8,000 g/mol, alternatively 1,000 g/mol to 2,000 g/mol, alternatively 1,100 g/mol to 1,900 g/mol, alternatively 1,200 g/mol to 1,800 g/mol, alternatively 1,300 g/mol to 1,700 g/mol, alternatively 1,400 g/mol to 1,600 g/mol, and alternatively 1,500 g/mol.

[0018] U.S. Patent 8,580,073 at col. 3, line 5 to col. 4, line 31, is hereby incorporated by reference for disclosing silicone resins, which are examples of polyorganosilicate resins described herein. The polyorganosilicate resin can be prepared by any suitable method, such as cohydrolysis of the corresponding silanes or by silica hydrosol capping methods. The polyorganosilicate resin may be prepared by silica hydrosol capping processes such as those disclosed in U.S. Patent 2,676,182 to Daudt, et al.; U.S. Patent 4,611,042 to Rivers-Farrell et al.; and U.S. Patent 4,774,310 to Butler, et al. The method of Daudt, et al. described above involves reacting a silica hydrosol under acidic conditions with a hydrolyzable triorganosilane such as trimethylchlorosilane, a siloxane such as hexamethyldisiloxane, or mixtures thereof, and recovering a copolymer having M-units and Q-units. The resulting copolymers generally contain from 2 to 5 percent by weight of silicon bonded hydroxyl (silanol) groups.

[0019] The intermediates used to prepare the polyorganosilicate resin may be triorganosilanes and silanes with four hydrolyzable substituents or alkali metal silicates. The triorganosilanes may have formula $R^M{}_3SiX^1$, where R^M is as described above and X^1 represents a hydrolyzable substituent such as halogen, alkoxy, acyloxy, hydroxyl, oximo, or ketoximo; alternatively, halogen, alkoxy or hydroxyl. Silanes with four hydrolyzable substituents may have formula $SiX^2{}_4$, where each X^2 is halogen, alkoxy or hydroxyl. Suitable alkali metal silicates include sodium silicate.

[0020] The polyorganosilicate resin prepared as described above typically contains silicon bonded hydroxyl groups, i.e., of formulae, $HOSi_{3/2}$ and/or $HOR^M{}_2SiO_{1/2}$. The polyorganosilicate resin may comprise up to 2% of silicon bonded hydroxyl groups. The concentration of silicon bonded hydroxyl groups present in the polyorganosilicate resin may be determined using FTIR spectroscopy according to ASTM Standard E-168-16. For certain applications, it may desirable for the amount of silicon bonded hydroxyl groups to be below 0.7%, alternatively below 0.3%, alternatively less than 1%, and alternatively 0 to 0.8%. Silicon bonded hydroxyl groups formed during preparation of the polyorganosilicate resin can be converted to trihydrocarbyl-siloxy groups or to a different hydrolyzable group by reacting the polyorganosilicate resin with a silane, disiloxane, or disilazane containing the appropriate terminal group. Silanes containing hydrolyzable groups may be added in molar excess of the quantity required to react with the silicon bonded hydroxyl groups on the polyorganosilicate resin.

[0021] Alternatively, the polyorganosilicate resin may further comprises 2% or less, alternatively 0.7% or less, and alternatively 0.3% or less, and alternatively 0.3% to 0.8% of units represented by formula $XSiO_{3/2}$ and/or $XR^M{}_2SiO_{1/2}$ where R^M is as described above, and X represents a hydrolyzable substituent, as described above for X^1.

[0022] The polyorganosilicate resin useful herein has terminal aliphatically unsaturated groups. The polyorganosilicate resin having terminal aliphatically unsaturated groups may be prepared by reacting the product of Daudt, *et al.* described above with an unsaturated organic group-containing endblocking agent and an endblocking agent free of aliphatic unsaturation, in an amount sufficient to provide from 3 to 30 mole percent of unsaturated organic groups in the final product. Examples of endblocking agents include, but are not limited to, silazanes, siloxanes, and silanes. Suitable endblocking agents are known in the art and exemplified in U.S. Patents 4,584,355; 4,591,622; and 4,585,836. A single endblocking agent or a mixture of such agents may be used to prepare such resin.

[0023] Alternatively, the polyorganosilicate resin may comprise unit formula: $(R^1{}_3SiO_{1/2})_e(R^1{}_2R^2SiO_{1/2})_f(SiO_{4/2})_g$, where R^1 and R^2 are as described above and subscripts e, f and g have average values such that e ≥ 0, f ≥ 0, g > 1, and (e + f) > 4, with the proviso that a quantity (e + f + g) is sufficient to give the polyorganosilicate resin the Mn described above.

[0024] Starting materials (A) and (B) may be present in relative amounts such that a resin/polymer weight ratio i.e., (B)/(A) ratio), is 1:10 to 10:1.

(C) Polyalkylhydrogensiloxane

[0025] The polyorganosiloxane release coating composition described herein further comprises starting material (C), a polyalkylhydrogensiloxane having at least two silicon-bonded hydrogen atoms per molecule, where the polyalkylhydrogensiloxane is present in an amount sufficient to provide 0.8 mole to 5 moles of silicon-bonded hydrogen atoms per mole of alkenyl groups in starting materials (A) and (B). Without wishing to be bound by theory, it is thought that starting material (C) may act as a crosslinker herein.

[0026] The polyalkylhydrogensiloxane may comprise unit formula (C1): $(R^1{}_3SiO_{1/2})_m(R^1HSiO_{2/2})_n(R^1{}_2SiO_{2/2})_o(R^1{}_2HSiO_{1/2})_p$, where R^1 is as described above, subscript m is 0 to 2, subscript p is 0 to 2, a quantity (m + p) has an average value of 2, subscript n > 0, subscript o > 0, a quantity (n + p) ≥ 3, and a quantity (m + n + o + p) has a value sufficient to give the polyalkylhydrogensiloxane a viscosity of 5 mPa·s to 500 mPa·s, alternatively 25 mPa·s to 200 mPa·s, and alternatively 25 mPa·s to 70 mPa·s measured at 25°C at 0.1 to 50 RPM on a Brookfield DV-III cone & plate viscometer with #CP-52 spindle.

[0027] Alternatively, the polyalkylhydrogensiloxane may comprise unit formula (C2): $(HR^1{}_2SiO_{1/2})_r(SiO_{4/2})_q$, where R^1 is as described above, and subscripts q and r are present in a molar ratio r/q of 0.5/1 to 2/1, alternatively >1/1 to 2/1, and a quantity (q + r) has a value sufficient to give the polyalkylhydrogensiloxane the viscosity described above.

[0028] Polyalkylhydrogensiloxanes for starting material (C) are exemplified by:
C-I) trimethylsiloxy-terminated poly(dimethyl/methylhydrogen)siloxane,
C-II) trimethylsiloxy-terminated polymethylhydrogensiloxane,
C-III) dimethylhydrogensiloxy-terminated poly(dimethyl/methylhydrogen)siloxane,
C-IV) dimethylhydrogensiloxy-terminated polymethylhydrogensiloxane,
C-V) dimethylhydrogensiloxy-terminated polysilicate, and
C-VI) a combination of any two or more of C-I to C-V. The polyalkylhydrogensiloxane may be one polyalkylhydrogensiloxane or a combination of two or more polyalkylhydrogensiloxanes that

differ in one or more properties selected from molecular weight, structure, siloxane units and sequence.

(D) Hydrosilylation Reaction Catalyst

[0029] The polyorganosiloxane release coating composition described herein further comprises starting material (D) a hydrosilylation reaction catalyst in a catalytic amount. Hydrosilylation reaction catalysts are known in the art and are commercially available. Hydrosilylation reaction catalysts include i) platinum group metal catalysts. Such hydrosilylation reaction catalysts can be a metal selected from platinum, rhodium, ruthenium, palladium, osmium, and iridium. Alternatively, the hydrosilylation reaction catalyst may be a ii) compound of such a metal, for example, chloridotris(triphenylphosphane)rhodium(I) (Wilkinson's Catalyst), a rhodium diphosphine chelate such as [1,2-bis(diphenylphosphino)ethane]dichlorodirhodium or [1,2-bis(diethylphospino)ethane]dichlorodirhodium, chloroplatinic acid (Speier's Catalyst), chloroplatinic acid hexahydrate, platinum dichloride, and iii) complexes of said compounds with low molecular weight organopolysiloxanes or iv) platinum group metal compounds microencapsulated in a matrix or coreshell type structure. Complexes of platinum with low molecular weight organopolysiloxanes include 1,3-diethenyl-1,1,3,3-tetramethyldisiloxane complexes with platinum (Karstedt's Catalyst). These complexes may be microencapsulated in a resin matrix. Exemplary hydrosilylation reaction catalysts are described in U.S. Patents 3,159,601; 3,220,972; 3,296,291; 3,419,593; 3,516,946; 3,814,730; 3,989,668; 4,784,879; 5,036,117; and 5,175,325; and EP 0 347 895 B. Microencapsulated hydrosilylation reaction catalysts and methods of preparing them are known in the art, as exemplified in U.S. Patents 4,766,176 and 5,017,654. Hydrosilylation reaction catalysts are commercially available, for example, SYL-OFF™ 4000 Catalyst and SYL-OFF™ 2700 are available from Dow Silicones Corporation.

[0030] The hydrosilylation reaction catalyst is present in a catalytic amount, i.e., a sufficient amount to catalyze hydrosilylation reaction of the silicon bonded hydrogen atoms of starting material (C) with the alkenyl groups of starting materials (A) and (B). The exact amount of hydrosilylation reaction catalyst used herein will depend on various factors including the selection of starting materials (A), (B), and (C) and their respective contents of silicon bonded hydrogen atoms and alkenyl groups and the content of the platinum group metal in the catalyst selected, however, the amount of hydrosilylation reaction catalyst may be sufficient to provide 1 ppm to 6,000 ppm of the platinum group metal based on combined weights of starting materials (A), (B), and (C) combined; alternatively 1 ppm to 1,000 ppm, and alternatively 1 ppm to 150 ppm, on the same basis.

[0031] Alternatively, the hydrosilylation reaction catalyst may be selected from the group consisting of (D-1) a platinum group metal, (D-2) a compound of the platinum group metal, (D-3) a complex of the platinum group metal compound with an organopolysiloxane, (D-4) the compound of the platinum group metal microencapsulated in a matrix or coreshell type structure, and (D-5) the complex microencapsulated in a matrix or coreshell type structure. Alternatively, (D) the hydrosilylation reaction catalyst may comprise Karstedt's catalyst.

(E) Hydrosilylation Reaction Inhibitor

[0032] The polyorganosiloxane release coating composition described herein further comprises starting material (E) a hydrosilylation reaction inhibitor (inhibitor) that may be used for altering rate of reaction of the silicon bonded hydrogen atoms of starting material (C) and the alkenyl groups of starting materials (A) and (B), as compared to reaction rate of the same starting materials but with the inhibitor omitted. Inhibitors are exemplified by acetylenic alcohols such as methyl butynol, ethynyl cyclohexanol, dimethyl hexynol, and 3,5-dimethyl-1-hexyn-3-ol, 1-butyn-3-ol, 1-propyn-3-ol, 2-methyl-3-butyn-2-ol, 3-methyl-1-butyn-3-ol, 3-methyl-1-pentyn-3-ol, 3-phenyl-1-butyn-3-ol, 4-ethyl-1-octyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol, and 1-ethynyl-1-cyclohexanol, and a combination thereof; olefinic siloxanes such as cycloalkenylsiloxanes exemplified by methylvinylcyclosiloxanes exemplified by 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenylcyclotetrasiloxane, and a combination thereof; ene-yne compounds such as 3-methyl-3-penten-1-yne, 3,5-dimethyl-3-hexen-1-yne, and a combination thereof; triazoles such as benzotriazole; phosphines; mercaptans; hydrazines; amines, such as tetramethyl ethylenediamine, 3-dimethylamino-1-propyne, n-methylpropargylamine, propargylamine, and 1-ethynylcyclohexylamine; dialkyl fumarates such as diethyl fumarate, dialkenyl fumarates such as diallyl fumarate, dialkoxyalkyl fumarates, maleates such as diallyl maleate and diethyl maleate; nitriles; ethers; carbon monoxide; alkenes such as cyclo-octadiene, divinyltetramethyldisiloxane; alcohols such as benzyl alcohol; and a combination thereof. Exemplary olefinic siloxanes are disclosed, for example, in U.S. Patent 3,989,667. Exemplary acetylenic alcohols are disclosed, for example, in U.S. Patent 3,445,420. Alternatively, the inhibitor used in the polyorganosiloxane release coating described herein may comprise an acetylenic alcohol. Alternatively, the inhibitor may comprise 1-ethynyl-1-cychohexanol.

[0033] Alternatively, the inhibitor may be a silylated acetylenic compound. Without wishing to be bound by theory, it is thought that adding a silylated acetylenic compound reduces yellowing of the reaction product prepared from hydrosilylation reaction as compared to a reaction product from hydrosilylation of starting materials that do not include a silylated acetylenic compound or that include an organic acetylenic alcohol inhibitor, such as those described above.

[0034] The silylated acetylenic compound is exemplified by (3-methyl-1-butyn-3-oxy)trimethylsilane, ((1,1-dimethyl-2-propynyl)oxy)trimethylsilane, bis(3-methyl-1-butyn-3-oxy)dimethylsilane, bis(3-methyl-1-butyn-3-oxy)silanemethylvinylsilane, bis((1,1-dimethyl-2-propynyl)oxy)dimethylsilane, methyl(tris(1,1-dimethyl-2-propynyloxy))silane, methyl(tris(3-methyl-1-butyn-3-oxy))silane, (3-methyl-1-butyn-3-oxy)dimethylphenylsilane, (3-methyl-1-butyn-3-oxy)dimethylhexenylsilane, (3-methyl-1-butyn-3-oxy)triethylsilane, bis(3-methyl-1-butyn-3-oxy)methyltrifluoropropylsilane, (3,5-dimethyl-1-hexyn-3-oxy)trimethylsilane, (3-phenyl-1-butyn-3-oxy)diphenylmethylsilane, (3-phenyl-1-butyn-3-oxy)dimethylphenylsilane, (3-phenyl-1-butyn-3-oxy)dimethylvinylsilane, (3-phenyl-1-butyn-3-oxy)dimethylhexenylsilane, (cyclohexyl-1-ethyn-1-oxy)dimethylhexenylsilane, (cyclohexyl-1-ethyn-1-oxy)dimethylvinylsilane, (cyclohexyl-1-ethyn-1-oxy)diphenylmethylsilane, (cyclohexyl-1-ethyn-1-oxy)trimethylsilane, and combinations thereof. Alternatively, the silylated acetylenic compound is exemplified by methyl(tris(1,1-dimethyl-2-propynyloxy))silane, ((1,1-dimethyl-2-propynyl)oxy)trimethylsilane, or a combination thereof. The silylated acetylenic compound useful as the inhibitor herein may be prepared by methods known in the art, for example, U.S. Patent 6,677,740 discloses silylating an acetylenic alcohol described above by reacting it with a chlorosilane in the presence of an acid receptor.

[0035] The amount of inhibitor added herein will depend on various factors including the desired reaction rate, the particular inhibitor used, and the selection and amount of starting materials (A), (B), and (C). However, the amount of inhibitor may be 0.001 part by weight to 2 parts by weight, per 100 parts by weight of starting materials (A) and (B).

(F) Anchorage Additive

[0036] The polyorganosiloxane release coating composition described herein further comprises starting material (F), an anchorage additive. Without wishing to be bound by theory, it is thought that the anchorage additive will facilitate bonding to a substrate by a release coating prepared by curing the polyorganosiloxane release coating composition described herein.

[0037] Suitable anchorage additives include silane coupling agents such as methyltrimethoxysilane, vinyltrimethoxysilane, allyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, bis(trimethoxysilyl)propane, and bis(trimethoxysilyl)hexane; and mixtures or reaction mixtures of said silane coupling agents. Alternatively, the anchorage additive may be tetramethoxysilane, tetraethoxysilane, dimethyldimethoxysilane, methylphenyldimethoxysilane, methylphenyldiethoxysilane, phenyltrimethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, vinyltriethoxysilane, allyltriethoxysilane, 3-

glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, -(3,4-epoxycyclohexyl)ethyltrimethoxysilane or 3-methacryloxypropyl trimethoxysilane.

[0038] Alternatively, the anchorage additive may be exemplified by a reaction product of an alkenyl-functional alkoxysilane (e.g., a vinyl alkoxysilane) and an epoxy-functional alkoxysilane; a reaction product of an alkenyl-functional acetoxysilane (such as vinyl acetoxysilane) and epoxy-functional alkoxysilane; and a combination (e.g., physical blend and/or a reaction product) of a polyorganosiloxane having at least one aliphatically unsaturated hydrocarbon group and at least one hydrolyzable group per molecule and an epoxy-functional alkoxysilane (e.g., a combination of a hydroxy-terminated, vinyl functional polydimethylsiloxane with glycidoxypropyltrimethoxysilane). Suitable anchorage additives and methods for their preparation are disclosed, for example, in U.S. Patent 9,562,149; U.S. Patent Application Publication Numbers 2003/0088042, 2004/0254274, 2005/0038188, 2012/0328863 at paragraph [0091], and U.S. Patent Publication 2017/0233612 at paragraph [0041]; and EP 0 556 023.

[0039] Anchorage additives are commercially available. For example, SYL-OFF™ 297, SYL-OFF™ 397, and SYL-OFF™ 9176 are available from Dow Silicones Corporation of Midland, Michigan, USA. Other exemplary anchorage additives include (F-1) vinyltriacetoxysilane, (F-2) glycidoxypropyltrimethoxysilane, (F-3) a combination of (F-1) and (F-2), (F-4) a combination of (F-3) and a polydimethylsiloxane terminated with hydroxyl groups, methoxy groups, or terminated with both a hydroxy group and a methoxy group, and (F-5) 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane. The combinations (F-3) and (F-4) may be physical blends and/or reaction products. Alternatively, the anchorage additive may comprise (F-5) 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

[0040] The amount of anchorage additive depends on various factors including the type of substrate to which the polyorganosiloxane release coating composition will be applied and whether a primer or other surface treatment will be used before application of the polyorganosiloxane release coating composition. However, the amount of anchorage additive may be 0.01 part to 10 parts per 100 parts of starting materials (A) and (B), alternatively 0.2 part to 1 part, and alternatively 0.3 part to 0.6 part on the same basis.

Starting Material (G) Solvent

[0041] The polyorganosiloxane release coating composition described herein may optionally further comprise starting material (G), a solvent. Suitable solvents include, polyalkylsiloxanes, alcohols, ketones, aromatic hydrocarbons, aliphatic hydrocarbons, glycol ethers, tetrahydrofuran, mineral spirits, naphtha, tetrahydrofuran, mineral spirits, naphtha, or a combination thereof. Polyalkylsiloxanes with suitable vapor pressures may be used as the solvent, and these include hexamethyldisiloxane, octamethyltrisiloxane, hexamethylcyclotrisiloxane and other low molecular weight polyalkylsiloxanes, such as 0.5 to 1.5 cSt DOWSIL™ 200 Fluids and DOWSIL™ OS FLUIDS, which are commercially available from Dow Silicones Corporation of Midland, Michigan, U.S.A.

[0042] Alternatively, starting material (G) may comprise an organic solvent. The organic solvent can be an alcohol such as methanol, ethanol, isopropanol, butanol, or n-propanol; a ketone such as acetone, methylethyl ketone, or methyl isobutyl ketone; an aromatic hydrocarbon such as benzene, toluene, or xylene; an aliphatic hydrocarbon such as heptane, hexane, or octane; a glycol ether such as propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, or ethylene glycol n-butyl ether, tetrahydrofuran; mineral spirits; naphtha; or a combination thereof.

[0043] The amount of solvent will depend on various factors including the type of solvent selected and the amount and type of other starting materials selected for the curable polyorganosiloxane release coating composition. However, the amount of solvent may be 0% to 96%, alternatively 2% to 50%, based on the weight of all starting materials in the polyorganosiloxane release coating composition. The solvent may be added during preparation of the polyorganosiloxane release coating composition, for example, to aid mixing and delivery of one or more starting materials. For example, the resin and/or the catalyst may be delivered in a solvent. All or a portion of the solvent may optionally be removed after the polyorganosiloxane release coating composition is prepared. Alternatively, a customer may dilute the polyorganosiloxane release coating composition after receipt and before use.

(H) Anti-Mist Additive

[0044] Starting material (H) is an anti-mist additive that may be added to the polyorganosiloxane release coating composition to reduce or suppress silicone mist formation in coating processes, particularly with high speed coating equipment. The anti-mist additive may be a polyorganosiloxane comprising unit formula: $(R^1{}_3SiO_{1/2})_h(R^1{}_2SiO_{2/2})_i(R^1{}_2R^2SiO_{1/2})_j$ and $(SiO_{4/2})_k$, where R^1 and R^2 are as described above, subscript $h > 0$, subscript $i > 0$, subscript $j > o$, subscript $k > 0$, and a quantity $(h + i + j + k)$ has a value sufficient to provide the branched polyorganosiloxane with a viscosity of 30,000 mPa·s to 50,000 mPa·s, alternatively from 35,000 mPa·s to 45,000 mPa·s at 25°C. Suitable anti-mist additives and methods for their preparation are known in the art, for example, in U.S. Patent Application 2011/0287267; U.S.

Patent 8,722,153; U.S. Patent 6,805,914; U.S. Patent 6,586,535; U.S. Patent 6,489,407; and U.S. Patent 5,625,023.

[0045] The amount of anti-mist additive will depend on various factors including the amount and type of other starting materials selected for the polyorganosiloxane release coating composition. However, the amount of anti-mist additive may be 0% to 10%, alternatively 0.1% to 3%, based on the weight of all starting materials in the polyorganosiloxane release coating composition.

[0046] Optional starting materials which may also be added to the polyorganosiloxane release coating composition described herein include, for example, reactive diluents, fragrances, preservatives and fillers, for example, silica, quartz or chalk.

[0047] Alternatively, the polyorganosiloxane release coating composition may be free of filler or contains only a limited amount of filler, such as 0 to 30% by weight of the polyorganosiloxane release coating composition. Fillers can agglomerate or otherwise stick to the coater equipment used to apply the release coating. They can hinder optical properties, for example transparency, of the release coating and of the release liner formed therewith. The fillers may be prejudicial to the adherence of the adherend.

[0048] The polyorganosiloxane release coating composition may be free of conventional release modifiers that have been used in the past to control (decrease) the level of release force (the adhesive force between the release coating and an adherend thereto, such as a label including a pressure sensitive adhesive). Examples of such release modifiers include trimethylsiloxy-terminated dimethyl, phenylmethylsiloxanes. Without wishing to be bound by theory, it is thought that including a trimethylsiloxy-terminated dimethyl, phenylmethylsiloxanes in a release coating composition may lower subsequent adhesion strength and/or increase migration of the release coatings prepared therefrom. Therefore, the polyorganosiloxane release coating composition described herein may be free of polyorganosiloxanes that contain silicon bonded aryl groups (e.g., silicon bonded phenyl groups) other than starting material (A) described herein.

[0049] The curable polyorganosiloxane release coating composition may be free from fluoroorganosilicone compounds. It is believed that, during the cure, a fluorocompound, because of its low surface tension, will rapidly migrate to the interface of a coating composition and a substrate, for example a polyorganosiloxane release coating composition/PET film interface, and prevent adherence of the release coating (prepared by curing the polyorganosiloxane release coating composition) to the substrate by making a fluorine containing barrier. By making a barrier, the fluorocompound prevents any component from reacting at the interface. Moreover, fluorosilicone compounds are usually expensive.

Method of Making Polyorganosiloxane Release Coating Composition and Release Liner

[0050] The polyorganosiloxane release coating composition of the present invention may be prepared by mixing the starting materials together, for example, to prepare a one part composition. However, it may be desirable to prepare the polyorganosiloxane release coating composition as a multiple part composition, in which the crosslinker and catalyst are stored in separate parts, until the parts are combined at the time of use (e.g., shortly before application to a substrate).

[0051] For example, a multiple part polyorganosiloxane release coating composition may comprise:

Part (*A*) a base part comprising the starting materials having silicon bonded alkenyl groups, i.e. starting materials (A) and (B); (D) the hydrosilylation reaction catalyst, and when present, (H) the anti-mist additive, and

Part (*B*) a curing agent part comprising (A) the polydiorganosiloxane and (C) the polyalkylhydrogensiloxane (crosslinker). Starting material (E), the hydrosilylation reaction inhibitor may be added to either Part (*A*), Part (*B*), or both. Starting material (F), the anchorage additive, can be incorporated in either of Part (*A*) or Part (*B*), or it can be added in a separate (third) part. When present, the (G) the solvent may be added to Part (*A*), Part (*B*), or both. Part (*A*) and Part (*B*) may be combined in a weight ratio (*A*):(*B*) of 1:1 to 10:1, alternatively 1:1 to 5:1, and alternatively 1:1 to 2:1. Part (*A*) and Part (*B*) may be provided in a kit with instructions for how to combine the parts to prepare the polyorganosiloxane release coating composition and/or how to apply the polyorganosiloxane release coating composition to a substrate.

[0052] A method for forming a release liner comprises:

1) combining starting materials comprising (A), (B), (C), (D), (E), and (F), and optionally one or more of (G) the solvent and (H) the anti-mist additive, thereby the polyorganosiloxane release coating composition as described above; and

2) applying the polyorganosiloxane release coating composition to a surface of a substrate.

[0053] The polyorganosiloxane release coating composition can for example be applied to the surface of the substrate by any convenient means such as spraying, doctor blade, dipping, screen printing or roll coating, by a roll coater, e.g. an offset web coater, kiss coater or etched cylinder coater.

[0054] The polyorganosiloxane release coating composition can be applied to a surface of any substrate, such as polymer film substrates, for example polyester, particularly polyethylene terephthalate (PET), polyethylene, polypropylene, or polystyrene films. The polyorganosiloxane release coating composition can alternatively be applied to a paper substrate, including plastic coated paper, for example paper coated with polyethylene, glassine, super calender paper, or clay coated kraft. The polyorganosiloxane release coating composition can alternatively be applied to a metal foil substrate, for example aluminum foil.

[0055] The method may further comprise: 3) treating the surface of the substrate before coating the polyorganosiloxane release coating composition on the surface of the substrate. Treating the surface of the substrate may be performed by any convenient means such as a plasma treatment or a corona discharge treatment. Alternatively, the surface of the substrate may be treated by applying a primer. In certain instances anchorage of the release coating may be improved if the surface of the substrate is treated before coating.

[0056] The method may further comprise: 4) removing solvent, which may be performed by any conventional means, such as heating at 50°C to 100°C for a time sufficient to remove all or a portion of the solvent. The method may further comprise: 5) curing the polyorganosiloxane release coating composition to form a release coating on the surface of the substrate. Curing may be performed by any conventional means such as heating at 100°C to 200°C.

[0057] Under production coater conditions cure can be affected in a residence time of 1 second to 60 seconds, alternatively 10 seconds to 60 seconds, alternatively 1 seconds to 30 seconds, alternatively 1 second to 6 seconds, and alternatively 1.5 seconds to 3 seconds, at an air temperature of 120°C to 160°C. Heating for steps 4) and/or 5) can be performed in an oven, e.g., an air circulation oven or tunnel furnace or by passing the coated film around heated cylinders.

[0058] The coat weight of the release coating may be 0.6 g/m^2 to 1.3 g/m^2, alternatively 0.6 g/m^2 to 0.8 g/m^2. Without wishing to be bound by theory, one benefit of the curable polyorganosiloxane release coating described herein is the ability to provide tight release force (e.g., > 100 g/inch at RT and > 200 g/inch at 70°C using tesa™ 7475 tape as tested by the method in Reference Example 3 (2) and (3) and high Subsequent Adhesive Strength (> 90% as tested by the method in Reference Example 3(4)) at low coat weights (e.g., 0.8 g/m^2 or less).

[0059] The release liners prepared as described above can be used to protect pressure sensitive adhesives. Customers may coat a liquid pressure sensitive adhesive composition directly on the release liner and remove the solvent or water by heat, alternatively by UV cure, then laminate with substrates and rewind to rolls. Alternatively, customers may laminate the release liner with dry pressure sensitive adhesive or sticky film for tapes, labels or die-cutting applications.

EXAMPLES

[0060] These examples are intended to illustrate the invention to one skilled in the art and are not to be interpreted as limiting the scope of the invention set forth in the claims. The following abbreviations were used: RF: Release Force (Release Tester), CW: Coat Weight (Oxford XRF), RO: Rub Off (Anchorage performance), and SAS: Subsequent Adhesion Strength (Migration performance).

Table 1, below, shows the starting materials used in these examples. Table 1

Starting Material	Description
(A1) Polymer 1	mixture of 30% vinyl-functional polydimethylsiloxane gum and 70% toluene
(A2) Polymer 2	vinyl-functional poly(dimethyl/methylphenyl)siloxane gum with Mn = 380,000 g/mol
(A3) Polymer 3	vinyl-functional polydimethylsiloxane
(A4) Polymer 4	vinyl functional poly(dimethyl/diphenyl)siloxane with Mn = 19,000 g/mol
(B1) Resin 1	polyorganosilicate resin of formula $M^{Vi}_{15}M_{45}Q_{40}$ with Mn = 1,500 g/mol and 5.1% to 5.6% vinyl content and no detectable free silanol, where M
(C1) Crosslinker 1	trimethylsiloxy-terminated poly(dimethyl/methylhydrogen)siloxane with viscosity of 70 mPa·s
(C2) Crosslinker 2	Dimethylhydrogensiloxy-modified silica of formula $M^{H}_{1.82}Q$ having viscosity of 25 mPa·s
(D1) Catalyst 1	Karstedt's Catalyst
(E1) Inhibitor 1	1-ethynyl-1-cyclohexanol
(F1) Anchorage Additive 1	alkoxy containing alkenyl/epoxy functional organopolysiloxane

Reference Example 1 – Preparation of Polyorganosiloxane Release Coating Compositions

[0061] Samples of polyorganosiloxane release coating compositions were prepared by adding starting material (A) the polydiorganosiloxane (having both alkenyl and aryl groups), starting material (E) the hydrosilylation reaction inhibitor, and, when present, starting material (G) the solvent to a vessel with mixing. Starting material (B) the polysiloxane resin was then added to the vessel. Starting material (C) the polyalkylhydrogensiloxane, starting material (F) the anchorage additive, and starting material (D) the hydrosilylation reaction catalyst were then added. The resulting polyorganosiloxane release coating composition is used as a coating bath.

Reference Example 2 – Preparation of Release Liners

[0062] The polyorganosiloxane release coating compositions prepared according to Reference Example 1 were coated on PET substrates. The polyorganosiloxane release coating compositions were then cured at 140°C for 30 seconds to form release coatings on the substrates. The resulting release liners were then evaluated.

Reference Example 3 - Release Coating Evaluation Procedures

[0063] (1) Coat weight (CW) in g/m^2 was evaluated using X-Ray to detect the coat weight of the release coating on the substrate with an Oxford lab-x 3500 instrument manufactured by Oxford Instruments PLC, Oxon, United Kingdom. Uncoated PET was used as a control sample (blank). The test method was FINAT Test Method No.7 (FINAT Technical Handbook 7th edition, 2005).

[0064] (2) Release force (RF-RT) in g/in was evaluated using the 180 degree peeling test to measure release force from the release liner. A tape was laminated on a cured release coating, a loaded weight of 20 g/cm^2 was placed on the laminated sample and left under RT for 20 hours. After 20 hours, the loaded weight was removed, and the sample was allowed to rest for 30 minutes. The release force was then tested by a ChemInstruments AR-1500 using FINAT Test Method No.10 (FINAT Technical Handbook 7th edition, 2005). The following were tested: 7475 RF-RT refers to the above test method with tesa™ 7475 tape, which is commercially available from Tesa SE – A Beiersdorf Company. 'Hotmelt RF-RT' refers to the same method, but with a rubber base hotmelt tape from UPM Raflatac. 'WB Acrylic RF-RT' refers to the same test method, but with waterborne acrylic tape from UPM Raflatac.

[0065] (3) Release force (RF-70ºC aging) in g/in was evaluated using the 180 degree peeling test to measure release force from the release liner. A tape was laminated on a cured release coating, a loaded weight of 20 g/cm^2 was placed on the laminated sample and left under 70ºC for 20 hours. After 20 hours, the loaded weight was removed and the sample allowed to rest for 30 minutes. Release force was then tested by ChemInstruments AR-1500 using FINAT Test Method No.10 (FINAT Technical Handbook 7th edition, 2005). The following were tested: 7475 RF-70°C refers to the above test method with tesa™ 7475 tape. 'Hotmelt RF-70°C' refers to the same method, but with a rubber base hotmelt tape from UPM Raflatac. 'WB Acrylic RF-70°C' refers to the same test method, but with waterborne acrylic tape from UPM Raflatac.

[0066] (4) SAS (Subsequent Adhesive Strength, indicator of migration) in % was evaluated as follows. A test tape was laminated by Nitto Denko 31B tape on a cured release coating under a loaded weight of 20 g/cm^2 and left under 70 ºC for 20 hours. After 20 hours, the loaded weight was removed and the sample was allowed to rest 30 minutes at room temperature. Then transfer the 31B tape on PET substrate and wait for another 1 hour. The release force was tested by ChemInstruments AR-1500 using FINAT Test Method No.11 (FINAT Technical

Handbook 7th edition, 2005). In this SAS test, a laminate 31B tape on a PTFE substrate was tested, and the PTFE sample was treated the same way as a cured release coating sample. The SAS value was recorded as $RF_{release}/RF_{PTFE}\times100\%$.

[0067] The starting materials used in each sample prepared according to Reference Example 1 are shown below in Tables 2 and 3. Amounts of each starting material are in weight parts, except amount of catalyst (C1) is sufficient to provide the amount of platinum shown, in ppm. The results of evaluations according to Reference Example 3 are shown below in Tables 4-7.

Table 2 – Starting Materials for Samples with Poly(dimethyl/methylphenyl)siloxane

Starting Material	C1	C2	C3	C4	C5	C6	W1	W2	W3	W4
(A1)	100	87.50	75	62.5	50	0	0	0	0	0
(A2)	0	0	0	0	0	100	87.5	75	62.5	50
(B1)	0	3.75	7.5	11.25	15	0	12.5	25	37.5	50
(E1)	0	0.06	0.06	0.06	0.06	0.2	0.2	0.2	0.2	0.2
(F1)	0.32	0.32	0.32	0.32	0.32	0.6	0.6	0.6	0.6	0.6
(C1)	0.6	1.44	2.42	3.41	4.51	0.48	3.79	7.02	10.54	14.04
(D1)	140	140	140	140	140	140	140	140	140	140
SiH/Vi Ratio	2.3	1.7	1.7	1.7	1.7	2.8	1.7	1.7	1.7	1.7

Table 3 – Starting Materials for Samples with Poly(dimethyl/diphenyl)siloxane

Starting Material	C7	C8	C9	W5	W6
(A3)	100	50	0	0	0
(A4)	0	0	100	75	50
(B1)	0	50	0	25	50
(E1)	0	0.2	0.2	0.36	0.52
(F1)	0.6	0.6	0.6	0.6	0.6
(C1)	1.84	0.92	0	0	0
(C2)	0	15	2.1	8.8	16.4
(D1)	100	100	100	100	100
SiH/Vi Ratio	1.7	1.7	1.7	1.7	1.7

Table 4 – Fresh Sample Evaluation Results, for the Comparative Samples in Table 2

Test	Units	C1	C2	C3	C4	C5	C6
C/W	g/m^2	0.625	0.625	0.671	0.612	0.625	0.569
7475 RF-RT	g/in	5.3	7.9	12.9	28.6	67.1	6.5
7475 RF-70C	g/in	7.7	14.9	26.1	50.9	102.7	14.9
Hotmelt RF-RT	g/in	2.1	2.2	6.0	42.6	194.3	1.5
Hotmelt RF-70C	g/in	2.6	2.9	8.3	38.4	193.4	2.4
WB Acrylic RF-RT	g/in	5.8	6.2	10.7	44.1	169.6	1.9
WB Acrylic RF-70C	g/in	6.1	6.4	12.5	47.7	187.1	3.8
SAS	%	94.8	95.5	93.5	95.2	91.8	90.1

Table 4 (continued) – Fresh Sample Evaluation Results, for the Working Samples in Table 2

Test	Units	W1	W2	W3	W4
C/W	g/m^2	0.692	0.672	0.659	0.659
7475 RF-RT	g/in	114.8	187.5	264.6	396.8
7475 RF-70C	g/in	210.3	337.1	545.7	709.7
Hotmelt RF-RT	g/in	29.1	195.1	258.7	281.7
Hotmelt RF-70C	g/in	21.6	166.8	236.6	267.1
WB Acrylic RF-RT	g/in	98.5	279.8	330.9	336.1
WB Acrylic RF-70C	g/in	60.8	235.5	304.5	300.3
SAS	%	96.7	96.6	96.7	92.1

Table 5– Fresh Sample Evaluation Results, for the Samples in Table 3

Test	Units	C7	C8	C9	W5	W6
C/W	g/m^2	0.757	0.762	0.725	0.766	0.778
7475 RF-RT	g/in	7.3	32.9	35.9	417.2	812.1
7475 RF-70C	g/in	8.4	51.2	62.7	735.0	1311.9
Hotmelt RF-RT	g/in	2.2	83.2	10.1	167.0	370.0
Hotmelt RF-70C	g/in	2.9	73.8	14.2	142.8	343.4
WB Acrylic RF-RT	g/in	3.0	86.4	22.3	251.0	364.9
WB Acrylic RF-70C	g/in	3.3	48.7	12.8	238.3	354.8
SAS	%	90.2	94.2	94.0	90.4	94.0

Table 6 – 3 Months Aged Sample Evaluation Results, for the samples in Table 2

Test	Units	C1	C2	C3	C4	C5	C6	W1	W2	W3	W4
7475 RF-RT	g/in	5.2	6.2	11.3	23.6	65.3	7.7	112.0	213.9	284.2	371.2
7475 RF-70C	g/in	7.2	11.2	28.2	55.9	108.8	16.6	158.9	396.3	507.5	650.6
Hotmelt RF-RT	g/in	2.1	2.5	6.1	40.1	197.7	2.3	25.2	146.6	240.3	262.0
Hotmelt RF-70C	g/in	2.6	3.4	10.8	47.4	211.6	5.5	25.2	135.5	225.2	270.6
WB Acrylic RF-RT	g/in	3.9	3.8	9.9	25.7	207.3	3.7	47.5	263.1	356.8	387.2
WB Acrylic RF-70C	g/in	3.8	4.5	11.4	34.8	249.9	5.1	33.9	212.0	328.1	1469.3

Table 7 – 3 Months Aged Sample Evaluation Results, for the samples in Table 3.

Test	Units	C7	C8	C9	W5	W6
7475 RF-RT	g/in	7.0	34.7	42.0	367.4	746.9
7475 RF-70C	g/in	9.1	56.5	67.6	765.3	1166.2
Hotmelt RF-RT	g/in	1.2	61.8	10.9	156.1	327.0
Hotmelt RF-70C	g/in	2.8	81.0	20.9	154.6	325.3

Test	Units	C7	C8	C9	W5	W6
WB Acrylic RF-RT	g/in	2.7	46.1	20.1	243.9	369.6
WB Acrylic RF-70C	g/in	2.5	47.6	17.3	229.6	370.1

INDUSTRIAL APPLICABILITY

[0068] The working examples (W) above showed that release coatings (on PET substrates) can be prepared with coat weights of 0.659 g/m^2 to 0.778 g/m^2; release force from tesa™ 7475 standard tape after aging at room temperature of 114.8 g/in to 812.1 g/in, release force from tesa™ 7475 standard tape after aging at 70°C of 210 g/in to 1312 g/in, and sustained adhesion strength of > 90% to 97%.

[0069] The working examples and comparative examples (C) above showed that release liners including release coatings prepared from the polyorganosiloxane release coating compositions disclosed herein had consistently higher release force than the comparative examples. For example, Working Examples W1 to W4 each had higher release force from 7475 at RT than Comparative Examples C1 to C6, with both freshly prepared samples and samples that were aged for 3 months (see Tables 4 and 6). Working Examples W1 to W4 each had higher release force from 7475 at 70°C than Comparative Examples C1 to C6, with both freshly prepared samples and samples that were aged for 3 months (see Tables 4 and 6).

[0070] Furthermore, the release coatings in Working Examples W5 and W6 had higher release force than Comparative Examples 7 and 8 under all conditions tested (see Tables 5 and 7).

DEFINITIONS AND USAGE OF TERMS

[0071] Unless otherwise indicated by the context of the specification: all amounts, ratios, and percentages herein are by weight; the articles ‘a’, ‘an’, and ‘the’ each refer to one or more; and the singular includes the plural. The SUMMARY and ABSTRACT are hereby incorporated by reference. The transitional phrases “comprising”, “consisting essentially of”, and “consisting of” are used as described in the Manual of Patent Examining Procedure Ninth Edition, Revision 08.2017, Last Revised January 2018 at section §2111.03 I., II., and III. The use of “for example,” “e.g.,” “such as,” and “including” to list illustrative examples does not limit to only the listed examples. Thus, “for example” or “such as” means “for example, but not limited to” or “such as, but not limited to” and encompasses other similar or equivalent examples. The abbreviations used herein have the definitions in Table 8.

Table 8 – Abbreviations

Abbreviation	Definition
°C	degrees Celsius
cm	centimeters
FTIR	Fourier Transform Infra Red
g	grams
g/cm^2	grams per square centimeter
g/in	grams per inch
g/m^2	grams per square meter
GPC	gel permeation chromatography
M	a siloxane unit of formula $(Me_3SiO_{1/2})$
Me	methyl
M^H	a siloxane unit of formula $(Me_2HSiO_{1/2})$
min	minutes
Mn	number average molecular weight
mPa·s	milliPascal·seconds
M^{Vi}	a siloxane unit of formula $(Me_2ViSiO_{1/2})$
N	normal
NMR	nuclear magnetic resonance
PTFE	polytetrafluoroethylene
PET	polyethylene terephthalate
Q	a siloxane unit of formula $(SiO_{4/2})$
RPM	revolutions per minute
RT	room temperature of 20°C to 25°C
Vi	vinyl
Vi-terminated PDMS	bis-vinyl-terminated polydimethylsiloxane

[0072] The following test methods were used to measure properties of the starting materials herein.

[0073] Viscosity of each polydiorganosiloxane was measured at 0.1 to 50 RPM on a Brookfield DV-III cone & plate viscometer with #CP-52 spindle. One skilled in the art would recognize that rotation rate decreases as viscosity increases and would be able to select the appropriate rotation rate when using this test method to measure viscosity.

[0074] ^{29}Si NMR and ^{13}C NMR spectroscopy can be used to quantify the R group (e.g., R^1, R^2, and/or R^3) group content in a polydiorganosiloxane. A ^{29}Si NMR spectrum should be acquired using the methodology outlined by Taylor et. al. in Chapter 12 of The Analytical Chemistry of Silicones, ed. A. Lee Smith, Vol. 112 in Chemical Analysis, John Wiley & Sons, Inc. (1991), pages 347-417, and section 5.5.3.1. In this chapter, the authors discuss general parameters unique to acquiring quantitative NMR spectra from Silicon nuclei. Each NMR spectrometer is different with respect to the electronic components, capabilities, sensitivity, frequency and operating procedures. One should consult instrument manuals for the spectrometer to be used in order to tune, shim and calibrate a pulse sequences sufficient for quantitative 1D measurement of ^{29}Si and ^{13}C nuclei in a sample.

[0075] A key output of a NMR analysis is the NMR spectrum. Without standards, it is recommended that the signal to noise ratio of signal height to average baseline noise be no less than 10:1 to be considered quantitative. A properly acquired and processed NMR spectrum results in signals that can be integrated using any commercially available NMR processing software package.

[0076] From these integrations, the weight percent of total R group content can be calculated from the ^{29}Si NMR spectrum according to the following: $(I^{M}) \cdot (U^{M}) = G^{M}$; $(I^{M(R)}) \cdot (U^{M(R')}) = G^{M(R)}$; $(I^{D}) \cdot (U^{D}) = G^{D}$; $(I^{D(R)}) \cdot (U^{D(R)}) = G^{D(R)}$; $U^{R} / U^{M(R)} = Y^{R'}$; $U^{R} / U^{D(R)} = Y^{R''}$; $Y^{R''} \cdot [G^{M(R)} / (G^{M} + G^{M(R)} + G^{D} + G^{D(R)}) \cdot 100] = W^{R'}$; $Y^{R'''} \cdot [G^{D(R)} / (G^{M} + G^{M(R)} + G^{D} + G^{D(R)}) \cdot 100] = W^{R''}$; and $W^{R'} + W^{R''} = \text{TOTAL } W^{R}$; where I is the integrated signal of the indicated siloxy group; U is the unit molecular weight of the indicated siloxy group; G is a placeholder representing the grams unit; W is the weight percent of the indicated siloxy unit; Y is a ratio value for the specified siloxy unit; R is as described above; R' represents R groups only from M(R); and R" represents R groups only from D(R) groups.

[0077] Number average molecular weight of polyorganosiloxane starting materials (*e.g.*, starting materials (A), (B), and (C) described herein) may be measured by GPC according to the test method in U.S. Patent 9,593,209, Reference Example 1 at col. 31.

[0078] The invention has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation. With respect to any Markush groups relied upon herein for describing particular features or aspects, different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and/or in combination and provides adequate support for specific embodiments within the scope of the appended claims.

[0079] Furthermore, any ranges and subranges relied upon in describing the present invention independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. One of skill in the art readily recognizes that the enumerated ranges and subranges sufficiently describe and enable various embodiments of the present invention, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range of "1 to 18" may be further delineated into a lower third, *i.e.*, 1 to 6, a middle third, *i.e.*, 7 to 12, and an upper third, *i.e.*, from 13 to 18, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the language which defines or modifies a range, such as "at least," "greater than," "less than," "no more than," and the like, it is to be understood that such language includes subranges and/or an upper or lower limit.

Embodiments of the Invention

[0080] In a first embodiment, a kit for preparing a polyorganosiloxane release coating composition comprises:

Part (*A*) a base part comprising

(A) a polydiorganosiloxane of unit formula:

$(R^1{}_2R^2SiO_{1/2})_a(R^1{}_2SiO_{2/2})_b(R^1R^3SiO_{2/2})_c(R^3{}_2SiO_{2/2})_d$, where each R^1 is an independently selected alkyl group of 1 to 18 carbon atoms, each R^2 is an independently selected alkenyl group of 2 to 18 carbon atoms, each R^3 is an independently selected aryl group of 5 to 20 carbon atoms, subscript a has an average value of 2, subscript b > 0, subscript c ≥ 0, subscript d ≥ 0 with the proviso that a quantity (c + d) > 0;

(B) a polyorganosilicate resin having silicon bonded alkenyl groups,

(C) a polyalkylhydrogensiloxane, having at least two silicon-bonded hydrogen atoms per a molecule, where the polyalkylhydrogensiloxane is present in an amount sufficient to provide 0.8 mole to 5 moles of silicon-bonded hydrogen atoms per mole of alkenyl groups in starting materials (A) and (B);

(E) a hydrosilylation reaction inhibitor;

optionally (F) an anchorage additive; and

optionally (G) a solvent;

Part (*B*) a curing agent part comprising

optionally (A) the polydiorganosiloxane as described above;

(D) a hydrosilylation reaction catalyst;

optionally (F) the anchorage additive as described above; and optionally (G) the solvent as described above; and

Instructions for combining Part (*A*) and Part (*B*) to prepare the polyorganosiloxane release coating composition and/or how to apply the polyorganosiloxane release coating composition to a substrate;

where starting material (C) is present in the polyorganosiloxane release coating composition in an amount sufficient to provide 0.8 mole to 5 moles of silicon-bonded hydrogen atoms per mole of alkenyl groups in starting materials (A) and (B); starting material (D) is present in the polyorganosiloxane release coating composition in an amount sufficient to provide 100 ppm to 1,0000 ppm of platinum group metal to the composition based on combined weights of all starting materials, starting material (E) is present in the polyorganosiloxane release coating composition in an amount of 0.001 part by weight to 2 parts by weight, per 100 parts by weight of starting materials (A) and (B); starting material (F) is present in the polyorganosiloxane release coating composition in an amount of 0.01 part by weight to 10 parts by weight per 100 parts by weight of starting materials (A) and (B); starting material (G) is present in the polyorganosiloxane release coating composition in an amount of > 0 to 96 weight % based on combined weights of all starting materials in the polyorganosiloxane release coating composition; and

where the composition is free of polydiorganosiloxanes that do not have silicon bonded aryl groups.

[0081] In a second embodiment, a method for preparing a release liner comprises:

1) forming the polyorganosiloxane release coating composition of the first embodiment according to the instructions,

2) applying the polyorganosiloxane release coating composition to a surface of a substrate,

optionally 3) treating the surface of the substrate before coating the polyorganosiloxane release coating composition on the surface of the substrate,

optionally 4) removing all or a portion of the solvent (when solvent is present), and

5) curing the polyorganosiloxane release coating composition to form a release coating on the surface of the substrate.

[0082] In a third embodiment, in the method of the second embodiment step 2) may be performed by a technique selected from the group consisting of spraying, doctor blade, dipping, screen printing, or roll coating.

[0083] In a fourth embodiment, in the method of the second or the third embodiments the substrate is selected from the group consisting of: (i) a polymer film substrate, for example polyester, particularly polyethylene terephthalate, polyethylene, polypropylene, or polystyrene films; (ii) a paper substrate, including plastic coated paper, for example paper coated with polyethylene, glassine, super calender paper, or clay coated kraft; and (iii) a metal foil substrate, for example aluminum foil.

[0084] In a fifth embodiment, in the method of any one of the second to fourth embodiments, step 3) is present, and step 3) is performed by a technique selected from the group consisting of a plasma treatment, a corona discharge treatment, and applying a primer.

[0085] In a sixth embodiment, in the method of any one of the second to fifth embodiments, where step 4) is present, and step 4) is performed by heating at 50°C to 100°C for a time sufficient to remove all or a portion of the solvent.

[0086] In a seventh embodiment, in the method of any one of the second to sixth embodiments step 5) is performed by heating at 100°C to 200°C for a time sufficient to cure the polyorganosiloxane release coating composition and form the release coating therefrom.

[0087] In an eighth embodiment, in the method of the seventh embodiment, step 5) is performed by heating for 10 seconds to 60 seconds at an air temperature of 120°C to 160°C.

WHAT IS CLAIMED IS:

1. A polyorganosiloxane release coating composition comprising:

(A) a polydiorganosiloxane of unit formula: $(R^1{}_2R^2SiO_{1/2})_a(R^1{}_2SiO_{2/2})_b(R^1R^3SiO_{2/2})_c(R^3{}_2SiO_{2/2})_d$, where each R^1 is an independently selected alkyl group of 1 to 18 carbon atoms, each R^2 is an independently selected alkenyl group of 2 to 18 carbon atoms, each R^3 is an independently selected aryl group of 5 to 20 carbon atoms, subscript a has an average value of 2, subscript b > 0, subscript c ≥ 0, subscript d ≥ 0 with the proviso that a quantity (c + d) > 0, and a quantity (a + b + c + d) is sufficient to give the polydiorganosiloxane a number average molecular weight ≥ 3,000 g/mol;

(B) a polyorganosilicate resin having silicon bonded alkenyl groups,

(C) a polyalkylhydrogensiloxane, having at least two silicon-bonded hydrogen atoms per a molecule, where the polyalkylhydrogensiloxane is present in an amount sufficient to provide 0.8 mole to 5 moles of silicon-bonded hydrogen atoms per mole of alkenyl groups in starting materials (A) and (B);

(D) a hydrosilylation reaction catalyst in a catalytic amount;

(E) a hydrosilylation reaction inhibitor, in an amount of 0.001 part by weight to 2 parts by weight, per 100 parts by weight of starting materials (A) and (B);

(F) an anchorage additive, in an amount of 0.01 part by weight to 10 parts by weight per 100 parts by weight of starting materials (A) and (B); and

optionally (G) a solvent;

where the composition is free of polydiorganosiloxanes that do not have silicon bonded aryl groups, other than starting material (A).

2. The composition of claim 1, where in starting material (A), the polydiorganosiloxane, each R^1 is methyl, each R^2 is vinyl, and each R^3 is phenyl.

3. The composition of claim 1 or claim 2, where in starting material (A), the polydiorganosiloxane, subscript c = 0, and subscript d > 0, and subscript d has a value sufficient to provide the polydiorganosiloxane with a Mn of 3,000 g/mol to 500,000 g/mol.

4. The composition of any one of claims 1 to 3, where in (B) the polyorganosilicate resin comprises unit formula: $(R^1{}_3SiO_{1/2})_e(R^1{}_2R^2SiO_{1/2})_f(SiO_{4/2})_g$, where R^1 and R^2 are as described above and subscripts m, n and o have average values such that e ≥ 0, f ≥ 0, g > 1, and (e + f) > 4, with the proviso that a quantity (e + f + g) is sufficient to give the polyorganosilicate resin a number average molecular weight of 1,000 g/mol to 8,000 g/mol.

5. The composition of any one of claims 1 to 4, where (C) the polyalkylhydrogensiloxane comprises unit formula (C1): $(R^1{}_3SiO_{1/2})_m(R^1HSiO_{2/2})_n(R^1{}_2SiO_{2/2})_o(R^1{}_2HSiO_{1/2})_p$, where subscript m is 0 to 2, subscript p is 0 to 2, a quantity (m + p) has an average value of 2, subscript n > 0, subscript o > 0, a quantity (n + p) ≥ 3, and a quantity (m + n + o + p) has a value sufficient to give the polyalkylhydrogensiloxane a viscosity of 5 mPa·s to 500 mPa·s measured at 25°C at 0.1 to 50 RPM on a Brookfield DV-III cone & plate viscometer with #CP-52 spindle.

6. The composition of any one of claims 1 to 4, where (C) the polyalkylhydrogensiloxane comprises unit formula (C2): $(HR^1{}_2SiO_{1/2})_r(SiO_{4/2})_q$, where subscripts q and r are present in a molar ratio r/q of 0.5/1 to 2/1 and a quantity (q + r) has a value sufficient to give the polyalkylhydrogensiloxane a viscosity of 5 mPa·s to 200 mPa·s.

7. The composition of any one of claims 1 to 6, where (D) the hydrosilylation reaction catalyst is selected from the group consisting of (D-1) a platinum group metal, (D-2) a compound of the platinum group metal, (D-3) a complex of the platinum group metal compound with an organopolysiloxane, (D-4) the compound of the platinum group metal microencapsulated in a matrix or coreshell type structure, and (D-5) the complex microencapsulated in a matrix or coreshell type structure.

8. The composition of claim 7, where (D) the hydrosilylation reaction catalyst comprises Karstedt's catalyst.

9. The composition of any one of claims 1 to 8, where starting material (E), the hydrosilylation reaction inhibitor, comprises an acetylenic alcohol.

10. The composition of claim 9, where the acetylenic alcohol comprises 1-ethynyl-1-cychohexanol.

11. The composition of any one of claims 1 to 10, where (F) the anchorage additive is present, and the anchorage additive is selected from the group consisting of (F-1) vinyltriacetoxysilane, (F-2) glycidoxypropyltrimethoxysilane, (F-3) a combination of (F-1) and (F-2), (F-4) a combination of (F-3) and a polydimethylsiloxane terminated with hydroxyl groups, methoxy groups, or terminated with both a hydroxy group and a methoxy group, and (F-5) 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

12. The composition of claim 11, where the anchorage additive comprises 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

13. The composition of any one of claims 1 to 12, where starting material (G), the solvent, is present in an amount up to 96 weight% based on combined weights of all starting materials in the composition, and the solvent comprises an aromatic hydrocarbon.

14. A method for preparing a release liner comprising:
1) coating the composition of any one of claims 1 to 13 on a surface of a substrate, and
2) curing the composition to form a release coating on the surface of the substrate.

15. A release liner prepared by the method of claim 14.

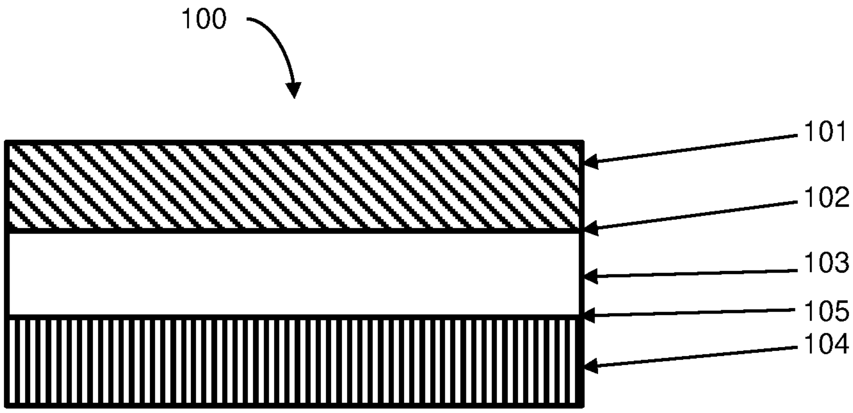

Figure 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2019/101940

A. CLASSIFICATION OF SUBJECT MATTER

C09D 5/20(2006.01)i； C09D 183/05(2006.01)i； C09D 183/07(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT;CNKI;DWPI: release,polydiorganosiloxane,alkenyl,aryl,hydrosilylation, inhibitor,anchorage additive,solvent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2018112911 A1 (DOW SHANGHAI HOLDING CO LTD) 28 June 2018 (2018-06-28) description， paragraphs [0004]-[0045]	1-15
X	WO 2018148504 A1 (DOW SILICONES CORP) 16 August 2018 (2018-08-16) description， paragraphs [0005]-[0090]	1-15
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A	CN 102300932 A (DOW CORNING TORAY CO LTD) 28 December 2011 (2011-12-28) the whole document	1-15
A	GB 2073765 A (GENERAL ELECTRIC CO) 21 October 1981 (1981-10-21) the whole document	1-15
A	TW 201925388 A (SHINETSU CHEM CO LTD) 01 July 2019 (2019-07-01) the whole document	1-15

☐ Further documents are listed in the continuation of Box C.   ☑ See patent family annex.

* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 April 2020	**18 May 2020**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2019/101940

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