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DURABLE, HIGH HEAT RESISTANT CERAMIC COATING**FIELD**

[0001] The present disclosure relates to a durable and heat resistant coating composition
5 for cookware or bakeware, a method of making the coating composition, and a method of
coating a substrate with the coating composition.

BACKGROUND

[0002] Heat resistant coatings are applied to substrates such as cookware, bakeware or
10 other cooking appliances to provide functions such as aiding in heat transfer, providing a non-
stick release surface, and/or providing a decorative color or aesthetic finish. Prior coating
compositions have used fluoropolymers, which could potentially contain per/polyfluoroalkyl
substances (PFAS), as binders or release agents. The regulatory landscape has become
increasingly concerned about PFAS, including fluoropolymers, as a constituent of substances
15 and/or mixtures.

SUMMARY

[0003] The present disclosure provides a method of forming a coating composition
including hydrolyzing and condensing at least two different siloxane monomers in the presence
20 of an acid catalyst, and colloidal silica to form an organosilica sol, the siloxane monomers of the
following formula: $R_xSi(OR')_{4-x}$, wherein R is a linear, branched, or cyclic alkyl or aryl group
with up to 10 carbon atoms; R' is a linear, branched, or cyclic alkyl group with up to 5 carbon
atoms; and x is 1, 2 or 3, and combining the organosilica sol with a silicone polyester resin and a
silicone oil.

25 [0004] The present disclosure further provides a coating composition including a silicone
polyester resin, a silicone oil, and an organosilica sol including the hydrolysis and condensation
reaction product of at least two different siloxane monomers, an acid catalyst, and colloidal
silica, the siloxane monomers of the formula $R_xSi(OR')_{4-x}$, wherein R is a linear, branched, or
cyclic alkyl or aryl group with up to 10 carbon atoms; R' is a linear, branched, or cyclic alkyl
30 group with up to 5 carbon atoms; and x is 1, 2 or 3, and a liquid medium.

[0005] The present disclosure further provides an article coated with a coating
composition including a silicone polyester resin, a silicone oil, and an organosilica sol
comprising the hydrolysis and condensation reaction product of at least two different siloxane
monomers, an acid catalyst, and colloidal silica, the siloxane monomers of the formula
35 $R_xSi(OR')_{4-x}$, wherein R is a linear, branched, or cyclic alkyl or aryl group with up to 10 carbon

atoms; R' is a linear, branched, or cyclic alkyl group with up to 5 carbon atoms; and x is 1, 2 or 3, and a liquid medium.

[0006] The present disclosure further provides a method of coating an article with a coating composition comprising applying, over a substrate, a coating composition comprising an organosilica sol, a silicone polyester resin, and a silicone oil, wherein the organosilica sol comprises the hydrolysis and condensation reaction product of at least two different siloxane monomers, an acid catalyst, and colloidal silica, the siloxane monomers of the formula $R_xSi(OR')_{4-x}$, wherein R is a linear, branched, or cyclic alkyl or aryl group with up to 10 carbon atoms; R' is a linear, branched, or cyclic alkyl group with up to 5 carbon atoms; and x is 1, 2 or 3; and curing the coating composition at a temperature from 100°C to 450°C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The above-mentioned and other features and advantages of this disclosure, and the manner of attaining them, will become more apparent and the disclosure itself will be better understood by reference to the following description taken in conjunction with the accompanying drawings. These above-mentioned and other features of the disclosure may be used in any combination or permutation.

[0008] FIG. 1 illustrates a substrate coated with the coating composition of the present disclosure;

[0009] FIG. 2 illustrates a substrate coated with an undercoat and an overcoat coating composition of the present disclosure; and

[0010] FIG. 3 is a graph illustrating thermoset behavior of a coating composition of the present disclosure and comparative coating compositions.

[0011] Corresponding reference characters indicate corresponding parts throughout the several views. The exemplifications set out herein illustrate the disclosure, and such exemplifications are not to be construed as limiting the scope of the disclosure in any manner.

DETAILED DESCRIPTION

[0012] The present disclosure provides a durable and heat resistant coating composition including an organosilica sol, a silicone polyester resin, and a silicone oil. The coating composition may be applied as a single layer onto a substrate, or as a multilayer system including an undercoat and an overcoat.

[0013] I. Definitions

[0014] For purposes of the following detailed description, it is to be understood that the disclosure may assume various alternative variations and step sequences, except where expressly

specified to the contrary. Moreover, other than in any operating examples or where otherwise indicated, all numbers expressing, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term "about." For example, numerical ranges provided for weight percentages of components or amounts of components added should be construed as being modified by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0015] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

[0016] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges from (and including) the recited minimum value of 1 to the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

[0017] The use of the singular includes the plural and plural encompasses singular, unless specifically stated otherwise. In addition, the use of "or" means "and/or" unless specifically stated otherwise, even though "and/or" may be explicitly used in certain instances.

[0018] "Wet" coating composition as used herein refers to an uncured coating composition.

[0019] "Dry" coating composition as used herein refers to a cured coating composition.

[0020] "Substrate" and "article" as used herein refers to an object or other item with a surface onto which a coating composition may be applied.

[0021] "Solids" refers to the non-volatile components present in a composition of volatile and non-volatile components. As used herein, a weight percentage based on "solids" refers to an amount of a component based on a total weight of the non-volatile components of a composition.

[0022] "Resin solids" refers to the solid components that make up the binder or film-forming components of the composition, as well as any optional crosslinkers present. As used

herein, a weight percentage based on “resin solids” refers to an amount of a component based on a total weight of the binder or film-forming components of a composition.

[0023] “Siloxane monomer” refers to a monomer including a silicon atom with one or more Si-O-R linkages (wherein R is an organic group) that is capable of reacting with other such monomers via hydrolysis and condensation to form silicone resins with Si-O-Si linkages.

[0024] II. Organosilica sol

[0025] An organosilica sol can be prepared by a sol-gel reaction. The sol-gel reaction comprises a hydrolysis step and a condensation step to form a silicon matrix.

[0026] The organosilica sol may include at least two siloxane monomers, such as organosilanes of general formula:



wherein R is an aryl or alkyl organic substituent with up to 10 carbon atoms;

OR' is an alkoxy substituent with up to 5 carbon atoms (wherein the alkoxy substituent may have 1, 2, 3, 4, or 5 carbon atoms); and

x is an integer ranging from 1 to 3 (wherein x may be 1, 2, or 3).

[0027] The siloxane monomers may be hydrolyzed and condensed in the presence of a colloidal silica, water, and a catalyst.

[0028] The organosilica sol of the present disclosure may have a molecular weight (M_w) from 500 g/mol, 1500 g/mol, 2500 g/mol to 3500 g/mol, 4500 g/mol, 5000 g/mol, or any range including any two of the forgoing values as endpoints, such as 500 g/mol to 5000 g/mol, 1500 g/mol to 4500 g/mol, or 2500 g/mol to 3500 g/mol, as determined by GPC chromatography using polystyrene standards.

[0029] The organosilica sol of the present disclosure may comprise aryl groups, such as phenyl groups. The aryl groups may be present in an amount from 1 wt. %, 2 wt. %, 3 wt. % to 4 wt. %, 5 wt. %, 6 wt. %, or any range including any two of the forgoing values as endpoints, such as 1 wt.% to 6 wt.%, 2 wt.% to 5 wt.%, or 3 wt.% to 4 wt.%, wherein the weight percent is based on the total solids weight of the organosilica sol.

[0030] The organosilica sol may comprise alkyl groups, such as methyl groups. The organosilica sol may comprise a molar ratio of aryl to alkyl groups of 0.1, 0.3, 0.5 to 1.5, 2.5, 3, or any range including any two of the forgoing values as endpoints, such as 0.1 to 3, 0.3 to 2.5, or 0.5 to 1.5.

[0031] The organosilica sol of the present disclosure may have a solids concentration from 20 wt. %, 25 wt. %, 30 wt. % to 40 wt. %, 50 wt. %, 60 wt. %, or any range including any two of the forgoing values as endpoints, such as 20 wt. % to 60 wt. %, 25 wt. % to 50 wt. %, or 30 wt. % to 35 wt. %, based on a total weight of the organosilica sol.

[0032] The coating composition provided by the present disclosure may comprise a weight percentage of organosilica sol from 10 wt.%, 30 wt.%, 40 wt.% to 60 wt.%, 70 wt.%, 90 wt. %, or any range including any of the foregoing values as endpoints, such as 10 wt.% to 90 wt.%, 30 wt.% to 70 wt.%, or 40 wt.% to 60 wt.%, wherein the weight percent is based on the total weight of the “wet” coating composition.

[0033] The organosilica may be present in the cured coating composition, in an amount from 10 wt.%, 30 wt.%, 40 wt.% to 60 wt.%, 70 wt.%, 90 wt. %, or any range including any of the foregoing values as endpoints, such as 10 wt.% to 90 wt.%, 30 wt.% to 70 wt.%, or 40 wt.% to 60 wt.%, wherein the weight percent is based on the total weight of the “dry” coating composition.

[0034] A. Siloxane Monomers

[0035] As shown in Table 1 below, siloxane monomers may be described according to the degree of oxygen substitution, or functionality, on the central silicone.

Table 1: Siloxane Monomer Types

Structural formula	Functionality	Symbol
$\text{R}_3\text{Si}-\text{O}-$	Monofunctional	M
$\begin{array}{c} \text{R} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{R} \end{array}$	Difunctional	D
$\begin{array}{c} \text{R} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{O} \\ \end{array}$	Trifunctional	T
$\begin{array}{c} \\ \text{O} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{O} \\ \end{array}$	Tetrafunctional	Q

[0036] Suitable trifunctional siloxane monomers used in the organosilica sol of the present disclosure may include methyltrimethoxy silane, methyltriethoxy silane, phenyltrimethoxy silane, phenyltriethoxy silane, ethyltrimethoxy silane, propyltrimethoxy silane, methyltriethoxy silane, and propyltriethoxy silane.

5 **[0037]** Suitable difunctional siloxane monomers used in the organosilica sol of the present disclosure may include dimethyldimethoxy silane, diphenyldipmethoxy silane, methylphenyldimethoxy silane, dimethyldiethoxy silane, diphenyldipethoxy silane, methylphenyldiethoxy silane, ethyltrimethoxy silane, propyltrimethoxy silane, ethyltriethoxy silane, and propyltriethoxy silane.

10 **[0038]** Suitable monofunctional siloxane monomers used in the organosilica sol of the present disclosure may include trimethylmethoxy silane, and trimethylethoxy silane.

[0039] The organosilica sol may be formed as the reaction product of two different siloxane monomers, such as any two of the foregoing listed siloxane monomers. Further, these monomers may be selected to provide the organosilica sol with any aryl and alkyl content.

15 **[0040]** The aryl groups may be phenyl groups and the alkyl groups may be methyl groups. The siloxane monomers may comprise a molar ratio of aryl to alkyl groups of 0.1, 0.3, 0.5 to 1.5, 2.5, 3, or any range including any two of the foregoing values as endpoints, such as 0.1 to 3, 0.3 to 2.5, or 0.5 to 1.5.

[0041] The organosilica sol may comprise a weight percentage of siloxane monomers
20 from 30 wt. %, 45 wt. %, 50 wt. % to 60 wt. %, 65 wt. %, 70 wt. %, or any range including any two of the foregoing values as endpoints, such as 30 wt. % to 70 wt. %, 45 wt. % to 65 wt. %, or 50 wt. % to 60 wt. %, wherein the weight percent is based on the total weight of the organosilica sol.

[0042] B. Colloidal Silica

25 **[0043]** The organosilica sol may include colloidal silica. Colloidal silica is a suspension of silica particles in a liquid phase.

[0044] Suitable colloidal silica may include nanometric silica with a volume based average particle diameter, or D50, from 20 nm, 30 nm, 40 nm, 50 nm, to 60 nm, 70 nm, 80 nm, 100 nm, or any range including any two of the foregoing values as endpoints, such as 20 nm to
30 100 nm, 30 nm to 80 nm, 40 nm to 70 nm, or 50 nm to 60 nm, as determined by dynamic light scattering measured through Mie scattering and Fraunhofer diffraction technique as per ISO 13320-1 practice.

[0045] Suitable colloidal silica may also have a concentration of nanometric silica from
35 20 wt.%, 25 wt.%, 30 wt.% to 35 wt.% 40 wt.%, 50 wt.%, or any range including any two of the foregoing values as endpoints, such as 20 wt.% to 50 wt.%, 25 wt.% to 40 wt.%, or 30 wt.% to 35

wt.%, wherein the weight percent is based on a total weight of the colloidal silica suspension.

The colloidal silica particles may also include surface functionality that can comprise hydroxides, aluminates, chlorides or others. The continuous phase for the colloidal silica suspension may be an organic solvent such as isopropanol, ethanol, xylene, toluene, methanol, methyl ethyl ketone, methyl isobutyl ketone, methoxy propyl acetate, and/or water, provided water is removed in subsequent reaction steps.

[0046] The organosilica sol may comprise a weight percentage of colloidal silica from 5 wt. %, 10 wt. %, 20 wt. % to 40 wt. %, 50 wt. %, 60 wt. %, or any range including any two of the forgoing values as endpoints, such as 5 wt. % to 60 wt. %, 10 wt. % to 50 wt. %, or 20 wt. % to 50 wt. %, wherein the weight percent is based on the total weight of the organosilica sol.

[0047] C. Catalyst

[0048] A catalyst may be used in in the coating composition of the present disclosure. Acid catalysts may be used to increase the shelf life of the resulting catalyst-containing mixture.

[0049] Suitable catalysts may be general organic acids or alkali, such as formic acid, acetic acid, maleic acid, oxalic acid, malic acid etc. or primary amines or ammonia.

[0050] The organosilica sol may comprise a weight percentage of a catalyst from 0.1 wt. %, 0.5 wt. %, 1 wt. % to 1.5 wt. %, 2 wt. %, 2.5 wt. %, or any range including any two of the forgoing values as endpoints, such as 0.1 wt. % to 2.5 wt. %, 0.5 wt. % to 2 wt. %, or 1 wt. % to 1.5 wt. %, wherein the weight percent is based on the total weight of the organosilica sol.

[0051] D. Hydrolyzing Reactant

[0052] To complete the hydrolysis step of the sol-gel reaction, a hydrolyzing reactant, such as water, may be used. The molar ratio of water to alkoxy (OR') groups of the siloxane monomers may be less than 2, less than 1.5, less than 1, less than 0.5, or any other range within the forgoing values.

[0053] During the condensation step of the sol-gel reaction, water may be removed from the mixture. The removal of water may be facilitated by quenching the reaction by absorbing the water onto hygroscopic salts, such as Na₂SO₄, zeolite, or silica gel materials. Other suitable chemical techniques may also be used to quench the reaction, such as azeotropic distillation and Dean-Stark apparatus.

[0054] The organosilica sol may comprise a weight percentage of a hydrolyzing agent of less than 0.1 wt. %, less than 0.5 wt. %, less than 1 wt. %, less than 1.5 wt. %, or less than 2 wt. %, 2.5 wt. %, wherein the weight percent is based on the total weight of the organosilica sol.

[0055] III. Silicone Polyester Resin

[0056] A silicone polyester resin may be used in the preparation of high temperature coatings, in particular baking enamels for non-stick and temperature resistant coatings for cookware, stove tops, chimneys or mufflers.

[0057] Silicone polyester resins may be co-polymers prepared by polycondensation of a diol and di-acid to which an alkoxy or hydroxy functional siloxane oligomer or monomer are grafted.

[0058] Silicone polyester resins may be supplied in dry form or dissolved in a solvent, such as, but not limited to, methoxy propyl acetate, toluene, xylene, butyl acetate, ethyl acetate, and methyl isobutyl ketone.

[0059] Silicone polyester resins may have a mass fraction of dry siloxane to dry polyester of less than 90 wt. %, less than 70 wt. %, less than 50 wt. %, less than 30 wt. %, less than 10 wt. %, or less than 5 wt. %.

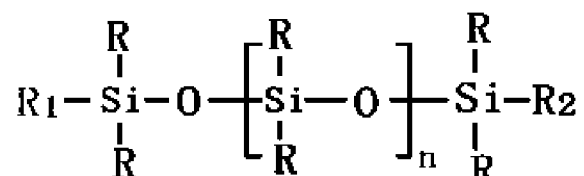
[0060] The coating composition provided by the present disclosure may comprise a weight percentage of silicone polyester resin from 10 wt. %, 30 wt. %, 40 wt. % to 50 wt. %, 60 wt. %, 70 wt. %, or any range including any two of the forgoing values as endpoints, such as 10 wt. % to 70 wt. %, 30 wt. % to 60 wt. %, or 40 wt. % to 50 wt. %, wherein the weight percent is based on the total weight of the “wet” coating composition.

[0061] The silicone polyester resin may be present in the cured coating composition, in an amount from 10 wt. %, 30 wt. %, 40 wt. % to 50 wt. %, 80 wt. %, 90 wt. %, or any range including any two of the forgoing values as endpoints, such as 10 wt. % to 90 wt. %, 30 wt. % to 80 wt. %, or 40 wt. % to 50 wt. %, wherein the weight percent is based on the total weight of the “dry” coating composition.

[0062] IV. Silicone Oil

[0063] Silicone oils may be used in coating compositions to improve non-stick and cleanability characteristics. The coating composition of the present disclosure may include one or more silicone oils, such as a medium molecular weight silicone oil, a high molecular weight silicone oil, or combinations thereof.

[0064] Suitable silicone oil may have the following structure:



where R is methyl or phenyl; R₁ is hydride, hydroxide or trimethyl silyl, and n is from 3 to more than 660.

[0065] A silicone oil may have a variable viscosity depending on the molecular weight and the organic substituents present along the chain. The viscosity of the silicone oil may be from 50 cP, 100 cP, 200 cP to 500 cP, 1000 cP, 5000 cP, or any range including any of the foregoing values as endpoints, such as 50 cP to 5000 cP, 100 cP to 1000 cP, or 200 cP to 500 cP, wherein the viscosity is measured at 25°C using a Brookfield rotational viscometer according to ASTM D2983-09.

[0066] The coating composition provided by the present disclosure may comprise a weight percentage of silicone oil from 0.1 wt. %, 0.5 wt. %, 1 wt. % to 10 wt. %, 15 wt. %, 20 wt. %, or any range including any two of the foregoing values as endpoints, such as 0.1 wt. % to 20 wt. %, 0.5 wt. % to 15 wt. %, or 1 wt. % to 10 wt. %, wherein the weight percent is based on the total weight of the “wet” coating composition.

[0067] The silicone oil may be present in the cured coating composition, in an amount from 1 wt.%, 2 wt.%, 5 wt.% to 10 wt.%, 20 wt.%, 40 wt. %], or any range including any of the foregoing values as endpoints, such as 1 wt.% to 40 wt.%, 2 wt.% to 20 wt.%, or 5 wt.% to 10 wt.%, wherein the weight percent is based on the total weight of the “dry” coating composition.

[0068] V. Additives

[0069] The coating composition formulated by the present disclosure can also include additives, such as fillers, pigments, wetting agents, rheology modifiers, defoamers, conductivity enhancers, smoke suppressors, dispersing agents, crosslinkers, and flexibilizers.

[0070] The coating composition provided by the present disclosure may comprise a weight percentage of total additives from 1 wt. %, 2 wt. %, 5 wt. % to 10 wt. %, 15 wt. %, 20 wt. %, or any range including any two of the foregoing values as endpoints, such as 1 wt. % to 20 wt. %, 2 wt. % to 15 wt. %, or 5 wt. % to 10 wt. %, wherein the weight percent is based on the total weight of the “wet” coating composition.

[0071] Some additives may be present in the cured coating composition, in an amount from 1 wt.%, 2 wt.%, 5 wt.% to 10 wt.%, 20 wt.%, 40 wt. %, or any range including any of the foregoing values as endpoints, such as 1 wt.% to 40 wt.%, 2 wt.% to 20 wt.%, or 5 wt.% to 10 wt.%, wherein the weight percent is based on the total weight of the “dry” coating composition.

[0072] VI. Coating Composition Application and Curing

[0073] The coating composition of the present application may be applied to a variety of substrates and cured. The coating composition of the present application may be applied as a single layer or as multiple layers. The multiple layers of the coating composition of the present application may comprise an undercoat and an overcoat.

[0074] FIG. 1 illustrates a single layer coated substrate 10. The single layer coated substrate 10 comprises a substrate 12, an optional phosphate conversion layer 14, and a coating composition of the present disclosure 16.

[0075] FIG. 2 illustrates a multiple layer coated substrate 20. The single layer coated substrate 20 comprises a substrate 12, an optional phosphate conversion layer 14, an undercoat coating composition 26 and an overcoat coating composition 28. The overcoat and undercoat coating compositions may comprise the coating composition formulation of the present disclosure.

[0076] A. Substrates

[0077] The coating composition may be applied to the surface of a substrate/article. Suitable substrates may include metals, ceramic materials, plastics, composites, and minerals. Suitable metals may include carbon steel, stainless steel, aluminum, and aluminized steel. Suitable ceramic materials may include glasses like borosilicate glass, porcelain enamels, various fired clays and other refractory materials. Suitable plastics and composites may include high melting point plastics and composites, such as plastics having a melting point higher than the cure temperature of the coating formulation, including polyester, polypropylene, ABS, polyethylene, carbon fiber epoxy composites, and glass fiber epoxy composites. Suitable minerals may include micas, basalts, aluminas, silicas, and wollastonites, marble and granite.

[0078] B. Pre-Treatment of a Substrate

[0079] The coating composition may be applied to the surface after a pre-treatment process. Suitable pre-treatment processes include, but are not limited to, de-greasing, acid or alkaline pickling, surface conversion layer with phosphate salts, brushing, grit blasting, or shot blasting.

[0080] As seen in FIGS. 1-2, a suitable substrate for coating with the coating composition of the present disclosure may also be pre-treated with an optional phosphate conversion layer. The phosphate conversion layer may be a coating on the substrate that creates a layer of iron, zinc, or manganese phosphates to increase corrosion resistance, lubrication, and act as a primer for the surface of the substrate before applying a coating composition.

[0081] The coating composition 16 of the present disclosure may be applied over a substrate 12 with an optional phosphate conversion layer 14 without a mechanical roughening step, such as grit blasting or shot blasting.

[0082] C. Coating Application

[0083] The coating compositions of the present disclosure may be applied to a substrate without pre-heating due to the stability of the organosilica sol within the coating.

[0084] The coating composition of the present disclosure may be applied to a substrate 12 as a single layer (16), as seen in FIG. 1, or in multiple layers (26, 28), as seen in FIG. 2, using spray coating or electrostatic spraying. For multiple layer coatings, an undercoat layer 26 may first be sprayed onto substrate 12. Without curing undercoat layer 26, an overcoat layer 28 may be sprayed onto substrate 12 coated in undercoat layer 26.

[0085] Spray coating may involve loading the coating composition into device wherein the coating composition is then forced through a nozzle such that the composition is made into a fine aerosol spray. The spray is then directed over a substrate for an even coating.

[0086] Electrostatic spraying may involve loading the coating composition into a device wherein, as the coating composition is forced through a nozzle and made into a fine aerosol spray, a small electrical charge is applied to the nozzle causing the aerosol spray droplets to be slightly charged. The charged fine aerosol spray may adhere to the sprayed substrate better than an uncharged spray.

[0087] D. Curing

[0088] The coating composition of the present disclosure may be cured at temperatures from 100°C, 200°C, 250°C to 350, 400°C, 450°C, or any range including any of the foregoing values as endpoints, such as 100°C to 450°C, 200°C to 400°C, or 250°C to 350°C.

[0089] VII. Coating Composition Properties

[0090] The coating composition of the present disclosure may have improved adhesion, storage stability, gloss, hardness, and release as compared to known coating compositions.

[0091] The coating of the present disclosure may also be substantially free, essentially free, or completely free of fluorine-containing components.

[0092] Fluorine-containing components may include per/polyfluoroalkyl substances (PFAS), such as fluoropolymers, fluorine-containing oligomers and/or fluorine containing small molecules.

[0093] By substantially free in relation to fluoropolymers, is meant that the coating composition may comprise less than 5 wt. % of fluoropolymers based on the total weight of the “wet” coating composition. By essentially free in relation to fluoropolymers, is meant that the coating composition may comprise less than 1 wt. % of fluoropolymers based on the total weight of the “wet” coating composition. By completely free in relation to fluoropolymers, is meant that the coating composition may comprise less than 0.01 wt. % of fluoropolymers based on the total weight of the “wet” coating composition.

[0094] A. Adhesion

[0095] Adhesion can be tested by a standard technique such as ASTM D3359 (standard test methods for measuring adhesion by tape test) or ASTM D2197-16 (Standard Test Method for Adhesion of Organic Coatings by Scrape Adhesion).

[0096] The coating composition of the present disclosure may exhibit excellent adhesion and pass the adhesion test.

[0097] B. Storage Stability

[0098] Storage stability can be measured by a combination of techniques such as ASTM D869-21 (Standard Test Method for Evaluating Degree of Settling of Paint); viscosity as per ASTM D5125-10 (Standard Test Method for Viscosity of Paints and Related Materials by ISO Flow Cups); and performance of the applied coating such as gloss retention. The storage stability of the composition may be measured at 25°C and a relative humidity of 60%.

[0099] The coating composition of the present disclosure may display a recoverable settlement over one week storage; a variation in viscosity no greater than 20% over one week storage; and a change in gloss no greater than 20% after one week storage.

[0100] C. Gloss

[0101] The gloss of a coating may be measured by comparing the specular reflectance of the coating to that of a black glass standard. This is done with an instrument that projects a beam of light at a fixed intensity and angle onto a surface and measuring the amount of reflected light at an equal but opposite angle.

[0102] The coating composition of the present disclosure may have a gloss from 40 GU, 45 GU, 50 GU, or 55 GU, 60 GU, 65 GU, or within any range using any two of the foregoing as endpoints, such as 40 GU to 65 GU, 45 GU to 60 GU, or 50 GU to 55 GU, where the gloss is measured at 60°C according to ASTM D523.

[0103] D. Pencil Hardness/Hot Pencil Hardness

[0104] Pencil Hardness describes the capacity of a coating on a substrate to resist scratching, marring or gouging. The test utilizes a pencil of known hardness at a 45-degree angle to the coated surface at a constant force to determine the hardest pencil that will not scratch the coating. The value scale of pencil hardness ranges from 6B-9H, 6B being the softest and 9H being the hardest.

[0105] The coating composition of the present disclosure may have a pencil hardness from 5H, 7H, to 8H, 9H, or within any range using any two of the foregoing as endpoints, such as 5H to 9H, to 7H to 8H where the pencil hardness is measured at ambient temperatures, e.g., at 23°C, according to ASTM D 3363.

[0106] Pencil hardness may also be tested at elevated temperatures to test the hardness of a coating when the coating is exposed to heat. The coating composition of the present disclosure

may have a pencil hardness from 3H, 5H, or 7H, 9H, or within any range using any two of the foregoing as endpoints, such as 3H to 9H, or 5H to 7H where the pencil hardness is measured at elevated temperatures, e.g., at 25°C-200°C, according to ASTM D 3363.

[0107] E. Dry RAT Test

5 **[0108]** The coating composition of the present disclosure may have a reciprocating abrasion resistance from 9000, 9500, 10000, 20000 to 70000, 80000, 90000, 100000, or within any range using any two of the foregoing as endpoints, such as 9000 to 100000, 9500 to 90000, 10000 to 80000, or 20000 to 70000, where the abrasion resistance is measured according to BSI norm BS 6079/1988.

10 **[0109]** F. Egg Release/Steak Release

[0110] A dry egg release test may be performed according to a test method developed internally within PPG Industries with the following procedure.

[0111] A cooking article is positioned on the heating source and stabilized at 150°C; a whole egg is broken into the cooking article and it is left to cook for 2 minutes. The cooked egg
15 is then turned over and left to cook for another 1 minute. The ease of removal is evaluated with a spatula, and the following score is assigned:

5 - Excellent - No sticking in center or around edges of the egg.

Egg removed intact.

20 4 - Good - Slight sticking around edges of utensil with or without a small amount of easily removed residue.

3 - Fair - Egg sticks on edges and in the center.

2 - Poor - Egg sticks and cannot be removed completely, leaving half of portion stuck on the surface.

1 - Failed - More than half of the egg stuck on the surface

25 **[0112]** The coating composition of the present disclosure may have excellent egg release properties, indicating that the coating provides a good non-stick surface to the substrate it is applied to.

[0113] The steak test quantifies the release properties of a coatings when a steak or other meat is cooked on the surface of a coated substrate. It is appropriate release test for certain
30 markets; EN13834 performance test results are recognized throughout the bakeware industry in Europe.

[0114] To test the steak release of a coating, a substrate coated with a cured coating composition is subjected to multiple steak test cycle. Each test cycle involves cooking a raw steak on the coated substrate. Once the steak is cooked, the steak is removed from the surface

and a natural sponge is used to clean the substrate. Repeated test cycles are conducted until the coated substrate has residue or staining following a test cycle.

[0115] The release properties are measured by evaluating the presence of remaining residue and level of staining following each test cycle. Use of a natural sponge is important to maintain the consistency of the result. The steak release of a coating composition may be characterized by the number of test cycles conducted before residue/staining occurs.

[0116] The coating composition of the present disclosure may successfully pass steak release cycles from 5, 10, 15, 20 to 25, 30, 35, 40 or within any range using any two of the foregoing as endpoints, such as 5 to 40, 10 to 35, 15 to 30, or 20 to 30, where the steak test is performed according to the norm EN13834 Annex D (Cookware - Ovenware for use in traditional domestic ovens).

EXAMPLES

[0117] Aspects of the present disclosure are further illustrated by reference to the following examples. It will be apparent to those skilled in the art that many modifications, both to materials, and methods, may be practiced without departing from the scope of the disclosure.

Example 1: Organosilica Sol Synthesis

[0118] An organosilica sol may be prepared using the formulation in Table 2 as follows.

[0119] In the amounts indicated in Table 2 and in the following order, colloidal silica, acetic acid, isopropyl alcohol, and mentoxy propanol are placed into a reactor. The mixture is stirred until it becomes homogeneous and slightly hazy, being careful to homogenize the acid entirely before adding the solvent.

[0120] Subsequently, in the amounts indicated in Table 2 and in the following order, under vigorous stirring and reflux, methyltrimethoxy silane, phenyltrimethoxy silane, and methoxy propyl acetate are added.

[0121] The mixture is left reacting for 2 to 24 hours under vigorous stirring and reflux. The reaction is heated for up to 48 hours at a moderate temperature of 40 to 80°C or carried out at room temperature (25°C), extending the reaction time.

[0122] To let down, the pH is adjusted to the range 2 to 3, and the water is removed from the batch by introducing a desiccant salt such as sodium sulfate anhydrous or by other suitable industrial method, to stop the reaction. The reacted sol is subsequently filtered and concentrated to a solid content of about 40%.

[0123] The organosilica sol prepared by such technique is a clear slightly hazy liquid that is storable at room temperature with a shelf life of several month, characterized by a molecular

weight M_w ranging from 2000 to 5000 Dalton, as measured by convenient GPC chromatography using polystyrene standards.

Table 2: Formulation of Organosilica Sol

Component	Wt. %
Colloidal silica, suspended 30% in water	25.4
Acetic acid, glacial	1.7
Isopropyl alcohol	12.7
Mentoxy propanol	2.3
Methyltrimethoxy silane	24.7
Phenyltrimethoxy silane	28.0
Methoxy propyl acetate	5.2

5

Example 2: Example Coating Composition Synthesis

[0124] Example coating compositions of the present disclosure were prepared according to Table 3 below.

[0125] A. Example Coatings 1 and 2

10 **[0126]** The sol produced in the Example 1 was blended, with the amounts specified in Table 3, with a silicone modified polyester, xylene, methoxy propyl acetate, butyl oxitol and isopropanol solvents under high-speed dispersion.

[0127] An amount of carbon black and pyrogenic silica were ground in the liquid by a basket mill filled with zirconia beads, operated at 1000 to 1500 RPM for 60 to 240 minutes
15 within a cooled vessel. Conditions may depend on batch size and viscosity.

[0128] After grinding, an amount of silicon carbide was stirred in by high-speed dispersion. The composition was finalized by the addition to the formula of silicone fluids and additives.

[0129] The composition was prepared as mentioned above and then sprayed by airmix
20 spraying onto a metal substrate made of carbon steel pre-treated with a phosphate conversion layer. After spraying, the composition was dried at 100°C for 5 minutes, and finally cured for 20 minutes at 290°C to produce a uniform non-stick film of 20-40 μm in dry film thickness.

[0130] The wt. % of each component in cured Examples Coatings 1 and 2 are illustrated in Table 5.

25 **[0131]** B. Example Coatings 3 and 4

[0132] To form Example Coatings 3 and 4, an undercoat was formulated by blending the sol produced in the Example 1 with the components and amounts specified in Table 3, with methoxy propyl acetate solvent. The undercoat composition was finalized by adding silicone fluids, additives, and pearlescent mica pigments.

5 **[0133]** The overcoat compositions of Examples 3 and 4 were produced by mixing the components in the amounts specified in Table 4. The entire preparation of the undercoat and overcoat compositions for Example coatings 3 and 4 were performed under high-speed dispersion.

[0134] The undercoat compositions of Examples 3 and 4 were applied by airmix spraying onto a metal substrate made of carbon steel pre-treated with a phosphate conversion layer.

[0135] Subsequently, the overcoat compositions of Examples 3 and 4 were applied on top of the undercoat, without a drying stage in between. After spraying, the compositions are dried at 100°C for 5 minutes, and finally cured for 20 minutes at 290°C to produce a uniform non-stick film of 20-40 μm in dry film thickness.

[0136] The wt. % of each component in cured Examples Coatings 3 and 4 are illustrated in Table 5 and Table 6.

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Table 3: Formulation of Coating Compositions (wt. %)

Undercoat		Component	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Binder		Example 1 organosilica sol	20	35	20	35
		SILICONE POLYESTER 60%	50	35	50	35
	Nanopol colloidal (40wt% resin)	Evonik NANOPOL C 764				
	REN168 (40wt% resin)	REN168 (40wt% solid)				
Release agent	Silicone fluid	XIAMETER PMX-200 FLUID 350	2	2		
		XIAMETER PMX-0156 SILANOL			0.2	0.2

Undercoat		Component	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Pigments and fillers	Silicon carbide	CARBOREX C6 F500	2	2	2	2
		CARBOREX BW F 800	2	2	2	2
	Pigment (100% solid)	SHEPHERD BLACK 430	4	4	4	4
	Filler (solid)	AEROSIL R-972	1	1	1	1
Solvents and additives	Solvent	1-METHOXY-2-PROPYLACETATE (PMA)	6	6	6	6
		XYLENE (Fusion Use)	9	9	9	9
		Butyl oxitol / cellosolve (EGBE) (Fusion Use)	3	3	3	3
		ISOPROPYL ALCOHOL	0.6	0.6	2.4	2.4
	Additive	TEGOGLIDE 407	0.4	0.4	0.4	0.4

Table 4: Overcoat Composition for Example Coatings 3 and 4 (wt. %)

Overcoat		Part Description	Ex. 3	Ex. 4
Binder	1K Quark	1K Quark	82.50	82.50
Release agent	Silicone fluid	XIAMETER PMX-0156 SILANOL (Fusion Use)	1.80	1.80
Pigments and fillers	Pigment	KC 153 K SILVER WHITE SERIES	0.30	0.30
Solvents and additives	Solvent	1-METHOXY-2-PROPYLACETATE (PMA)	15.00	15.00
	Additive	TEGOGLIDE 407	0.40	0.40

Undercoat		Component	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Binder		Example 1 organosilica sol	16.19	30.17	16.81	31.39
		SILICONE POLYESTER 60%	60.73	45.26	63.03	47.09
	Nanopol colloidal (40wt% resin)	Evonik NANOPOL C 764				
	REN168 (40wt% resin)	REN168 (40wt% solid)				
Release agent	Silicone fluid	XIAMETER PMX- 200 FLUID 350	4.05	4.31		
		XIAMETER PMX- 0156 SILANOL			0.42	0.45
Pigments and fillers	Silicon carbide	CARBOREX C6 F500	4.05	4.31	4.20	4.48
		CARBOREX BW F 800	4.05	4.31	4.20	4.48
	Pigment (100% solid)	SHEPHERD BLACK 430	8.10	8.62	8.40	8.97
	Filler (solid)	AEROSIL R-972	2.02	2.16	2.10	2.24
Solvents and additives	Solvent	1-METHOXY-2- PROPYLACETATE (PMA)				
		XYLENE (Fusion Use)				
		Butyl oxitol / cellosolve (EGBE) (Fusion Use)				
		ISOPROPYL ALCOHOL				
	Additive	TEGOGLIDE 407	0.81	0.86	0.84	0.90

Table 6: Solids wt. % of Cured Overcoat for Example Coatings 3 and 4

Overcoat		Part Description	Ex. 3	Ex. 4
Binder	1K Quark	1K Quark	92.96	92.96

Overcoat		Part Description	Ex. 3	Ex. 4
Release agent	Silicone fluid	XIAMETER PMX-0156 SILANOL (Fusion Use)	5.07	5.07
Pigments and fillers	Pigment	KC 153 K SILVER WHITE SERIES	0.85	0.85
Solvents and additives	Solvent	1-METHOXY-2- PROPYLACETATE (PMA)		
	Additive	TEGOGLIDE 407	1.13	1.13

Example 3: Organosilica Sol Synthesis

[0137] An organosilica sol was prepared using the formulation in Table 7.

[0138] In the amounts indicated in Table 7 and in the following order, acetic acid,
5 methyltrimethoxy silane, and colloidal silica were mixed together.

Table 7: Formulation of Organosilica Sol

Component	Wt. %
Acetic acid, glacial	0.58
Methyltrimethoxy silane	27.83
Colloidal silica, suspended 30% in water	41.37

[0139] The mixture was stirred until it became homogeneous and slightly hazy, being
10 careful to homogenize the acid entirely before adding the colloidal silica. The mixture was left reacting for 2 hours at room temperature.

Example 4: Comparative Coating Composition Synthesis

[0140] Comparative coating compositions were prepared according to Table 8 below.

15 [0141] A. Comparative Coating Composition 1

[0142] A silicone modified polyester resin was blended, with the wt. % amounts specified in Table 8 of xylene, methoxy propyl acetate, butyl oxitol and isopropanol solvents under high-speed dispersion.

[0143] An amount of carbon black and pyrogenic silica were ground in the liquid by a
20 basket mill filled with zirconia beads, operated at 1000 to 1500 RPM for 60 to 240 minutes within a cooled vessel. Conditions may depend on batch size and viscosity.

[0144] After grinding, an amount of silicon carbide was stirred in by high-speed dispersion. The composition was finalized by the addition of silicone fluids and additives.

[0145] Comparative composition 1 was prepared as above and then sprayed by airmix spraying onto a metal substrate made of carbon steel pre-treated with a phosphate conversion layer. After spraying, comparative composition 1 was dried at 100°C for 5 minutes, and finally cured for 20 minutes at 290°C to produce a uniform non-stick film of 20-40 μm in dry film thickness.

[0146] The wt. % of each component in cured Comparative Coating 1 is illustrated in Table 10.

[0147] B. Comparative Coating Composition 2

[0148] The sol produced in the Example 1 (table 2) was blended with the amounts specified in Table 8 of xylene, methoxy propyl acetate, butyl oxitol and isopropanol solvents under high speed dispersion.

[0149] An amount of carbon black and pyrogenic silica were ground in the liquid by a basket mill filled with zirconia beads, operated at 1000 to 1500 RPM for 60 to 240 minutes within a cooled vessel. Conditions may depend on batch size and viscosity.

[0150] After grinding, an amount of silicon carbide was stirred in by high speed dispersion. The composition was finalized by the addition to the formula of silicone fluids and additives.

[0151] Comparative composition 2 was prepared and then sprayed by airmix spraying onto a metal substrate made of carbon steel pre-treated with a phosphate conversion layer. After spraying, comparative composition 2 was dried at 100°C for 5 minutes, and finally cured for 20 minutes at 290°C to produce a uniform non-stick film of 20-40 μm in dry film thickness.

[0152] The wt. % of each component in cured Comparative Coating 2 is illustrated in Table 10.

[0153] C. Comparative Coating Composition 3

[0154] The organosilica sol from Example 3 (table 7) was blended with the recipe amounts specified in Table 8, with isopropyl alcohol.

[0155] An amount of carbon black and pyrogenic silica were ground in the liquid by a basket mill filled with zirconia beads, operated at 1000 to 1500 RPM for 60 to 240 minutes within a cooled vessel. Conditions may depend on batch size and viscosity.

[0156] After grinding, an amount of silicon carbide was stirred in by high-speed dispersion. Comparative composition 3 was finalized by the addition of silicone fluids and additives.

[0157] Comparative composition 3 was prepared and then sprayed by airmix spraying onto a metal substrate made of carbon steel pre-treated with a phosphate conversion layer. After spraying, the composition was dried at 100°C for 5 minutes, and finally cured for 20 minutes at 290°C to produce a uniform non-stick film of 20-40 μm in dry film thickness.

5 [0158] The wt. % of each component in cured Comparative Coating 3 is illustrated in Table 10.

[0159] D. Comparative Coating Composition 4

[0160] A silicone modified polyester resin was blended, with the recipe amounts specified in Table 8, with, xylene, methoxy propyl acetate, butyl oxitol and isopropanol solvents
10 under high speed dispersion. It was then blended with an amount of solvent stabilized colloidal silica such as Evonik Nanopol C764.

[0161] An amount of carbon black and pyrogenic silica were ground in the liquid by a basket mill filled with zirconia beads, operated at 1000 to 1500 RPM for 60 to 240 minutes within a cooled vessel. Conditions may depend on batch size and viscosity.

15 [0162] After grinding, an amount of silicon carbide was stirred in by high speed dispersion. Comparative coating composition 4 was finalized by the addition to the formula of silicone fluids and additives.

[0163] Comparative coating composition 4 was prepared and then sprayed by airmix spraying onto a metal substrate made of carbon steel pre-treated with a phosphate conversion
20 layer. After spraying the composition is dried at 100°C for 5 minutes, and finally cured for 20 minutes at 290°C to produce a uniform non-stick film of 20-40 μm in dry film thickness.

[0164] The wt. % of each component in cured Comparative Coating 4 is illustrated in Table 10.

[0165] E. Comparative Coating Composition 5

25 [0166] For the preparation of an undercoat, a silicone modified polyester resin was blended, with the amounts specified in Table 8 of xylene, methoxy propyl acetate, butyl oxitol and isopropanol solvents under high-speed dispersion.

[0167] Subsequently, the composition was blended with a silicone T resin prepared primarily of methyl and phenyl siloxanes with a degree of crosslinking close to 75%, such as
30 Silres REN168 supplied by Wacker.

[0168] An amount of carbon black and pyrogenic silica were ground in the liquid by a basket mill filled with zirconia beads, operated at 1000 to 1500 RPM for 60 to 240 minutes within a cooled vessel. Conditions may depend on batch size and viscosity.

[0169] After grinding, an amount of silicon carbide was stirred in by high-speed dispersion. The undercoat was finalized by the addition to the formula of silicone fluids and additives.

[0170] For the preparation of the overcoat, a second composition was prepared by blending a silicone T resin prepared primarily of methyl and phenyl siloxanes with a degree of crosslinking close to 75%, such as Silres REN168 supplied by Wacker, with the amounts specified in Table 9, with methoxy propyl acetate solvent. The overcoat was finalized by the addition to the formula of silicone fluids and additives and pearlescent mica pigments. All the preparation was performed under high-speed dispersion.

[0171] The undercoat was sprayed by airmix spraying onto a metal substrate made of carbon steel pre-treated with a phosphate conversion layer. Subsequently the overcoat was applied on top of the undercoat, without a drying stage in between, creating comparative coating composition 5. After spraying, comparative coating composition 5 was dried at 100°C for 5 minutes, and finally cured for 20 minutes at 290°C to produce a uniform non-stick film of 20-40 µm in dry film thickness.

[0172] The wt. % of each component in cured Comparative Coating 5 is illustrated in Tables 10 and 11.

[0173] F. Comparative Coating Composition 6

[0174] For the preparation of the undercoat, a silicone modified polyester resin was blended, with the amounts specified in Table 8 of, xylene, methoxy propyl acetate, butyl oxitol and isopropanol solvents under high-speed dispersion. Subsequently the composition was blended with a silicone T resin prepared primarily of methyl and phenyl siloxanes with a degree of crosslinking close to 75%, such as Silres REN168 supplied by Wacker and an amount of solvent stabilized colloidal silica such as Evonik Nanopol C764.

[0175] An amount of carbon black and pyrogenic silica were ground in the liquid by a basket mill filled with zirconia beads, operated at 1000 to 1500 RPM for 60 to 240 minutes within a cooled vessel. Conditions may depend on batch size and viscosity.

[0176] After grinding, an amount of silicon carbide was stirred in by high-speed dispersion. The undercoat was finalized by the addition to the formula of silicone fluids and additives.

[0177] For the preparation of the overcoat, a second composition was prepared by blending a silicone T resin prepared primarily of methyl and phenyl siloxanes with a degree of crosslinking close to 75%, such as Silres REN168 supplied by Wacker, with the amounts specified in Table 9 of methoxy propyl acetate solvent with an amount of solvent stabilized colloidal silica such as Evonik Nanopol C764.

[0178] The overcoat composition was finalized by the addition to the formula of silicone fluids and additives and pearlescent mica pigments. All the preparation is performed under high-speed dispersion.

[0179] The undercoat was sprayed by airmix spraying onto a metal substrate made of

5 carbon steel pre-treated with a phosphate conversion layer. Subsequently, the overcoat was applied on top of the undercoat, without a drying stage in between, creating comparative coating composition 6. After spraying, comparative coating composition 6 was dried at 100°C for 5 minutes, and finally cured for 20 minutes at 290°C to produce a uniform non-stick film of 20-40 μm in dry film thickness.

10 **[0180]** The wt. % of each component in cured Comparative Coating 6 is illustrated in Tables 10 and 11.

Table 8: Comparative Coating Composition Formulation (wt. %)

Undercoat		Component	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6
Binder		Example 1 organosilica sol		70				
		Silicone polyester 60%	70			35	35	35
	MTMS + Colloidal silica	Example 3 organosilica sol			70			
	Nanopol colloidal (40wt% resin)	Evonik NANOPOL C 764				35		20
	REN168 (40wt% resin)	REN168 (40wt% solid)					35	15
Release agent	Silicone fluid	XIAMETER PMX-200 FLUID 350	2	2	2	2		
		XIAMETER PMX-0156 SILANOL					0.2	0.2
Pigments and fillers	Silicon carbide	CARBOREX C6 F500	2	2	2	2	2	2
		CARBOREX BW F 800	2	2	2	2	2	2

Undercoat		Component	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6
	Pigment (100% solid)	SHEPHERD BLACK 430	4	4	4	4	4	4
	Filler (solid)	AEROSIL R-972	1	1	1	1	1	1
Solvents and additives	Solvent	1-METHOXY-2- PROPYLACET ATE (PMA)	6	6		6	6	6
		XYLENE (Fusion Use)	9	9		9	9	9
		Butyl oxitol/cellosolve (EGBE) (Fusion Use)	3	3		3	3	3
		ISOPROPYL ALCOHOL	0.6	0.6	18.6	0.6	2.4	2.4
	Additive	TEGOGLIDE 407	0.4	0.4	0.4	0.4	0.4	0.4

Table 9: Overcoat Composition for Comparative Coatings 5 and 6 (wt. %)

Overcoat		Part Description	Comp. 5	Comp. 6
Binder	REN168 (40 wt. % resin	REN168 (40wt% solid)	82.50	57.50
	Nissan chemical colloidal (40 wt. % resin)	Evonik NANOPOL C 764		25.00
Release agent	Silicone fluid	XIAMETER PMX-0156 SILANOL (Fusion Use)	1.80	1.80
Pigments and fillers	Pigment	KC 153 K SILVER WHITE SERIES	0.30	0.30
Solvents and additives	Solvent	1-METHOXY-2- PROPYLACETATE (PMA)	15.00	15.00
	Additive	TEGOGLIDE 407	0.40	0.40

Table 10: Solids wt. % of Cured Coating

Undercoat		Component	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6
Binder		Example 1 organosilica sol		71.07				

Undercoat		Component	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6
		Silicone polyester 60%	78.65			44.26	47.09	46.46
	MTMS + Colloidal silica	Example 3 organosilica sol			73.43			
	Nanopol colloidal (40wt% resin)	Evonik NANOPOL C 764				31.72		19.03
	REN168 (40wt% resin)	REN168 (40wt% solid)					31.39	13.27
Release agent	Silicone fluid	XIAMETER PMX-200 FLUID 350	3.75	5.08	4.66	4.21		
		XIAMETER PMX-0156 SILANOL					0.45	0.44
Pigments and fillers	Silicon carbide	CARBOREX C6 F500	3.75	5.08	4.66	4.21	4.48	4.42
		CARBOREX BW F 800	3.75	5.08	4.66	4.21	4.48	4.42
	Pigment (100% solid)	SHEPHERD BLACK 430	7.49	10.15	9.32	8.43	8.97	8.85
	Filler (solid)	AEROSIL R-972	1.87	2.54	2.33	2.11	2.24	2.21
Solvents and additives	Solvent	1-METHOXY-2-PROPYLACETATE (PMA)						
		XYLENE (Fusion Use)						
		Butyl oxitol/cellosolve (EGBE) (Fusion Use)						
		ISOPROPYL ALCOHOL						
	Additive	TEGOGLIDE 407	0.75	1.02	0.93	0.84	0.90	0.88

Table 11: Solids wt. % of Cured Overcoat for Comparative Coatings 5 and 6

Overcoat		Part Description	Comp. 5	Comp. 6
Binder	REN168 (40 wt. % resin)	REN168 (40wt% solid)	92.96	63.45
	Nissan chemical colloidal (40 wt. % resin)	Evonik NANOPOL C 764		29.66
Release agent	Silicone fluid	XIAMETER PMX-0156 SILANOL (Fusion Use)	5.07	4.97
Pigments and fillers	Pigment	KC 153 K SILVER WHITE SERIES	0.85	0.83
Solvents and additives	Solvent	1-METHOXY-2- PROPYLACETATE (PMA)		
	Additive	TEGOGLIDE 407	1.13	1.10

Example 5: Coating Composition Properties

[0181] All the example compositions presented in Tables 2 and 4 were applied by spraying about 20-30 μm of dry film thickness on phosphated carbon steel substrate. The applied coating was dried at 100°C for about 5 minutes and subsequently baked for 20 minutes at 290°C in order to cure the coating. The examples relative to a 2-coat system were applied wet on wet, without any drying step in between the two coats. The properties of each coating composition were measured and recorded, as seen in Table 12.

[0182] Coating composition Ex. 1 and 2 displayed the synergistic performance of the combination of the silicone modified polyester and the organosilica sol such as prepared in Example 1, jointly with an amount of silicone fluid. Coating composition Ex. 1 and 2 show different ratios of sol and silicone polyester resin. Coating composition Ex. 1 and 2 show good adhesion and performance in durability compared to the other solutions presented as 1-coat system.

[0183] Comparative coating composition 1 contained a silicone polyester without organosilica sol. Comparative coating composition 1 was soft thermoplastic that was not durable and not non-stick.

[0184] Comparative coating composition 2 contained the organosilica sol without silicone polyester. Comparative coating composition 2 showed good non-stick durability and abrasion resistance, but limited adhesion to the phosphate carbon steel substrate.

[0185] Comparative coating composition 3 contained an organosilica sol prepared by traditional methods in the absence of phenyl and without stabilization. Comparative coating composition 3 showed outstanding abrasion resistance and thermoset properties. However, the nature of the binder prevents a proper adhesion over the phosphate carbon steel substrate, therefore it was impossible to test against the other examples prepared in absence of gritblasting. Additionally, Comparative coating composition 3 underwent a fast reaction that caused a gelation of the material within a few days.

[0186] Comparative coating composition 4 contained a silicone polyester combined with a silica sol in absence of the organic modification of the same. Comparative coating composition 4 showed a dull surface unsuitable for nonstick application, but definitely an enhanced mechanical resistance compared to the comparative coating composition 2. In comparison with coating composition examples 1 and 2 of the present disclosure, comparative coating composition 4 lacked the organosilicon structure to shell the silica adopted in the preparation to behave effectively.

[0187] Coating composition Ex. 3 and 4 had the most effective combination by blending the organosilica sol and the silicone polyester to form an undercoat where the superior adhesion of the silicone polyester was maximized, and by subsequently adding an overcoat where the superior thermoplastic properties of the organosilica sol is exploited. Coating composition Ex. 3 and 4 show two possible ratios of the main resins.

[0188] Comparative coating composition 5 displayed a combination of silicone polyester resin and a silicone T resin, where the absence of colloidal silica in the resin is responsible for softness and reduced non-stick durability. Compared to Ex. 1-4 coating compositions, Comp. 5 had a greatly reduced pencil hardness.

[0189] Comparative coating composition 6 displays the cold blend combination of the key ingredients of the disclosure, such as the silicone polyester, the silicone T resin, and the silica sol. Compared to Ex. 1-4 coating compositions, Comp. 6 had reduced pencil hardness.

Table 12: Coating Composition Properties

Coating	Primer	Overcoat	Adhesion	Storage Stability	Gloss	Pencil Hardness	Hot Pencil Hardness	Dry RAT	Egg Release	Steak Release
Ex. 1	Yes		Pass	4 months	50	7H	4H	10000	5	15
Ex. 2	Yes		Pass	4 months	50	7H	5H	15000	5	20
Comp. 1	Yes		Pass	12 months	65	2H	H	5000	5	6
Comp. 2	Yes		Fail	1 day	NA	7H	6H	20000	5	15
Comp. 3	Yes		Fail	6 months	15	NA	NA	NA	NA	NA

Coating	Primer	Overcoat	Adhesion	Storage Stability	Gloss	Pencil Hardness	Hot Pencil Hardness	Dry RAT	Egg Release	Steak Release
Comp. 4	Yes		Pass	4 months	65	3H	1H	15000	5	12
Ex. 3	Yes	Yes	Pass	4 months	65	7H	5H	38000	5	26
Ex. 4	Yes	Yes	Pass	4 months	65	7H	6H	45000	5	30
Comp. 5	Yes	Yes	Pass	6 months	75	HB	B	10000	5	12
Comp. 6	Yes	Yes	Pass	6 months	35	2H	1H	15000	5	15

Example 6: Coating Composition Thermo-Mechanical Properties

[0190] The thermo-mechanical properties were investigated by the use of TMA (thermo-mechanical analyzer) where the coated samples were placed on a stage into a furnace capable of controlled temperature ramp, and a penetrating probe was applied to the coating with a constant load. The softening point of the coating, if present, was measured by an inflection in the otherwise linear thermal dilatation curve of the samples.

[0191] From Fig. 3, it is apparent that the coating formulated as per comparative coating composition 1 has a strong thermoplastic behavior, while comparative coating composition 2 made with the organosilica sol does not. The coating composition Ex. 1 of the present disclosure surprisingly inherited the thermoset behavior of the organosilica sol despite the presence of the silicone polyester resin in the blend.

Example 7: Coating Compositions and Scratch Resistance

[0192] Example coating compositions of the present disclosure and comparative coating compositions were prepared using the amounts indicated in Table 13 below.

[0193] The ratio of organosilica sol and silicone modified polyester was varied between the coating compositions to determine which ratio results in superior scratch resistance.

[0194] The coating compositions were applied onto phosphate carbon steel panels by spraying and cured for 20 minutes at 290°C resulting in a clear film with a thickness of 10-20 μm.

Table 13: Coating Composition Formulations (wt. %)

Function	Part Description	Comp. 7	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Comp. 8
Binder	Example 1 organosilica sol (40% solid)		14	28	42	56	70
	silicone modified polyester (40% in MPA)	70	56	42	28	14	
Release agent	Silicone oil 350 cSt	1.2	1.2	1.2	1.2	1.2	1.2

Function	Part Description	Comp. 7	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Comp. 8
Solvent	1-METHOXY-2- PROPYLACETATE (PMA)	28.8	28.8	28.8	28.8	28.8	28.8

[0195] The coated panels were tested with a scratch tester analyzer Nanovea PB1000, equipped with a 40N load cell, a rockwell type of indenter and a heated stage capable of reaching 400°C. The panels were tested for scratch resistance over a run of 20mm and a progressive load applied up to 10N. the breakdown load (LC2) at which the coating was disbanded was captured and reported in Table 14.

[0196] Surprisingly it is observed that the combination of the organosilica sol and the silicone polyester gives a critical load that is superior, in all combinations, to each of the extremes of the range at room temperature.

[0197] The same experiment was performed at elevated temperature. The combinations of the two components had a better scratch resistance at 200°C than the individual components measured separately, indicating a surprising synergistic effect.

Table 14: Scratch Resistance

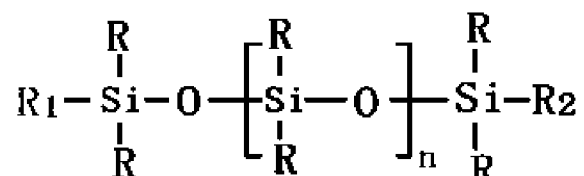
Coating	25°C	100°C	150°C	200°C
Comp. 8	3.16	2.56	2.65	3.12
Ex. 5	6.47	5.16	4.84	3.17
Ex. 6	6.87	5.68	4.26	3.34
Ex. 7	8.33	6.23	4.33	3.68
Ex. 8	7.65	5.00	3.52	3.05
Comp. 7	5.68	4.71	1.70	0.85

[0198] Wherein particular examples of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the invention as defined in the appended claims. This application is therefore intended to cover any variations, uses, or adaptations of the disclosure using its general principles. Further, this application is intended to cover such departures from the present disclosure as come within known or customary practice in the art to which this disclosure pertains and which fall within the limits of the appended claims.

CLAIMS

What is claimed is:

1. A method of forming a coating composition, comprising:
hydrolyzing and condensing at least two different siloxane monomers, an acid catalyst, and colloidal silica to form an organosilica sol, the siloxane monomers of the following formula:
$$R_xSi(OR')_{4-x}$$
wherein:
R is a linear, branched, or cyclic alkyl or aryl group with up to 10 carbon atoms;
R' is linear, branched, or cyclic alkyl group with up to 5 carbon atoms; and
x is 1, 2 or 3; and
combining the organosilica sol with:
a silicone polyester resin; and
a silicone oil.
2. The method of claim 1, wherein the organosilica sol comprises aryl groups, the aryl to alkyl molar ratio ranging from 0.1 to 3.0.
3. The method of claim 1 or claim 2, wherein the organosilica sol has a molecular weight (Mw) of from 2,000 to 5,000 Daltons, as determined by GPC chromatography using polystyrene standards.
4. The method of any one of claims 1-3, wherein in the hydrolyzing and condensing step, a molar ratio of water to the alkoxy (OR') groups of the siloxane monomers is less than 1.
5. The method of any one of claims 1-4, wherein the hydrolyzing and condensing step is conducted at a pH from 2 to 5.
6. The method of any one of claims 1-5, wherein the organosilica sol has a water content of less than 2.5 wt. %, based on the total weight of organosilica sol.
7. The method of any one of claims 1-6, wherein the silicone oil is of the following formula:



wherein:

R is methyl or phenyl;

R₁ is hydride, hydroxide or trimethyl silyl; and

n is from 3 to 600.

8. The method of any one of claims 1-7, wherein the silicone oil has a viscosity from 50 cP to 5,000 cP as measured using a Brookfield rotational viscometer according to ASTM D2983-09.

9. The method of any one of claims 1-8, wherein the siloxane monomers comprise methyltrimethoxy silane and phenyltrimethoxy silane.

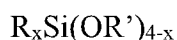
10. The method of any one of claims 1-9, wherein the coating composition comprises less than 5 wt. % of fluorine-containing components, based on a total weight of the coating composition.

11. A coating composition, comprising:

a silicone polyester resin;

a silicone oil;

an organosilica sol comprising the hydrolysis and condensation reaction product of at least two different siloxane monomers, an acid catalyst, and colloidal silica, the siloxane monomers of the following formula:



wherein:

R is a linear, branched, or cyclic alkyl or aryl group with up to 10 carbon atoms;

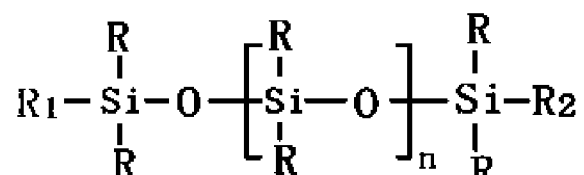
R' is a linear, branched, or cyclic alkyl group with up to 5 carbon atoms; and

x is 1, 2 or 3; and

a liquid medium.

12. The coating composition of claim 11, wherein the organosilica sol comprises aryl groups, the aryl to alkyl molar ratio ranging from 0.1 to 3.0.

13. The coating composition of claim 11 or claim 12, wherein the organosilica sol has a water content of less than 2.5 wt. %, based on the total weight of organosilica sol.
14. The coating composition of any one of claims 11-13, wherein the coating composition comprises at least one of:
- 10 to 70 wt.% silicon polyester resin, based on a total weight of the coating composition;
 - 0.1 to 10 wt.% silicon oil, based on a total weight of the coating composition; and
 - 10 to 90 wt.% organosilica sol, based on a total weight of the coating composition.
15. The coating composition of any one of claims 10-14, wherein the siloxane monomers comprise methyltrimethoxy silane and phenyltrimethoxy silane.
16. The coating composition of any one of claims 10-15, wherein the silicone oil is of the following formula:



wherein:

R is methyl or phenyl;

R₁ is hydride, hydroxide or trimethyl silyl; and

n is from 3 to 600.

17. The coating composition of claim 16, wherein the silicone oil has a viscosity of 50 to 5000 cP as measured using a Brookfield rotational viscometer according to ASTM D2983-09.
18. The coating composition of any one of claims 11-17, wherein the coating composition comprises less than 5 wt. % of fluorine-containing components, based on a total weight of the coating composition.
19. The coating composition of any one of claims 11-18, wherein the coating composition has a storage stability of 3 to 5 months as determined by ASTM D869-21.
20. An article comprising a coating, the coating comprising a cured composition of the coating composition of any one of claims 11-19.

21. The article of claim 20, wherein the cured composition comprises at least one of the following:

10 to 70 wt.% of silicone polyester resin, based on a total weight of the coating composition;

1 to 40 wt.% of silicone oil, based on a total weight of the coating composition; and

10 to 90 wt.% of organosilica sol, based on a total weight of the coating composition.

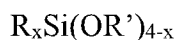
22. The article of any one of claims 19-21, wherein the coating composition has at least one of the following:

a pencil hardness of 5H to 9H at 23°C, according to ASTM D 3363; and

a pencil hardness of 3H to 9H at 25°C-200°C, according to ASTM D 3363.

23. A method of coating an article with a coating composition, comprising:

applying, over a substrate, a coating composition comprising an organosilica sol, a silicone polyester resin, and a silicone oil, wherein the organosilica sol comprises the hydrolysis and condensation reaction product of at least two different siloxane monomers, an acid catalyst, and colloidal silica, the siloxane monomers of the following formula:



wherein:

R is a linear, branched, or cyclic alkyl or aryl group with up to 10 carbon atoms;

R' is a linear, branched, or cyclic alkyl group with up to 5 carbon atoms; and

x is 1, 2 or 3; and

curing the coating composition at a temperature from 100°C to 450°C.

24. The method of claim 23, wherein the organosilica sol comprises aryl groups, the aryl to alkyl molar ratio ranging from 0.1 to 3.0.

25. The method of claim 23 or claim 24, wherein the organosilica sol has a water content of less than 2.5 wt. %, based on the total weight of organosilica sol.

26. The method of any one of claims 23-25, further comprising applying an overcoat over the coating composition, the overcoat comprising an organosilica sol and a silicone oil.

27. The method of any one of claims 22-26 further comprising applying a phosphate conversion layer over the substrate prior to applying the coating composition over the substrate.
28. The method of any one of claims 22-27, wherein the coating composition comprises less than 5 wt. % of fluorine-containing components, based on a total weight of the coating composition.

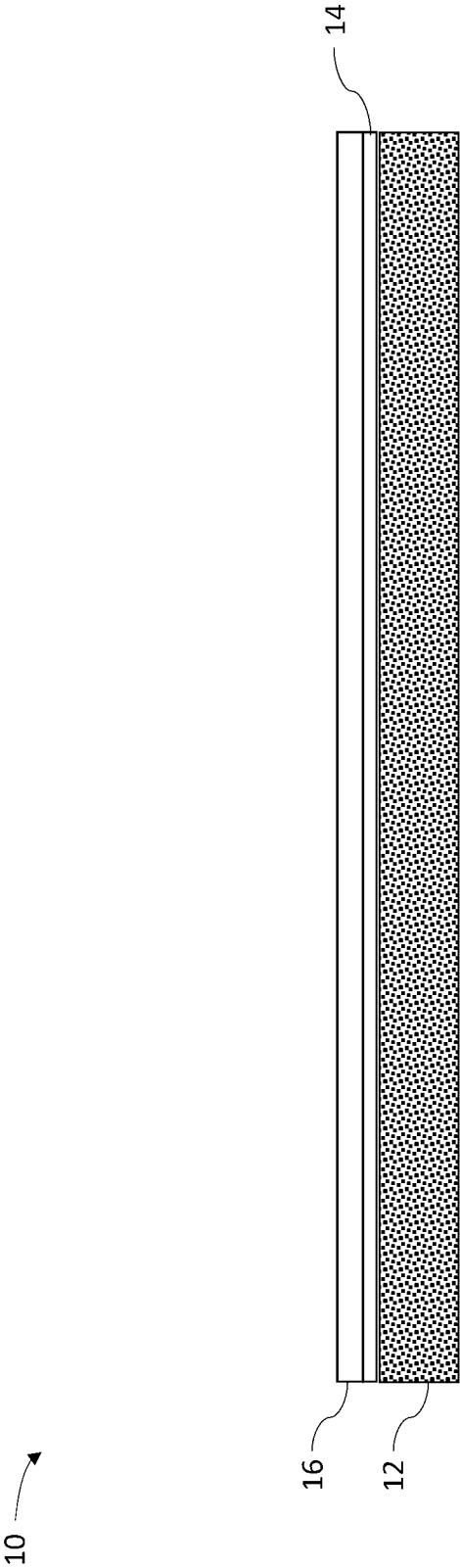


FIG. 1

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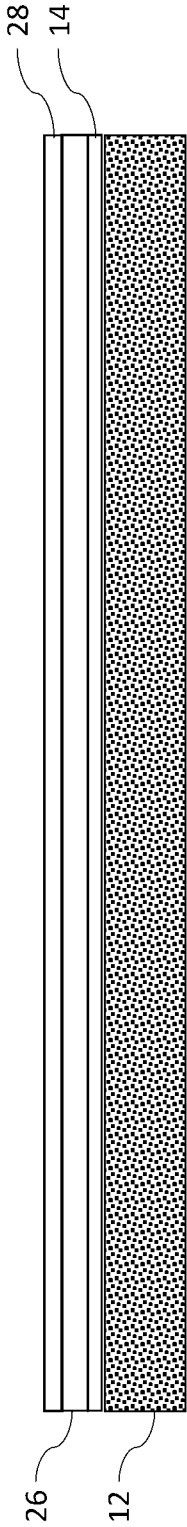


FIG. 2

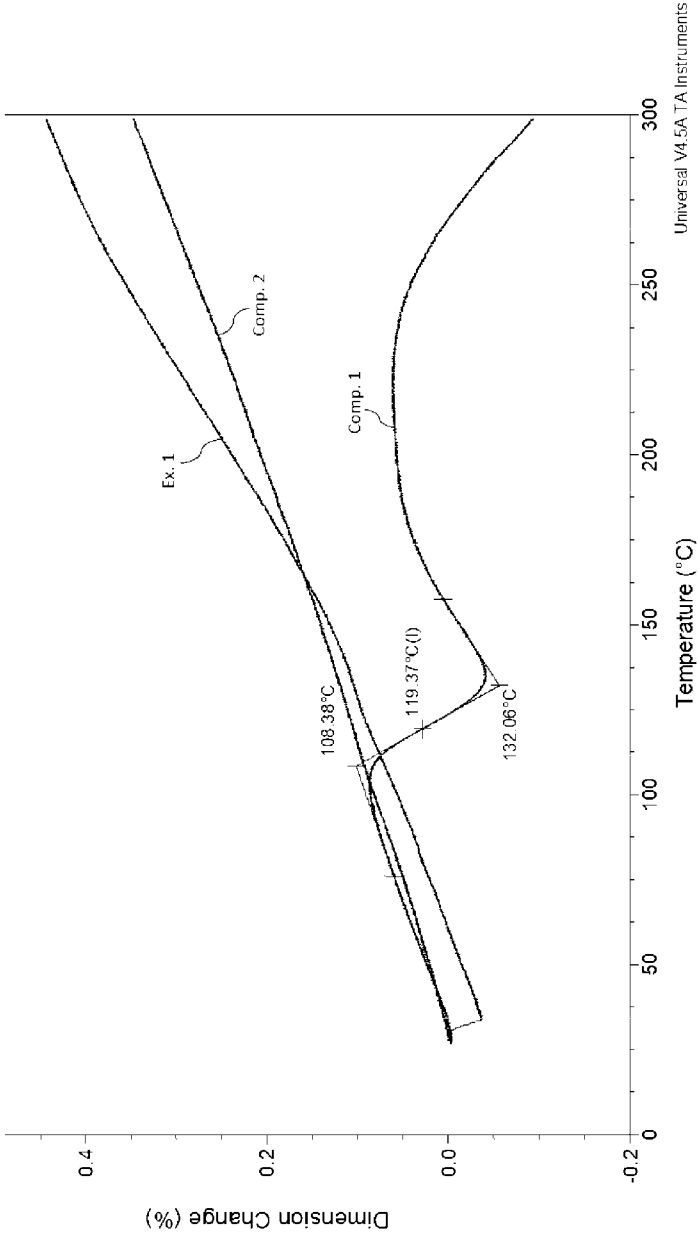


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No

PCT/CN2023/095496

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D183/04 C09D183/10
ADD.

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)

C08G 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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 9 096 777 B2 (BOCKMEYER MATTHIAS [DE]; RUDIGIER-VOIGT EVELINE [DE] ET AL.) 4 August 2015 (2015-08-04) column 2, line 14 - column 4, line 47 examples 4-6 -----	1-28
A	US 2017/020331 A1 (BERRUX AURELIEN [FR]) 26 January 2017 (2017-01-26) paragraphs [0001], [0011] - [0015] paragraphs [0050] - [0056] paragraphs [0069] - [0083] examples 7, 8 -----	1-28
A	US 2020/308406 A1 (SEYFRIED MONA [DE] ET AL) 1 October 2020 (2020-10-01) paragraphs [0143] - [0146] paragraphs [0186] - [0200] -----	1-28

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search

6 November 2023

Date of mailing of the international search report

14/11/2023

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/CN2023/095496

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