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(54) **ANTICORROSION MATERIAL**

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(57) **ABSTRACT**

An anticorrosion material comprising colloidal particles and multivalent metal ions is disclosed. The particles are preferably silica. The metal ions may be Al, Ga, Ti, Zr, Hf, Zn, Mg, Ca, Nb, Ta, Fe, Cu, Sn, Co, W or Ce. The material can be added to a conversion coating liquid, mixed with a polymeric binder or used as such to form a coating.

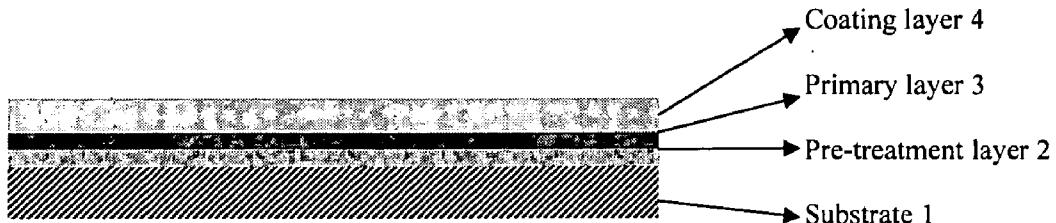
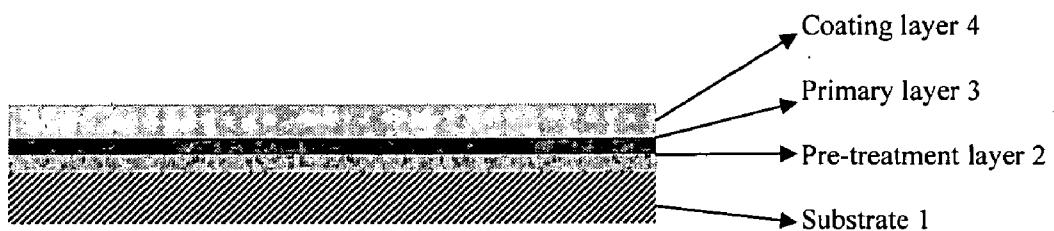


FIG. 1

ANTICORROSION MATERIAL

FIELD OF THE INVENTION

[0001] The present invention is directed to anticorrosion material, compositions, formulations including the anticorrosion composition, and methods of making the anticorrosion composition.

BACKGROUND OF THE INVENTION

[0002] There is a need in the metal treatment and coatings industry for anticorrosion compositions and formulations having good corrosion resistance, and being free of toxic metals while maintaining other desirable film properties, such as adhesion, strength, anti-corrosion performance, thin film thickness, etc. There is also a need in the art for methods of making and using the anticorrosion compositions and formulations.

SUMMARY OF THE INVENTION

[0003] The present invention addresses some of the difficulties and problems discussed above by the discovery of new anticorrosion compositions, formulations and films prepared therefrom. The composition includes two nano-sized metal oxide particles in combination with divalent and trivalent metal ions.

[0004] In an exemplary embodiment, an anticorrosion composition of the present invention comprises a solvent; colloidal particles; and at least one multivalent metal ion present in an amount of at least about 0.001% up to about 10% by weight based on the total weight of the composition.

[0005] In a further exemplary embodiment, an anticorrosion composition of the present invention comprises a solvent; colloidal particles; and at least one multivalent metal ion, wherein the composition remains stable for at least 60 minutes at 60° C. or at least 8 hours at 25° C.

[0006] In an even further exemplary embodiment, an anticorrosion composition of the present invention comprises a solvent; colloidal particles; and at least one multivalent metal ion, wherein the ratio of metal ion to metal oxide is greater than about 0.001 up to about 0.1. The ratio of multivalent metal ion to colloidal particle may be at least about 0.005, preferably at least about 0.008, more preferably at least about 0.01, and even more preferably at least about 0.01 to about 0.1.

[0007] The present invention is further directed to methods of forming the exemplary anticorrosion compositions. One exemplary method comprises forming a dispersion of colloidal metal oxide particles in water including the steps of adding up to 40 wt % metal oxide particles to water, wherein the weight percent is based on a total weight of the dispersion; adding a multivalent metal salt to the dispersion and then mixing the composition. The resulting dispersion desirably has a stable viscosity for at least 60 minutes at 60° C. or at least 8 hours at 25° C.

[0008] In another exemplary embodiment, an anticorrosion formulation of the present invention comprises a binder; a solvent; colloidal particles; and at least one multivalent metal ion, wherein the ratio of metal ion to metal oxide is greater than about 0.001 up to about 0.1. The ratio of multivalent metal ion to colloidal particle may be at least about 0.005, preferably at least about 0.008, more preferably at least about 0.01, and even more preferably at least about 0.01 to about 0.1.

[0009] In a further exemplary method of using the anticorrosion formulation, the method comprises a method of forming a coated substrate comprising the steps of providing a substrate having a first surface; coating the formulation onto the first surface of the substrate; and drying the coated substrate. The resulting coating provides the substrate with desirable anticorrosion resistance that is particularly useful in corrosive environments.

[0010] In one exemplary embodiment, a corrosion resistant material of the present invention comprises a substrate; and an anticorrosion coating on the substrate having colloidal particles; and at least one multivalent metal ion, wherein the ratio of metal ion to metal oxide is greater than about 0.001 up to about 0.1. The ratio of multivalent metal ion to colloidal particle may be at least about 0.005, preferably at least about 0.008, more preferably at least about 0.01, and even more preferably at least about 0.01 to about 0.1.

[0011] These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

BRIEF DESCRIPTION OF THE FIGURE

[0012] FIG. 1 depicts a cross-sectional view of the exemplary article of the present invention, wherein the exemplary article comprises at least one layer containing anticorrosion material of this invention.

DETAILED DESCRIPTION OF THE INVENTION

[0013] To promote an understanding of the principles of the present invention, descriptions of specific embodiments of the invention follow and specific language is used to describe the specific embodiments. It will nevertheless be understood that no limitation of the scope of the invention is intended by the use of specific language. Alterations, further modifications, and such further applications of the principles of the present invention discussed are contemplated as would normally occur to one ordinarily skilled in the art to which the invention pertains.

[0014] The present invention is directed to anticorrosion coatings and formulations and dispersions suitable for making anticorrosion coatings. The present invention is further directed to methods of making anticorrosion materials, as well as methods of using such materials. A description of exemplary anticorrosion materials, coatings, formulations and dispersions for making anticorrosion materials, and methods of making anticorrosion materials, coatings, formulations and dispersions are provided below.

[0015] The anticorrosion compositions and formulations of the present invention have good corrosion resistance, and are free of toxic metals while still maintaining other desirable film properties, such as adhesion, strength, thin film thickness, anti-corrosion performance, etc.

[0016] In an exemplary embodiment, an anticorrosion composition of the present invention comprises a solvent; colloidal particles; and at least one multivalent metal ion present in an amount of at least about 0.001% up to about 5% by weight based on the total weight of the composition. The multivalent metal ion may be present in the composition in an amount of about 0.1% by weight up to about 4%, preferably from about 0.1% up to about 3% by weight, more preferably from about 0.1% up to about 2% by weight, and even more preferably from about 0.1% up to about 1% by weight based

upon the total weight of the composition of which contains 20-40% solids. Depending on the solids content, the above-mentioned amount of multivalent metal ion in the composition may either increase or decrease as the solids content increases or decreases, respectively.

[0017] In an even further exemplary embodiment, an anticorrosion composition of the present invention comprises a solvent; colloidal particles; and at least one multivalent metal ion, wherein the ratio of metal ion to colloidal particle may be greater than about 0.001 up to about 0.1. The ratio of multivalent metal ion to colloidal particle may be at least about 0.005, preferably at least about 0.008, more preferably at least about 0.01, and even more preferably at least about 0.01 to about 0.1.

[0018] The particles may be composed of metal oxides, sulfides, hydroxides, carbonates, silicates, phosphates, etc., but are preferably metal oxides. As used herein, "metal oxides" is defined as binary oxygen compounds where the metal is the cation and the oxide is the anion. The metals may also include metalloids. Metals include those elements on the left of the diagonal line drawn from boron to polonium on the periodic table. Metalloids or semi-metals include those elements that are on this line. Examples of metal oxides include silica, alumina, titania, zirconia, etc., and mixtures thereof. The particles may be a variety of different symmetrical, asymmetrical or irregular shapes, including chain, rod or lath shape. The particles may have different structures including amorphous or crystalline, and may be in various forms, such as gels, sols, precipitates, fumed, etc. The particles may include mixtures of particles comprising different compositions, sizes, shapes or physical structures, or that may be the same except for different surface treatments. Preferably, the metal oxide particles are amorphous, such as, for example, colloidal silica.

[0019] By the term "colloidal particles" or "colloidal sol" it is meant particles originating from dispersions or sols in which the particles do not settle from dispersion over relatively long periods of time. Such particles are typically below one micron in size. Colloidal sols having an average particle size in the range of about 1 to about 300 nanometers and processes for making the same are well known in the art. See U.S. Pat. Nos. 2,244,325; 2,574,902; 2,577,484; 2,577,485; 2,631,134; 2,750,345; 2,892,797; 3,012,972; and 3,440,174, the contents of which are incorporated herein by reference. Colloidal sols having average particle sizes in the range of 5 to 100 nanometers are more preferred for this invention. Colloidal sols may have a specific surface area (as measured by BET nitrogen adsorption) in the range of 9 to about 2700 m^2/g SiO_2 .

[0020] Even though many types of colloidal sols may be utilized in the anticorrosion composition of the present invention, the following describes an exemplary colloidal silica sol. Most colloidal silica sols contain an alkali to stabilize the silica particles from aggregation or gelation. The alkali is usually an alkali metal hydroxide the alkali metals being from Group IA of the Periodic Table (hydroxides of lithium, sodium, potassium, etc.) Most commercially available colloidal silica sols contain sodium, which originates, at least partially, from the sodium silicate used to make the colloidal silica, although sodium hydroxide may also be added to stabilize the sol against gelation. Some alkaline colloidal silica sols are stabilized with aqueous ammonia. Such alkaline colloidal silica sols are not suitable to this invention. Most multivalent metal ions suitable to this invention form insoluble

metal hydroxides in alkaline solutions, limiting the processing of the anticorrosive formulation. Acidifying the alkaline colloidal silica sol with, e.g., a mineral or organic acid is disadvantageous because the resulting alkali metal salt will reduce the stability of the colloidal silica sol and anticorrosion composition of this invention and additionally may be deleterious to the anticorrosive performance of the coating.

[0021] Deionized colloidal silica sols are suitable for this invention. By "deionized," it is meant that any metal ions, e.g., alkali metal ions such as sodium, have been essentially removed from the colloidal silica solution phase and have been replaced with hydronium (H_3O or H^+) or acid ions. Methods to remove alkali metal ions are well known and include ion exchange with a suitable ion exchange resin (U.S. Pat. Nos. 2,577,484 and 2,577,485), dialysis (U.S. Pat. No. 2,773,028) and electrodialysis (U.S. Pat. No. 3,969,266).

[0022] To impart stability of the colloidal silica sol against gelation at acidic pH, the particles may also be surface modified with aluminum as described in U.S. Pat. No. 2,892,797 (the contents therein incorporated herein by reference), and then the modified silica is deionized.

[0023] As defined herein, the term "multivalent metal ion" means metal ions that possess a valence of two or three. Examples of the multivalent metal ions include, but are not limited to, Al, Ga, Ti, Zr, Hf, Zn, Mg, Ca, Nb, Ta, Fe, Cu, Sn, Co, W, Ce, Ba, Mn, Mo, V and the like.

[0024] In an exemplary embodiment of the present invention, the solids content (or amount of colloidal particles) of the anticorrosion composition ranges from about 1 to about 40 wt %, preferably from about 1 to about 30 wt %, more preferably from about 1 to about 25 wt %, and even preferably from about 1 to about 20 wt %, based on the total weight of the composition.

[0025] In a further exemplary embodiment, an anticorrosion composition of the present invention comprises a solvent; colloidal particles; and at least one multivalent metal ion, wherein the composition remains stable for at least 60 minutes at 60° C. or at least 120 minutes at 60° C. The composition typically may remain stable for at least about 3 hours at 60° C., preferably at least about 6 hours at 60° C., more preferably at least about 12 hours at 60° C., and even more preferably at least about 24 hours at 60° C. The composition typically may remain stable for at least about 24 hours at 25° C., preferably at least about 2 days at 25° C., more preferably at least about 4 days at 25° C., and even more preferably at least about 8 days at 25° C. As defined herein the term "stable" means a dispersion of particles that does not gel over time.

[0026] The anticorrosion composition of the present invention may be prepared by mixing colloidal particles with a solvent and multivalent metal ion in the form of a salt. The solvent may be any solvent that is compatible with the colloidal particles and multivalent metal ion salt. Water is a preferred solvent but mixtures of water and water miscible organic solvents may be used (e.g., methanol, ethanol, propanol, acetone, etc.). Useful multivalent metal ion salts are those which have a multivalent metal ion and a multifunctional soluble anion. Preferably, the anion does not promote metal corrosion. Examples of such anion include, but are not limited to, nitrates, nitrites, lactates, phosphates, hydrogen phosphates, sulfates, molybdates or mixtures thereof.

[0027] Mixing may be accomplished by conventional mixing and blending equipment common to laboratory or industrial processes. High shear mixers may be used but are not

necessary. Because concentrated solutions of the multivalent metal ion salt solution can cause gelation of the colloidal particles on contact, the multivalent metal ion salt solution should be as dilute as possible to achieve the target metal ion to colloidal particle ratio and total solids level of the anticorrosion formulation. Typically, this can be accomplished with solutions containing 0.1-1 mole per liter of the multivalent metal ion, preferably 0.1-0.5 mole per liter of the multivalent metal ion.

[0028] In a further exemplary method of using the anticorrosion formulation, the method comprises a method of forming a coated substrate comprising the steps of providing a substrate having a first surface; coating the formulation onto the first surface of the substrate; and drying the coated substrate. The resulting coating provides the substrate with desirable anticorrosion resistance that is particularly useful in corrosive environments. The dispersions may be used to coat a surface of a variety of substrates including, but not limited to, a metal substrate, a surface treated metal substrate, a metal substrate having a pretreatment layer or other layer thereon, a metal composite substrate, or any other substrate that requires corrosion resistance, and combinations thereof. The resulting coated substrate may be used in a number of applications including, but not limited to, chemical conversion applications, direct painting applications, etc.

[0029] In another exemplary embodiment, an anticorrosion composition of the present invention comprises a binder. In this embodiment, a binder is utilized to provide desirable film properties upon application to a substrate.

[0030] The anticorrosion composition may be incorporated in conventional coating binders to form an anticorrosion coating. The binder not only acts to bind the colloidal particles and to form a film, it also provides adhesiveness to the interface between the coating and the substrate or any intermediate layer between the anticorrosion coating and substrate.

[0031] Water-soluble or water-compatible binders such as latexes are particularly suitable in the present invention and may, for example, be epoxy, polyester, polypropylene, polyethylene, acrylic silicone, polyurethane, polyamine, acrylic emulsion, polyvinyl butyral, etc. Other suitable binders include starch derivatives such as oxidized starch, a etherified starch or phosphate starch; a cellulose derivative such as carboxymethyl cellulose or hydroxymethyl cellulose; casein, gelatin, soybean protein, polyvinyl alcohol or a derivative thereof; polyacrylates; vinyl alcohol/acrylamide copolymers; cellulose polymers; starch polymers; isobutylene/maleic anhydride copolymer; vinyl alcohol/acrylic acid copolymer; polyethylene oxide modified products; dimethyl ammonium polydiallylpyridine; and quaternary ammonium polyacrylate, and the like. Suitable materials for forming optional primary layer 3 may include, but are not limited to, polyethylene, polypropylene, polyesters, and other polymeric materials. Substrate 1 may be composed of a variety of materials that corrode over time such as any metal or metalloid.

vinyl chloride-vinyl acetate copolymer, polyvinyl butyral or an alkyd resin; or mixtures thereof may also be used.

[0032] The binder may be combined with the anticorrosion composition using conventional blenders and mixers. The components may be combined and mixed at ambient conditions.

[0033] In an exemplary embodiment of the present invention, the solids content (or amount of colloidal particles and binder) of the anticorrosion composition ranges from about 1 to about 50 wt %, preferably from about 1 to about 30 wt %, more preferably from about 1 to about 25 wt %, and even preferably from about 1 to about 20 wt %, based on the total weight of the composition. Colloidal particles and binder solids may be present in the coating formulation at a ratio of at least 1:1, and more preferably 6:4 to 4:1 by weight. The ratio can be as high as 9.9:1.

[0034] It may also be desirable to include additional components in the coating composition of this invention. The coating of this invention can contain one or more of the following: dispersant, thickener, fluidity-improving agent, defoaming agent, foam-suppressing agent, release agent, blowing agent, penetrating agent, coloring dye, coloring pigment, fluorescent brightener, ultraviolet absorber, anti-oxidant, preservative, waterproofing agent, etc.

[0035] In one exemplary embodiment, a corrosion resistant material of the present invention comprises a substrate; and an anticorrosion coating on the substrate having colloidal particles; and at least one multivalent metal ion, wherein the weight ratio of metal ion to metal oxide is greater than about 0.001 up to about 0.1. The ratio of multivalent metal ion to colloidal particle may be at least about 0.005, preferably at least about 0.008, more preferably at least about 0.01, and even more preferably at least about 0.01 to about 0.1. An exemplary coated substrate is provided in FIG. 1.

[0036] As shown in FIG. 1, exemplary coated substrate 1 comprises thin pre-treatment layer 2, a primary layer 3, a top coating layer 4. All layers may comprise the anticorrosion composition of the present invention, although typically top coating layer 4 does not contain this composition. Preferably, the pre-treatment layer 2 includes the anticorrosion composition of the present invention. Suitable binder materials for forming the thin pre-treatment layer 2 may include, but are not limited to, water absorptive materials such as polyacrylates; vinyl alcohol/acrylamide copolymers; cellulose polymers; starch polymers; isobutylene/maleic anhydride copolymer; vinyl alcohol/acrylic acid copolymer; polyethylene oxide modified products; dimethyl ammonium polydiallylpyridine; and quaternary ammonium polyacrylate, and the like. Suitable materials for forming optional primary layer 3 may include, but are not limited to, polyethylene, polypropylene, polyesters, and other polymeric materials. Substrate 1 may be composed of a variety of materials that corrode over time such as any metal or metalloid.

[0037] In a further exemplary embodiment of the present invention, the anticorrosion composition may be used in a method of making a treated or coated anticorrosion material. In one exemplary method, the method of making the material comprises the steps of providing a substrate having a first surface; and applying the anticorrosion composition onto the first surface of the substrate, which forms an anticorrosion coating layer thereon. The coating layer may be subsequently dried to form a coated substrate. The coated substrate may be used to form a pre-treated anti-corrosive substrate. In one exemplary method of the present invention, the anticorrosion

material may be utilized in chemical conversion coating and thin painting surface treatment.

EXAMPLES

[0038] The present invention is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

Example 1

[0039] Three colloidal silica sols are prepared:
 [0040] Sol 1. 22 nm particles, ammonia stabilized, pH~9;
 [0041] Sol 2. 22 nm particles, alkaline (pH~9) containing sodium ion
 [0042] Sol 3. 22 nm particles, stabilized with aluminate according to the method disclosed in U.S. Pat. No. 2,892,797 and deionized to pH 4; and
 [0043] Sol 4. 12 nm particles, stabilized with aluminate according to U.S. Pat. No. 2,892,797 and deionized to pH 4.
 [0044] A mixture of 0.5M $\text{Ca}(\text{NO}_3)_2$ and water is added to each of these sols with agitation such that the samples contained 20% SiO_2 and Ca/SiO_2 weight ratio is 0.005, 0.01, 0.02 and 0.03. Observation of these samples at room temperature over an 8-day period are as follows:
 [0045] Samples made from Sol 1 and Sol 2 gelled almost immediately, showing that alkaline sols cannot be used. Samples made from Sol 3 are stable at ratio=0.005 for the length of the test. All other Sol 3 samples gelled after 5 days. Samples made from Sol 4 are stable at ratios 0.005 and 0.01 for the length of the test. At ratio of 0.02, the sample gelled after 8 days and at ratio of 0.03, the sample gelled after 1 day. This shows that colloidal particle size plays a significant role on formulation stability and the choice should be made based on the needed stability and anticorrosion performance.

Example 2

[0046] Calcium lactate (0.57M) solution is added to Sol 4 of Example 1 to make a sample with Ca/SiO_2 weight ratio of 0.03 and containing 20 weight % SiO_2 . This sample gelled after 7 days at room temperature. This shows that this calcium compound may also be used.

Example 3

[0047] This experiment shows that suitably selected metal ions work with SiO_2 to give better anti-corrosion performance in chemical conversion coatings on galvanized steel and galvalume steel, compared to using colloidal silica alone. Sol 3 of Example 1 is used for all samples, all of which are adjusted to about pH 1.5 to 2 with phosphoric acid (H_3PO_4).

[0048] Sample 1: Sol 3 20% SiO_2 adjusted to pH~2 with phosphoric acid having no multivalent metal ion.

[0049] Sample 2: A mixture of Sol 3, calcium hydrogen phosphate (CaHPO_4) and phosphoric acid containing 20% SiO_2 , and Ca/SiO_2 weight ratio=0.03 at pH~2.

[0050] Sample 3: A mixture of Sol 3, vanadium in the 4+ oxidation state (V^{4+}) prepared by reduction of vanadium pen-

toxide (V_2O_5) by conventional means, and phosphoric acid containing 20% SiO_2 , a V/SiO_2 weight ratio=0.06 and pH~1.5.

[0051] Sample 4: A mixture of Sol 3, vanadium in 4+ oxidation state (V^{4+}) prepared by reduction of vanadium pentoxide (V_2O_5) by conventional means, and phosphoric acid containing 20% SiO_2 , a V/SiO_2 weight ratio=0.03 and pH~1.5.

[0052] These samples are added to a conventional chemical conversion solution such that the treating composition contained 1-5% solids and exhibited pH 1 to 3. Galvanized and galvalume substrates are cleaned with 1-3% alkaline solution at 50-80° C. for 30-120 seconds, water washed, then treated with the chemical conversion solutions containing the samples 1 to 4 as set forth above at pH 3-4.5 for 30-90 seconds. Sample solids content is about 1-5%. This treatment deposits an anticorrosion layer on the substrate. The results set forth in Table 1 indicate that the substrates treated with the anticorrosion composition (i.e., with multivalent metal ions) of the present invention perform significantly better than the substrates treated without multivalent metal ions.

TABLE 1

Sample	Element content in treated layer				Anti-corrosion performance	
	SiO_2	Ca	V	P	Galvanized	Galvalume
1	99.4	—	—	0.6	2	1
2	91.2	2.2	—	6.7	3	1
3	95.3	—	4.6	0.1	3	3
4	97.0	—	2.4	0.6	3	3

Note:

3 - good;
 2 - intermediate;
 1 - poor

[0053] It must be noted that as used herein and in the appended claims, the singular forms "a", "and", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "an oxide" includes a plurality of such oxides and reference to "oxide" includes reference to one or more oxides and equivalents thereof known to those skilled in the art, and so forth.

[0054] "About" modifying, for example, the quantity of an ingredient in a composition, concentrations, volumes, process temperatures, process times, recoveries or yields, flow rates, and like values, and ranges thereof, employed in describing the embodiments of the disclosure, refers to variation in the numerical quantity that can occur, for example, through typical measuring and handling procedures; through inadvertent error in these procedures; through differences in the ingredients used to carry out the methods; and like proximate considerations. The term "about" also encompasses amounts that differ due to aging of a formulation with a particular initial concentration or mixture, and amounts that differ due to mixing or processing a formulation with a particular initial concentration or mixture. Whether modified by the term "about" the claims appended hereto include equivalents to these quantities.

[0055] While the invention has been described with a limited number of embodiments, these specific embodiments are not intended to limit the scope of the invention as otherwise described and claimed herein. It may be evident to those of ordinary skill in the art upon review of the exemplary embodiments herein that further modifications, equivalents, and variations are possible. All parts and percentages in the

examples, as well as in the remainder of the specification, are by weight unless otherwise specified. Further, any range of numbers recited in the specification or claims, such as that representing a particular set of properties, units of measure, conditions, physical states or percentages, is intended to literally incorporate expressly herein by reference or otherwise, any number falling within such range, including any subset of numbers within any range so recited. For example, whenever a numerical range with a lower limit, R_L , and an upper limit R_U , is disclosed, any number R falling within the range is specifically disclosed. In particular, the following numbers R within the range are specifically disclosed: $R=R_L+k(R_U-R_L)$, where k is a variable ranging from 1% to 100% with a 1% increment, e.g., k is 1%, 2%, 3%, 4%, 5% . . . 50%, 51%, 52% . . . 95%, 96%, 97%, 98%, 99%, or 100%. Moreover, any numerical range represented by any two values of R , as calculated above is also specifically disclosed. Any modifications of the invention, in addition to those shown and described herein, will become apparent to those skilled in the art from the foregoing description and accompanying drawings. Such modifications are intended to fall within the scope of the appended claims. All publications cited herein are incorporated by reference in their entirety.

What is claimed is:

1. An anticorrosion composition comprising:
solvent;
colloidal particles; and
at least one multivalent metal ion, wherein the weight ratio of metal ion to colloidal particle is greater than about 0.001 up to about 0.1.
2. The anticorrosion composition according to claim 1, wherein said colloidal particles comprise silica, alumina, titania, zirconia, or mixtures thereof.
3. The anticorrosion composition according to claim 1, wherein said colloidal particles comprise silica.
4. The anticorrosion composition according to claim 1, wherein said multivalent metal ion comprises Al, Ga, Ti, Zr, Hf, Zn, Mg, Ca, Nb, Ta, Fe, Cu, Sn, Co, W, Ce, or mixtures thereof.
5. The anticorrosion composition according to claim 1, wherein said multivalent metal ion comprises Sn, Zn, Ca, or mixtures thereof.
6. The anticorrosion composition according to claim 1, wherein said weight ratio is greater than about 0.005 up to about 0.08.
7. The anticorrosion composition according to claim 1, wherein said weight ratio is greater than about 0.01 up to about 0.05.
8. An anticorrosion composition comprising:
solvent;
colloidal particles; and
at least one multivalent metal ion present in an amount of at least about 0.001% up to about 4% % by weight based on the total weight of the composition.
9. The anticorrosion composition according to claim 8, wherein said colloidal particles comprise silica, alumina, titania, zirconia, or mixtures thereof.
10. The anticorrosion composition according to claim 8, wherein said colloidal particles comprise silica.
11. The anticorrosion composition according to claim 8, wherein said multivalent metal ion comprises Al, Ga, Ti, Zr, Hf, Zn, Mg, Ca, Nb, Ta, Fe, Cu, Sn, Co, W, Ce, or mixtures thereof.
12. The anticorrosion composition according to claim 8, wherein said multivalent metal ion comprises Sn, Zn, Ca, or mixtures thereof.
13. The anticorrosion composition according to claim 8, wherein said at least one multivalent metal ion present in an amount of at least about 0.005 wt % up to about 3 wt % by weight based on the total weight of the composition.
14. The anticorrosion composition according to claim 8, wherein said at least one multivalent metal ion present in an amount of at least about 0.01% up to about 2% by weight based on the total weight of the composition.
15. An anticorrosion composition comprises:
solvent;
colloidal particles; and
at least one multivalent metal ion, wherein the composition remains stable for at least 8 hours at 25° C.
16. The anticorrosion composition according to claim 15, wherein said colloidal particles comprise silica, alumina, titania, zirconia, or mixtures thereof.
17. The anticorrosion composition according to claim 15, wherein said colloidal particles comprise silica.
18. The anticorrosion composition according to claim 15, wherein said multivalent metal ion comprises Al, Ga, Ti, Zr, Hf, Zn, Mg, Ca, Nb, Ta, Fe, Cu, Sn, Co, W, Ce, or mixtures thereof.
19. The anticorrosion composition according to claim 15, wherein said multivalent metal ion comprises Sn, Zn, Ca, or mixtures thereof.
20. The anticorrosion composition according to claim 15, wherein said composition remains stable for at least 10 hours at 25° C.
21. The anticorrosion composition according to claim 15, wherein said composition remains stable for at least 60 minutes at 60° C.
22. An anticorrosion formulation comprises:
binder;
solvent;
colloidal particles; and
at least one multivalent metal ion, wherein the ratio of metal ion to colloidal particles is greater than about 0.001 up to about 0.1.
23. The anticorrosion composition according to claim 22, wherein said colloidal particles comprise silica, alumina, titania, zirconia, or mixtures thereof.
24. The anticorrosion composition according to claim 22, wherein said colloidal particles comprise silica.
25. The anticorrosion composition according to claim 22, wherein said multivalent metal ion comprises Al, Ga, Ti, Zr, Hf, Zn, Mg, Ca, Nb, Ta, Fe, Cu, Sn, Co, W, Ce, or mixtures thereof.
26. The anticorrosion composition according to claim 22, wherein said multivalent metal ion comprises Sn, Zn, Ca, or mixtures thereof.
27. The anticorrosion composition according to claim 22, wherein said weight ratio is greater than about 0.005 up to about 0.08.
28. The anticorrosion composition according to claim 22, wherein said weight ratio is greater than about 0.01 up to about 0.05.

29. A corrosion resistant material comprising:
a substrate; and
an anticorrosion coating on the substrate having colloidal
particles; and at least one multivalent metal ion, wherein
the ratio of metal ion to metal oxide is greater than about
0.001 up to about 0.1.

30. The anticorrosion composition according to claim **29**,
wherein said colloidal particles comprise silica, alumina, tita-
nia, zirconia, or mixtures thereof.

31. The anticorrosion composition according to claim **29**,
wherein said colloidal particles comprise silica.

32. The anticorrosion composition according to claim **29**,
wherein said multivalent metal ion comprises Al, Ga, Ti, Zr,

Hf, Zn, Mg, Ca, Nb, Ta, Fe, Cu, Sn, Co, W, Ce, or mixtures
thereof.

33. The anticorrosion composition according to claim **29**,
wherein said multivalent metal ion comprises Sn, Zn, Ca, or
mixtures thereof.

34. The anticorrosion composition according to claim **29**,
wherein said weight ratio is greater than about 0.005 up to
about 0.08.

35. The anticorrosion composition according to claim **29**,
wherein said weight ratio is greater than about 0.01 up to
about 0.05.

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