

SUBSTANTIALLY NICKEL-FREE PHOSPHATE CONVERSION COATING COMPOSITION AND PROCESS

BACKGROUND OF THE INVENTION

Field of the Invention

5 This invention relates to a composition and process for forming a phosphate conversion coating on active metal surfaces in order to increase the corrosion resistance of the surfaces, either as treated or after subsequent conventional overcoating of the conversion coating layer formed by an organic based protective coating such as a paint or lacquer. A composition according to this invention is well adapted to treating any of a variety of
10 base metals, including at least steel and galvanized steel and aluminum and aluminum based alloys.

Statement of Related Art

A wide variety of phosphate conversion coating compositions and processes are already described in the art. Those believed to be generally considered of highest quality at
15 present include zinc, nickel, and at least one other divalent metal such as manganese in the composition.

DESCRIPTION OF THE INVENTION

In this description, except in the working examples and claims and wherever expressly indicated to the contrary, all numerical specifications of amounts of materials or
20 conditions of reaction or use are to be understood as modified by the term "about" in describing the broadest scope of the invention. Practice of the invention within the numerical limits given is generally preferred.

Object of the Invention

Nickel has been implicated as a carcinogen in some studies, so that avoidance of its use
25 in metal finishing is desirable for health reasons. Nickel is also considered a serious pollutant, and at the levels of 0.5 - 1.5 grams per liter (hereinafter often abbreviated "g/L") at which it is conventionally used, nickel contributes significantly to the cost of the zinc phosphate conversion coating compositions. It is an object of this invention to minimize or eliminate the use of nickel, without worsening the quality of conversion
30 coating obtained with conventional compositions containing zinc, nickel, and manganese.

Summary of the Invention

A working composition according to this invention is an aqueous liquid composition that comprises, preferably consists essentially of, still more preferably consists of, water and:

- (A) from 3 to 50, more preferably from 5 - 20, still more preferably from 13 - 18 g/L of dissolved phosphate ions;
- (B) from 0.2 to 3, or with increasing preference in the order given, from 0.45 to 2.0, 0.57 to 1.24, 0.60 to 0.95, or 0.71 to 0.87, g/L of dissolved Zn^{+2} ions;
- 5 (C) from 1 to 200, or with increasing preference in the order given, from 20 to 100, 24 to 74, or 24 to 60 milligrams per liter ("mg/L") of dissolved Cu^{+2} ions;
- (D) an effective amount of a conventional accelerator exclusive of nitrate ions;
- (E) from 5 to 40, or with increasing preference in the order given, from 7 to 25, 13 to 24, 16 to 22, or 18 to 21 "points" of total acid; and
- 10 (F) from -1.0 to +3.0, or with increasing preference in the order given, from -0.5 to +1.5 or -0.5 to +1.0 points of free acid; for substrates other than aluminum and operating temperatures above 40°C, ranges of 0.0 to 0.8, or better, 0.35 to 0.65 points of free acid are still more preferable; but if operation is at a temperature lower than 40°C or the substrate is aluminum, ranges of -0.5 to 0.0, or better, -0.5 to
15 -0.2, points of free acid are still more preferable; and, optionally,
- (G) up to 2 g/L, preferably from 0.1 to 0.8 g/L, or still more preferably from 0.40 to 0.65 g/L of a total of Mn^{+2} and Co^{+2} ions;
- (H) up to 2 g/L, preferably from 0.5 to 1.0, or still more preferably from 0.70 to 0.80 g/L of Mg^{+2} ions; and, optionally,
- 20 (J) up to 5.5, preferably 1.0 to 4.0, still more preferably from 1.5 to 2.5 g/L of free fluoride as measured by a fluoride sensitive electrode; and, optionally,
- (K) not more than 40, or with increasing preference in the order given, not more than 20 or 11 g/L of SO_4^{-2} ions; and, optionally,
- (L) not more than 4.5, or, with increasing preference in the order given, not more than
25 3.4, 2.0, 1.8, 1.3, or 1.0 g/L of NO_3^- ions.

It is to be understood that the specification of constituents in ionic form herein implies the presence of some counterions of opposite charge if needed to maintain charge neutrality in the composition as a whole.

- "Points" of free acid and total acid are defined for use herein as the number of milliliters
30 (hereinafter "ml") of 0.1 N NaOH solution required to titrate a 10 ml sample of the composition, to a phenolphthalein end point (pH 9.0) for total acid and a bromthymol blue end point (pH 3.8) for free acid, except that if the composition has a pH greater than 3.8 initially, the points of free acid are defined as the negative of the number of ml of 0.1 N strong acid solution required to titrate a 10 ml sample of the composition to a pH of 3.8.

A process according to this invention comprises at a minimum a step of contacting a metal surface to be treated with a composition according to the invention for a sufficient time to form on the metal surface a detectable conversion coating. Conventional metal surface cleaning and/or activation steps before contact between the metal to be treated and compositions according to the invention may be used if desired, and are generally preferred, as part of a process according to this invention. A process according to the invention also may, and usually preferably does, include conventional steps subsequent to the contact between the metal surface to be treated and the compositions according to the invention. These subsequent steps, *e.g.*, may include rinsing with water, any conventional reactive post treatments, *e.g.*, with compositions according to the teachings of U.S. Patent 4,963,596 or with chromate containing solutions, and painting or otherwise protecting the surface with an outer coating of an organic based solid material.

Another embodiment of the invention is a concentrate composition, from which a working composition as defined above can be prepared by dilution with water only, or by dilution with water and addition of an unstable accelerator component such as nitrite ions.

Description of Preferred Embodiments of the Invention

The phosphate ions required for the compositions according to this invention are preferably PO_4^{3-} ions or other ions derivable from less complete ionization of orthophosphoric acid (H_3PO_4). Any free unionized phosphoric acid that may be present is considered part of the content of phosphate ions, to the extent of its stoichiometric correspondence to PO_4^{3-} ions. Other free phosphoric acids such as metaphosphoric acid and condensed phosphoric acids such as pyrophosphoric acid and all anions derivable from them may also be used to supply the necessary phosphate ions. Preferably the phosphate ions are derived from orthophosphoric acid and/or its neutral or acid salts of the metal cations also specified above as part of the compositions according to this invention.

The zinc cations required as part of the compositions are preferably derived from neutral or acid zinc salts of orthophosphoric acid, which may be formed *in situ* by dissolving zinc or zinc oxide or hydroxide in a solution containing the acid.

The cupric cations required as part of the compositions according to this invention may be derived from salts such as cupric sulfate and/or nitrate, or may be obtained by dissolving cupric oxide in part of the phosphoric acid used.

The accelerator component required in compositions according to the invention preferably includes at least one of the following: (i) from 0.01 to 0.2 g/l of nitrite ions, (ii) from 0.5 to 5 g/l of H_2O_2 , (iii) from 0.05 to 2 g/l of m-nitrobenzenesulfonate ions, (iv) from 0.05 to 2 g/l of m-nitrobenzoate ions, (v) from 0.05 to 2 g/l of p-nitro-phenol, and (vi) from 0.1 to 10, more preferably from 0.5 to 6, or still more preferably from 0.5 to 2.0, g/L, measured as

it stoichiometric equivalent as hydroxylamine, of a component capable of furnishing hydroxylamine in water solution. Most preferably, the accelerator is hydroxylamine sulfate (hereinafter often abbreviated "HAS") or a similar safe and readily available source of dissolved hydroxylamine. The second most preferable accelerator is nitrite ions.

- 5 The acidity of the compositions according to the invention is preferably derived from phosphoric, sulfuric, and/or nitric acids.

Part or even all of the free fluoride may be derived from complex fluoride ions such as fluoborate (BF_4^{-3}), fluohafnate (HfF_6^{-2}), fluosilicate (SiF_6^{-2}), fluotitanate (TiF_6^{-2}), fluozirconate (ZrF_6^{-2}), and mixtures thereof; more preferably, from fluoborate and
10 fluosilicate and mixtures thereof. However, simple fluorides such as alkali metal fluorides are also entirely satisfactory sources of free fluoride.

With increasing preference in the order given and with independent preference for each noted component, compositions according to the invention contain no more than 0.5, 0.2, 0.10, 0.07, 0.03, 0.01, 0.005, or 0.001 g/L of each of Ni^{+2} , any cation with a valence of
15 three or higher, chloride ions including complex chloride ions, and chlorate ions. Independently, if chloride ions are present in sufficient quantity to be readily determined analytically, it is preferred that the ratio of the concentration in g/L of complex fluoride ions to the concentration in g/L of chloride ions have a value of at least 8:1, or more preferably a value of at least 14:1.

- 20 In a process according to the invention, contact between the metal surface to be treated and a composition according to the invention may be accomplished by spraying, dipping, or any other convenient method or combination of methods. The temperature during contact between the metal treated and the composition according to the invention preferably is, with increasing preference in the order given, in the range from 21 to 85, 25 to 55, or 31 to
25 44, °C. The total time of contact between the composition according to the invention and the metal surface to be conversion coated preferably is, with increasing preference in the order given, in the range from 5 sec to 15 minutes (hereinafter often abbreviated "min"), 15 seconds (hereinafter often abbreviated "sec") to 10 min, 30 sec to 5 min, or 90 to 120 sec. The add-on mass of the phosphate coating formed preferably is, with increasing preference
30 in the order given, in the range from 1.1 to 5.4, 1.6 to 4.3, or 2.2 to 3.8, grams per square meter (hereinafter "g/m²") of surface treated. The weight percent of copper in the coating formed preferably is, with increasing preference in the order given, from 0.50 to 10, 1.0 to 8.0, 2.0 to 6.0, 3.0 to 4.1.

- Further appreciation of the present invention may be had from considering the following
35 examples and comparative examples which are intended to illustrate, but not limit, the invention.

Composition Examples and Comparison Examples Group 1

These compositions, except for one comparison example, illustrate the use of HAS accelerator. Specific compositions are shown in Table 1 below. These compositions, except for comparison example 13 which was prepared from a commercially compounded concentrate, were prepared according to the following general procedure:

An amount of water equal to about three-quarters of the volume eventually desired for the composition was initially used, and an amount of zinc dihydrogen phosphate sufficient to provide the desired zinc ion concentration in the final desired volume was dissolved in this water. An amount of 75% aqueous solution of orthophosphoric acid that was sufficient, together with the previously added zinc dihydrogen phosphate, to provide the desired final concentration of phosphate ions in the desired final volume was then added. Sufficient amounts of sodium fluoride to provide the desired fluoride ion content, of HAS to provide the desired hydroxylamine content and some sulfate, of cupric sulfate pentahydrate to provide the cupric ion and part of the sulfate ion contents, of manganous nitrate to provide any desired manganese cation content, and of magnesium hydroxide or magnesium nitrate to provide any desired magnesium ion content were then added to the previously prepared solution in any order. Finally, the composition was adjusted with additions of sodium hydroxide solution and additional water as needed to produce the specified free acid and total acid concentrations.

20 Process Examples and Comparison Examples with Compositions of Group I

Test panels of cold rolled steel, galvanized steel, and/or conventional aluminum alloys used in automobile and appliance manufacture were used and subjected to the following general sequence of process steps: (1) Conventional alkaline cleaner for 120 sec at 43°C; (2) Water rinse at 38°C for 60 sec; (3) Conventional colloidal titanium phosphate activator for 30 sec at 38°C; (4) Contact with one of Compositions 1 - 12 from Table 1 below for 120 sec at 35°C or at 43°C; (5) Cold water rinse at 20 - 25°C for 60 sec; (6) Post treatment for 30 sec with a conventional commercial post treatment composition containing hexavalent and trivalent chromium; and (7) Rinse with deionized water for 30 sec at 20 - 25°C.

Table 1

IDENTIFYING NUMBER	POINTS OF:		CONCENTRATION IN g/L OF:								mg/L of Cu ⁺²
	TA	FA	ACC	FREE F	Zn ⁺²	PO ₄ ⁻³	Mn ⁺²	Mg ⁺²	SO ₄ ⁻²	NO ₃ ⁻	
1	19.0	0.5	1.60	0.53	0.94	15	0	0	8.4	1.2	0
2	19.0	0.5	1.60	0.46	0.79	15	0.46	0	9.9	1.1	0
3	19.0	0.5	1.56	0.18	0.64	15	0	0	9.9	1.1	27
4	18.5	0.5	1.60	0.48	0.62	15	0.46	0	8.8	1.0	26
5	18.5	0.5	1.60	0.51	0.71	15	0	0	8.8	1.2	52
6	19.0	0.5	1.60	0.49	0.77	15	0.48	0	8.4	0.95	60
7	18.5	0.5	1.60	0.18	0.87	15	0	0.79	9.2	1.2	0
8	19.3	0.5	1.68	0.16	0.87	15	0.49	0.71	9.2	1.2	0
9	19.5	0.5	1.52	0.16	0.78	15	0	0.77	8.8	1.1	28
10	20.5	0.5	1.60	0.18	0.79	15	0.47	0.72	9.0	1.0	24
11	18.5	0.5	1.56	0.18	0.76	15	0	0.73	9.2	1.3	57
12	19.0	0.5	1.60	0.18	0.62	15	0.47	0.73	11	1.1	55
13		0.6	0.12	0.40	1.1	16	0.66	0	0	0	0

Notes for Table 1

"TA" = total acid; "FA" = free acid; "ACC" - accelerator. The accelerator was nitrite ions for the composition with Identification Number 13 and HAS for all the others. # 13 also contained 1.3 g/L of Ni⁺² and thus is a Zn-Ni-Mn phosphating bath.

Composition and Process Examples Group II

These compositions were prepared in the same general manner as for Group I, except that sodium nitrite instead of HAS was used as the accelerator and cupric nitrate with an average of 2.5 molecules of water of hydration per cupric ion was used as the copper source. Compositions are as follows:

<u>Component</u>	<u>g/L of Component in:</u>	
	<u>Example 14</u>	<u>Example 15</u>
Zn(NO ₃) ₂	4.74	3.6
75% by weight aqueous H ₃ PO ₄	12.4	20.4
Cu(NO ₃) ₂ - 2½ H ₂ O	0.44	0.29
NaF	1.1	1.5
NaNO ₂	0.12	0.11
Mn(NO ₃) ₂	2.3	-
Total Acid Points	17.0	18
Free Acid Points	-0.3	0.4

Example 14 was used for spray phosphating at 33°C in a process sequence otherwise like those of Group I above. Example 14 was used for immersion phosphating at 57°C in a process sequence otherwise like those of Group I above.

10 Benefits of the Invention

Not only were the cost reduction and pollution reduction objectives of the invention achieved, but also there were several unexpected and surprising benefits from the invention, at least in its most preferred embodiments: Improved corrosion resistance, particularly to alkaline corrosion; operation at a lower temperature than for conventional Zn-Ni-Mn phosphating compositions, with at least comparable and sometimes better quality; better adhesion to paint applied over the conversion coatings; and improved coatings on zinciferous surfaces such as galvanized steel.

**CLAIMS**

1. An aqueous liquid composition consisting essentially of water and:
 - (A) from about 3 to about 50 g/L of dissolved phosphate ions;
 - (B) from about 0.2 to about 3 g/L of dissolved Zn^{+2} ions;
 - 5 (C) from about 1 to about 200 mg/L of dissolved Cu^{+2} ions;
 - (D) an effective amount of a conventional accelerator exclusive of nitrate ions;
 - (E) from about 5 to about 40 points of total acid; and
 - (F) from about -1.0 to about +3.0 points of free acid; and, optionally,
 - (G) up to about 2 g/L g/L in total of Mn^{+2} and Co^{+2} ions; and, optionally,
 - 10 (H) up to about 2 g/L of Mg^{+2} ions; and, optionally,
 - (J) up to about 5.5 g/L of free fluoride as measured by a fluoride sensitive electrode; and, optionally,
 - (K) not more than about 40 g/L of SO_4^{-2} ions; and, optionally,
 - (L) not more than about 4.5 g/L of NO_3^- ions; and, optionally,
 - 15 (M) not more than about 0.2 g/L of Ni^{+2} ions.
2. A composition according to claim 1, wherein:
 - (A) the amount of dissolved phosphate ions is from about 5 to about 20 g/L;
 - (B) the amount of dissolved Zn^{+2} ions is from about 0.45 to about 2.0 g/L;
 - (C) the amount of dissolved Cu^{+2} ions is from about 20 to about 100 mg/L;
 - 20 (D) the accelerator includes at least one of (i) from about 0.01 to 0.2 g/l of nitrite ions, (ii) from about 0.5 to about 5 g/l of HO_2O_2 , (iii) from about 0.05 to about 2 g/l of m-nitrobenzenesulfonate ions, (iv) from about 0.05 to about 2 g/l of m-nitrobenzoate ions, (v) from about 0.05 to about 2 g/l of p-nitrophenol, and (vi) from about 0.1 to about 10 g/L, measured as its stoichiometric equivalent as
 - 25 hydroxylamine, of a component capable of furnishing hydroxylamine in water solution;
 - (E) the "points" of total acid are from about 7 to about 25;
 - (F) the points of free acid are from about -0.5 to about +1.5;
 - (G) (i) the total concentration of Mn^{+2} and Co^{+2} ions is about 0.1 to about 0.8 g/L; or
 - 30 (ii) the concentration of Mg^{+2} ions is from about 0.5 to about 1.0; or (iii) the



concentrations of both the total of Mn^{+2} and Co^{+2} ions and of Mg^{+2} ions are within the ranges specified for the individual ions in parts (i) and (ii);

- (J) the concentration of free fluoride as measured by a fluoride sensitive electrode is from about 1.0 to about 4.0 g/L;
- 5 (K) the concentration of SO_4^{-2} ions is not more than about 11 g/L; and
- (L) the concentration of NO_3^{-} ions is not more than about 3.4 g/L.
3. A composition according to claim 2, wherein:
- (B) the amount of dissolved Zn^{+2} ions is from about 0.57 to about 1.24 g/L;
- (C) the amount of dissolved Cu^{+2} ions is from about 24 to about 74 mg/L;
- 10 (E) the "points" of total acid are from 13 to about 24;
- (F) the points of free acid are from about -0.5 to about +1.0; and
- (L) the concentration of NO_3^{-} ions is not more than about 2.0 g/L.
4. A composition according to claim 3, wherein:
- (B) the amount of dissolved Zn^{+2} ions is from about 0.60 to about 0.95 g/L;
- 15 (D) the accelerator includes at least one of from about 0.01 to about 0.2 g/l of nitrite ions and from about 0.5 to about 6 g/L, measured as its stoichiometric equivalent as hydroxylamine, of a component capable of furnishing hydroxylamine in water solution;
- (E) the "points" of total acid are from about 16 to about 22;
- 20 (F) the points of free acid are from about 0.0 to about 0.8; and
- (L) the concentration of NO_3^{-} ions is not more than about 1.8 g/L.
5. A composition according to claim 3, wherein:
- (B) the amount of dissolved Zn^{+2} ions is from about 0.60 to about 0.95 g/L;
- (D) the accelerator includes at least one of from about 0.01 to about 0.2 g/l of nitrite
- 25 ions and from about 0.5 to about 6 g/L, measured as its stoichiometric equivalent as hydroxylamine, of a component capable of furnishing hydroxylamine in water solution;
- (E) the "points" of total acid are from about 16 to about 22;
- (F) the points of free acid are from about -0.5 to about 0.0; and
- 30 (L) the concentration of NO_3^{-} ions is not more than about 1.8 g/L.



6. A composition according to claim 5, wherein:
- (A) the amount of dissolved phosphate ions is from about 13 to about 18 g/L;
 - (B) the amount of dissolved Zn^{+2} ions is from about 0.71 to about 0.87 g/L;
 - (C) the amount of dissolved Cu^{+2} ions is from about 24 to about 60 mg/L;
 - 5 (D) the accelerator includes at least one of from 0.01 to 0.2 g/l of nitrite ions and from about 0.5 to about 2 g/L, measured as it stoichiometric equivalent as hydroxylamine, of HAS;
 - (E) the points of total acid are from about 18 to about 21;
 - (F) the points of free acid are from about -0.5 to about -0.2;
 - 10 (G) (i) the concentration of the total of Mn^{+2} and Co^{+2} ions is from about 0.40 to about 0.65 g/L; or (ii) the concentration of Mg^{+2} ions is from about 0.70 to 0.80 g/L; or (iii) the concentration of both the total of Mn^{+2} and Co^{+2} ions and of Mg^{+2} ions are within the ranges already specified for the individual ions in items (G)(i) and (ii); and
 - 15 (L) the concentration of NO_3^- ions is not more than about 1.3 g/L.
7. A composition according to claim 4, wherein:
- (A) the amount of dissolved phosphate ions is from about 13 to about 18 g/L;
 - (B) the amount of dissolved Zn^{+2} ions is from about 0.71 to about 0.87 g/L;
 - (C) the amount of dissolved Cu^{+2} ions is from about 24 to about 60 mg/L;
 - 20 (D) the accelerator includes at least one of from 0.01 to 0.2 g/l of nitrite ions and from about 0.5 to about 2 g/L, measured as it stoichiometric equivalent as hydroxylamine, of HAS;
 - (E) the points of total acid are from about 18 to about 21;
 - (F) the points of free acid are from about 0.35 to about 0.65;
 - 25 (G) (i) the concentration of the total of Mn^{+2} and Co^{+2} ions is from about 0.40 to about 0.65 g/L; or (ii) the concentration of Mg^{+2} ions is from about 0.70 to 0.80 g/L; or (iii) the concentration of both the total of Mn^{+2} and Co^{+2} ions and of Mg^{+2} ions are within the ranges already specified for the individual ions in items (G)(i) and (ii); and
 - 30 (L) the concentration of NO_3^- ions is not more than about 1.3 g/L.



8. A process for forming a phosphate coating on the surface of a metal substrate that does not include aluminum as part of its surface, wherein the surface of the substrate is contacted for a time within the range from about 90 to about 120 sec at a temperature within the range from about 40 to about 44°C with a composition according to claim 7, the
5 add-on mass of the phosphate coating formed is in the range from about 2.2 to about 3.8 g/m², and the weight percent of copper in the phosphate coating formed is within the range from about 3.0 to about 4.1.

9. A process for forming a phosphate coating on the surface of a metal substrate that includes aluminum as part of its surface, wherein the surface of the substrate is contacted
10 for a time within the range from about 90 to about 120 sec at a temperature within the range from about 31 to about 44°C with a composition according to claim 6, the add-on mass of the phosphate coating formed is in the range from about 2.2 to about 3.8 g/m², and the weight percent of copper in the phosphate coating formed is within the range from about 3.0 to about 4.1.

15 10. A process for forming a phosphate coating on the surface of a metal substrate that includes aluminum as part of its surface, wherein the surface of the substrate is contacted for a time within the range from about 30 sec to about 5 min at a temperature within the range from about 25 to about 55°C with a composition according to claim 5, the add-on
20 mass of the phosphate coating formed is in the range from about 1.6 to about 4.3 g/m², and the weight percent of copper in the phosphate coating formed is within the range from about 2.0 to about 6.0.

11. A process for forming a phosphate coating on the surface of a metal substrate that does not include aluminum as part of its surface, wherein the surface of the substrate is contacted for a time within the range from about 30 sec to about 5 min at a temperature
25 within the range from about 40 to about 55°C with a composition according to claim 4, the add-on mass of the phosphate coating formed is in the range from about 1.6 to about 4.3 g/m², and the weight percent of copper in the phosphate coating formed is within the range from about 2.0 to about 6.0.

12. A process for forming a phosphate coating on the surface of a metal substrate,
30 wherein the surface of the substrate is contacted for a time within the range from about 15 sec to about 10 min at a temperature within the range from about 25 to about 55°C with a composition according to claim 3, the add-on mass of the phosphate coating formed is in the range from about 1.1 to about 5.4 g/m², and the weight percent of copper in the phosphate coating formed is within the range from about 1.0 to about 8.0.



13. A process for forming a phosphate coating on the surface of a metal substrate, wherein the surface of the substrate is contacted for a time within the range from about 5 sec to about 15 min at a temperature within the range from about 21 to about 85°C with a composition according to claim 2, the add-on mass of the phosphate coating formed is in
5 the range from about 1.1 to about 5.4 g/m², and the weight percent of copper in the phosphate coating formed is within the range from about 0.50 to about 10.0.

14. A process for forming a phosphate coating on the surface of a metal substrate, wherein the surface of the substrate is contacted for a time within the range from about 5 sec to about 15 min at a temperature within the range from about 21 to about 85°C with a
10 composition according to claim 1, the add-on mass of the phosphate coating formed is in the range from about 1.1 to about 5.4 g/m², and the weight percent of copper in the phosphate coating formed is within the range from about 0.50 to about 10.0.

15. A process for forming a protective coating on the surface of a metal substrate, said process comprising steps of:

- 15 (1) cleaning the surface;
- (2) contacting the cleaned surface with an activating composition containing colloidal titanium;
- (3) forming a phosphate coating on the cleaned and activated surface by a process according to claim 14; and
- 20 (4) applying an outer solid organic based coating over the phosphate coating formed in step (3).

16. A process for forming a protective coating on the surface of a metal substrate, said process comprising steps of:

- (1) cleaning the surface;
- 25 (2) contacting the cleaned surface with an activating composition containing colloidal titanium;
- (3) forming a phosphate coating on the cleaned and activated surface by a process according to claim 12; and
- (4) applying an outer solid organic based coating over the phosphate coating formed in
30 step (3).

17. A process for forming a protective coating on the surface of a metal substrate that does not include aluminum as part of its surface, and process comprising steps of:



- (1) cleaning the surface;
- (2) contacting the cleaned surface with an activating composition containing colloidal titanium;
- (3) forming a phosphate coating on the cleaned and activated surface by a process according to claim 11; and
- (4) applying an outer solid organic based coating over the phosphate coating formed in step (3).

18. A process for forming a protective coating on the surface of a metal substrate that includes aluminum as part of its surface, said process comprising steps of:

- (1) cleaning the surface;
- (2) contacting the cleaned surface with an activating composition containing colloidal titanium;
- (3) forming a phosphate coating on the cleaned and activated surface by a process according to claim 10; and
- (4) applying an outer solid organic based coating over the phosphate coating formed in step (3).

19. A process for forming a protective coating on the surface of a metal substrate that includes aluminum as part of its surface, said process comprising steps of:

- (1) cleaning the surface;
- (2) contacting the cleaned surface with an activating composition containing colloidal titanium;
- (3) forming a phosphate coating on the cleaned and activated surface by a process according to claim 9; and
- (4) applying an outer solid organic based coating over the phosphate coating formed in step (3).

20. A process for forming a protective coating on the surface of a metal substrate that does not include aluminum as part of its surface, said process comprising steps of:

- (1) cleaning the surface;
- (2) contacting the cleaned surface with an activating composition containing colloidal titanium;



- (3) forming a phosphate coating on the cleaned and activated surface by a process according to claim 8; and
- (4) applying an outer solid organic based coating over the phosphate coating formed in step (3).