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PROTECTION OF METALS FROM
CORROSION

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1

This invention relates to a process of making metallic articles corrosion-resistant by depositing on the article from an aqueous solution an amorphous film or coating formed by the interaction of one or more coating metal ions with one or more molecularly dehydrated phosphate radicals, the solution being of such character that the film is deposited without visible attack on the surface of the article. The amorphous films characteristic of my invention are substantially even in thickness, continuous and flexible as contrasted with the hard granular crystalline deposits obtained from orthophosphoric acid metal-treating solutions. They are superior to the crystalline deposits, particularly for those uses where the metal is first treated to improve its corrosion-resistance and then is formed to shape, as by bending or drawing, since the flexible amorphous films have less tendency to crack when bent or drawn.

This application is a continuation-in-part of my application Serial No. 468,690, filed December 11, 1942, and now abandoned.

The invention is particularly applicable to making steel or other ferrous metals corrosion resistant to the atmosphere but may be used for treating other metals, such as copper, zinc and their alloys in order to improve their resistance to corrosion. It provides a quick, simple process whereby mild carbon steel sheets can be protected from corrosion by the atmosphere during the period of time after the rolling is completed until the sheet is subjected to a further treatment such as lithographing, in case the sheet is to be made into containers or until enamelling, in case it is to be enamelled. The invention is applicable to preventing or retarding corrosion of the steel sheet by the atmosphere, irrespective of the particular use to which the steel is to be put; but the above have been given merely by way of example of certain applications of the invention.

The invention will be described as applied to improving the corrosion-resistance of steel sheets, it being understood that other metals or their alloys may be treated according to my process to improve their resistance to corrosion.

The steel sheet is first cleaned by any suitable method and is then treated with an aqueous solution which forms an amorphous protective film or coating on the sheet. The aqueous treating solution may be applied to the sheet by any suitable method, for example, immersion of the sheet in the treating solution or by spraying the treating solution on the sheet. The treating solu-

2

tion is of such character that there is formed on the sheet an amorphous protective film of material produced by the interaction of one or more molecularly dehydrated phosphate radicals and one or more coating metals of the group consisting of calcium, strontium, barium, zinc, cadmium, nickel, cobalt and manganese. As an example of the material which can be deposited to form the amorphous protective coating, I mention calcium metaphosphate $\text{Ca}(\text{PO}_3)_2$. The calcium metaphosphate film is formed on the sheet by providing in the treating solution calcium ion and metaphosphate radical in the proper concentrations and ratios and treating the sheet with the solution under the proper conditions of pH and temperature all as will be explained more fully hereinafter.

In order to form the desired amorphous protective film of calcium metaphosphate, for example, there must be a sufficient concentration of calcium and of metaphosphate radical to form the film by subjecting the sheet to the treating solution for a reasonable period of time. Also the weight ratio of metaphosphate to calcium must be within certain limits. If the ratio of metaphosphate to calcium is too low, the solution does not provide sufficient metaphosphate radical for uniting with the calcium to form the protective film of calcium metaphosphate. On the other hand, if the ratio of metaphosphate to calcium is too high, the effect is to prevent the formation of the calcium metaphosphate film.

For purposes of practical short-time treatment of iron and steel, to render them corrosion-resistant when they are exposed to the atmosphere for relatively short periods of time, the minimum effective concentration of calcium is about 100 P. P. M. (parts per million by weight). For a calcium concentration of 100 P. P. M., the amount of sodium phosphate glass having a molar ratio of Na_2O to P_2O_5 of 1.1:1, often referred to as technical grade Graham's salt or sodium hexametaphosphate, should be in the range of about 200 to 1000 P. P. M. but preferably about 500 P. P. M. Since this sodium phosphate glass contains about 67% P_2O_5 , this means that the P_2O_5 content, said P_2O_5 being derived from the aforementioned sodium phosphate glass, should amount to about 134-670 P. P. M. The pH value of this particular treating solution should be in the range of 4 to 7, preferably about pH 5. The treatment may be given by immersion of clean ferrous metal in the solution for ten minutes at room temperature or for one minute at 65° C. The optimum weight

ratio of this phosphate glass to calcium in the stated concentration of 100 P. P. M. is about 5:1, the optimum weight ratio of the P_2O_5 to calcium being about 3.4:1. In the case of low concentrations such as 100 P. P. M. of calcium, the effective weight ratio of this phosphate glass to calcium is about 2:1 to 10:1. However, as the calcium concentration level is increased, the range of effective ratios of this phosphate glass to calcium is widened downwardly, so that a concentration of 5000 P. P. M. calcium the effective weight ratio of this phosphate glass to calcium is between about 0.05:1 and 10:1, which means a weight ratio of P_2O_5 to calcium between about 0.03:1 and 7:1. Thus there appears to be a minimum effective concentration of this phosphate glass at about 200 P. P. M. whereas the maximum effective concentration bears a constant relation to the calcium concentration, i. e., about 10:1. The 5:1 ratio of this phosphate glass to calcium is the optimum ratio and gives satisfactory results over the whole range of calcium concentrations from 100 P. P. M. up to 5000 P. P. M. or even higher.

There appears to be no real upper limit to the concentrations of calcium and phosphate glass in solution so long as the proper ratio between them is maintained. However, due to the bulk of undissolved or precipitated material present, it probably is neither practical nor economical to operate above the 1000 P. P. M. calcium level if the pH of the solution is 5 or above. Since the amount of calcium which can be held in solution in a solution having a pH of 5 is around 300 P. P. M. calcium at room temperature and is lower at elevated temperatures, the optimum concentration of calcium in a solution having this pH value appears to be about 300 P. P. M. Lower concentrations than this are spent more rapidly whereas higher concentrations lead to waste of treating material. However, higher concentrations of calcium can be employed if the pH of the solution is lowered.

In one example of the process, a steel sheet was treated in a solution having a pH of 5 for one minute at 65° C., the solution containing 300 P. P. M. calcium and 1500 P. P. M. phosphate glass having a molar ratio of Na_2O to P_2O_5 of 1.1:1. The sheet was then rinsed with water and allowed to dry at room temperature. No rust spots could be found on this sheet after drying, while an untreated sheet similarly rinsed with water and allowed to dry at room temperature showed many rust spots.

Within practical limits, the higher the temperature and the longer the time of exposure to the solution, the more effective the treatment becomes. A one-minute exposure at 65° C. is roughly equivalent to 10 minutes exposure at room temperature. At 100° C., an amorphous film can be produced in less than one minute, but since high temperature causes decomposition of the phosphate glass, the use of such high temperature is uneconomical.

The invention has been described thus far principally in connection with the formation of a film of calcium metaphosphate. However, other coating metals may be substituted in whole or in part for the calcium, and other molecularly dehydrated phosphate radicals, for example, tripolyphosphate radical P_3O_{10} or pyrophosphate radical P_2O_7 may be substituted in whole or in part for the metaphosphate radical PO_3 .

In place of calcium, I may use as coating metals strontium, barium, zinc, cadmium, nickel, co-

balt and manganese. All of these coating metals have the common property of reacting in solution with molecularly dehydrated phosphate radicals when in proper concentrations and ratios and at proper pH values to form amorphous protective films on base metals without visible attack on the base metal. The nature of the anions in compounds of the coating metals does not appear to be critical. Apparently any compound of these metals can be used which provides one or more of the coating metals in solution in the treating bath. I may, for example, use the soluble chlorides, sulphates, acetates, chromates, nitrates or hydroxides of the metals for supplying the metal ions to the solution. Certain compounds of the metals are especially effective due to their pH value or neutralizing or buffer value. For example, calcium chloride is a very effective compound for use with a phosphate glass having a molar ratio of Na_2O to P_2O_5 of 1.1:1, because the pH values of aqueous solutions containing effective amounts of calcium chloride and such phosphate glass are about 5, which has been found to be the optimum pH value of the treating solution when the solution contains about 100-300 P. P. M. of calcium. If a more acid phosphate glass, for example, one having a ratio of Na_2O to P_2O_5 of 0.7:1 is employed in the treating solution, desirable coating metal compounds are the carbonates or hydroxides. Such compounds not only supply part or all of the necessary coating metal which is to react with the molecularly dehydrated phosphate radical to form the protective film but act as neutralizing agents as well.

The whole range of molecularly dehydrated phosphates, starting with tetrasodium pyrophosphate and extending to metaphosphoric acid (fresh P_2O_5 solution) appears to be effective in forming the protective film when the pH value is adjusted to the proper level. By "molecularly dehydrated phosphate" is meant any phosphate or phosphoric acid which can be considered as derived from monobasic or dibasic orthophosphate or orthophosphoric acid or mixtures thereof by removal of water of constitution. Included in this term are the sodium phosphate glass commonly referred to as technical grade Graham's salt, which has a molar ratio of Na_2O to P_2O_5 of 1.1:1, pentasodium tripolyphosphate $Na_5P_3O_{10}$, which has a molar ratio of Na_2O to P_2O_5 of 5:3, and tetrasodium pyrophosphate $Na_4P_2O_7$ having a molar ratio of Na_2O to P_2O_5 of 2:1. These are given merely by way of example, as illustrating the more common alkali-metal molecularly dehydrated phosphates which are either substantially neutral or alkaline in reaction. The preferred molecularly dehydrated phosphates for use according to the invention are the glasses which extend from P_2O_5 at the acid end of the materials through the phosphate glasses made by rapidly chilling a melt of the proper composition including the acid phosphate glasses, the neutral phosphate glasses and the alkaline phosphate glasses up to a composition at the alkaline end of the range of materials in the vicinity of sodium tripolyphosphate $Na_5P_3O_{10}$, which has a molar ratio of Na_2O to P_2O_5 of 5:3. The sodium phosphate glass with a molar ratio of Na_2O to P_2O_5 of 5:3 is more effective than crystalline sodium tripolyphosphate $Na_5P_3O_{10}$. Acid sodium phosphate glass with a molar ratio of Na_2O to P_2O_5 of 0.87:1 (pH 2.8) and freshly dissolved P_2O_5 both give good results when the pH value of the solution is adjusted to the proper level. The water soluble crystalline pentasodium tripoly-

phosphate and the tetrasodium pyrophosphate and sodium trimetaphosphate are not nearly as effective in producing the amorphous protective film as are the glassy molecularly dehydrated phosphates.

As has been pointed out previously herein, where calcium is employed as the coating metal and is used in the minimum concentration of about 100 P. P. M., the optimum pH value of the solution is about 5 and the effective pH range is from 4 to 7. The optimum pH value of the solution, according to my invention, will vary depending upon such factors as the coating metal employed, the concentration of the coating metal in the treating solution, the concentration of the molecularly dehydrated phosphate in the treating solution and the P_2O_5 content of the molecularly dehydrated phosphate. In general, lower pH values can be employed with higher concentrations of coating metal. Thus, a pH of 3 can be used if the calcium concentration is, say, 1500 P. P. M. or higher, whereas if the calcium concentration is of the order of 300 P. P. M. or lower, the pH should be 4 or higher. The pH of the solution should not be above about 8 or 9 because with a higher pH than this no substantial amount of coating is formed. In general, the pH should not be above 7 and I prefer to employ a pH of about 4 or 5.

The weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate to the coating metal varies over a fairly wide range for some coating metals and over a narrower range for other coating metals. The optimum ratio and the effective range of this ratio for each of the coating metals is given in Table I.

Table I

Weight Ratio P_2O_5 content of molecularly dehydrated phosphate
Coating Metal

Coating Metal	Optimum Ratio	Range of Ratios
Calcium	3.4	.03-7.0
Strontium	1.5	.7-2.0
Barium	1.0	.5-1.5
Zinc	1.0	.3-3.5
Cadmium	0.7	.3-1.5
Nickel	0.1	.07-3.5
Cobalt	1.4	.3-3.5
Manganese	0.7	.07-3.5

Table II which follows, gives numerous examples embodying widely varying conditions under which my process can be carried out in the treatment of mild carbon steel. In this table, column 1 shows the molecularly dehydrated phosphate used in the treating solution. Column 2 shows the molar ratio of $Na_2O:P_2O_5$ of the molecularly dehydrated phosphate. Column 3 shows the concentration in parts per million of the molecularly dehydrated phosphate. Column 4 shows the coating metal compound employed in the treating solution and column 5 the concentration in parts per million of the coating metal. Column 6 shows the weight ratio of P_2O_5 content of the molecularly dehydrated phosphate to the coating metal employed. Column 7 shows the pH value of the treating solution and columns 8 and 9 show respectively the temperature of the treating solution and the time of treatment in minutes.

Table II

No.	Molecularly Dehydrated Phosphate			Coating Metal		Weight Ratio— P_2O_5 in Phosphate: Coating Metal	Treating Solution		Time of Treatment, Minutes
	Compound	Molar Ratio $Na_2O:P_2O_5$	Concentration, P. P. M.	Compound	Concentration P. P. M.		pH	Temp., °C.	
1	$Na_4P_2O_7$ (cryst)	2	500	$CaCl_2$	300	0.89	5.0	25	10
2	do	2	1,500	do	300	2.67	5.0	25	10
3	$Na_3P_3O_{10}$ (cryst)	1.7	1,500	do	300	2.90	5.0	25	10
4	do	1.7	1,500	do	300	2.90	5.0	65	1
5	do	1.7	1,500	do	300	2.90	6.0	25	10
6	do	1.7	1,500	do	300	2.90	5.5	65	10
7	do	1.7	1,000	do	300	1.93	5.0	25	10
8	do	1.7	2,000	do	300	3.86	5.0	25	10
9	P_2O_5	0	500	do	300	1.67	5.0	25	10
10	do	0	1,500	do	300	5.0	5.0	65	10
11	do	0	500	do	300	1.67	5.0	65	1
12	do	0	2,000	do	300	6.67	5.0	65	1
13	Sodium Phosphate Glass	0.87	500	$Ca(OH)_2$	300	1.21	5.0	25	10
14	do	0.87	2,000	do	300	4.83	5.0	25	10
15	do	0.87	500	$CaCl_2$	300	1.21	5.0	25	10
16	do	0.87	2,000	do	300	4.83	5.0	25	10
17	do	0.87	1,000	do	300	2.42	5.0	65	10
18	do	0.87	500	do	300	1.21	5.0	65	1
19	do	0.87	2,500	do	300	6.03	5.0	65	1
20	do	1.5	500	do	300	1.04	5.0	25	10
21	do	1.5	2,000	do	300	4.16	5.0	25	10
22	do	1.5	500	do	300	1.04	5.0	65	1
23	do	1.5	2,500	do	300	5.20	5.0	65	1
24	do	1.7	500	do	300	0.97	5.0	25	10
25	do	1.7	2,500	do	300	4.83	5.0	25	10
26	do	1.1	7,500	$Ca(NO_3)_2$	1,500	3.38	3.0	49	5
27	do	1.1	7,500	do	1,500	3.38	3.0	49	30
28	do	1.1	1,500	$CaCrO_4$	300	3.38	5.0	49	5
29	do	1.1	7,500	$CaCl_2$	1,500	3.38	3.2	49	30
30	do	1.1	7,500	do	1,500	3.38	3.5	24	10
31	do	1.1	7,500	do	1,500	3.38	3.5	49	5
32	do	1.1	7,500	do	1,500	3.38	3.5	49	30
33	do	1.1	7,500	do	1,500	3.38	3.5	49	5
34	do	1.1	7,500	$Ca(NO_3)_2$	1,500	3.38	3.5	49	30
35	do	1.1	7,500	do	1,500	3.38	3.5	49	1
36	do	1.1	4,500	$CaCl_2$	900	3.38	3.7	49	10
37	do	1.1	750	do	150	3.38	4.0	49	10
38	do	1.1	4,500	do	900	3.38	4.0	49	10
39	do	1.1	750	do	150	3.38	5.0	49	10
40	do	1.1	4,500	do	900	3.38	5.0	49	10
41	do	1.1	1,500	do	300	3.38	6.0	65	1
42	do	1.1	3,000	do	600	3.38	7.0	48	10

Table II.—Continued

No.	Molecularly Dehydrated Phosphate			Coating Metal		Weight Ratio— P ₂ O ₅ in Phos- phate: Coating Metal	Treating Solu- tion		Time of Treatment, Minutes
	Compound	Molar Ratio Na ₂ O P ₂ O ₅	Concentra- tion, P. P. M.	Compound	Concentra- tion, P. P. M.		pH	Temp., °C.	
43.	Sodium Phosphate Glass	1.1	7,500	Zn(NO ₃) ₂	5,000	1.01	3.0	49	5
44.	do.	1.1	4,500	do.	5,500	0.55	3.5	48	10
45.	do.	1.1	4,500	do.	5,500	0.55	4.0	48	10
46.	do.	1.1	4,500	do.	5,500	0.55	5.0	48	10
47.	do.	1.1	3,750	ZnSO ₄	3,750	0.68	5.0	49	10
48.	do.	1.1	500	ZnCl ₂	500	0.68	5.0	25	10
49.	do.	1.1	2,500	do.	500	3.38	5.0	25	10
50.	do.	1.1	7,500	BaCl ₂	5,000	1.96	4.0	48	10
51.	do.	1.1	7,500	SrCl ₂	3,300	1.89	3.0	48	10
52.	do.	1.1	7,500	do.	3,300	1.89	4.5	48	10
53.	do.	1.1	500	CdSO ₄	1,000	0.34	5.0	25	10
54.	do.	1.1	2,000	do.	1,000	1.35	5.0	25	10
55.	do.	1.1	278	NiSO ₄	2,222	0.08	4.0	49	10
56.	do.	1.1	278	do.	2,222	0.08	5.0	49	10
57.	do.	1.1	1,250	do.	1,250	0.68	5.0	49	10
58.	do.	1.1	500	NiCl ₂	500	0.68	5.0	25	10
59.	do.	1.1	2,500	do.	500	3.38	5.0	25	10
60.	do.	1.1	1,500	do.	500	2.03	5.0	65	1
61.	do.	1.1	1,500	CoCl ₂	500	2.03	4.0	25	10
62.	do.	1.1	1,500	do.	500	2.03	5.0	25	10
63.	do.	1.1	1,500	do.	500	2.03	6.0	25	10
64.	do.	1.1	1,500	do.	500	2.03	7.0	25	10
65.	do.	1.1	500	do.	500	0.68	5.0	25	10
66.	do.	1.1	2,500	do.	500	3.38	5.0	25	10
67.	do.	1.1	250	do.	250	0.68	5.0	25	10
68.	do.	1.1	750	do.	250	2.03	5.0	25	10
69.	do.	1.1	1,250	do.	250	3.38	5.0	25	10
70.	do.	1.1	4,500	MnSO ₄	4,500	0.68	3.5	48	10
71.	do.	1.1	4,500	do.	4,500	0.68	4.0	48	10
72.	do.	1.1	800	do.	8,200	0.07	4.0	48	10
73.	do.	1.1	800	do.	8,200	0.07	5.0	48	10
74.	do.	1.1	4,500	do.	4,500	0.68	5.0	48	10
75.	do.	1.1	7,500	do.	1,500	3.37	5.0	48	10

Instead of making up the treating solution by dissolving a coating metal compound and a molecularly dehydrated phosphate in water, I may dissolve a material containing both coating metal and molecularly dehydrated phosphate radical in water. I may, for example, form the treating solution by dissolving a calcium phosphate glass in water or I may maintain the strength of the treating solution by adding calcium phosphate glass to a bath previously formed by dissolving a calcium compound and a sodium phosphate glass in water. The calcium phosphate glass is quite slowly soluble and this is advantageous because it provides an effective means for continuously supplying calcium and molecularly dehydrated phosphate to replace that which is removed in the formation of the film on the metal being treated to render it corrosion resistant. When a glass with a molar ratio of CaO to P₂O₅ of 1:1, corresponding to calcium metaphosphate, is dissolved in water, it provides molecularly dehydrated phosphate radical and calcium in substantially the optimum ratio for preventing corrosion.

I may use a sodium calcium phosphate glass, for example, that having the formula



or any sodium-calcium phosphate glass having less sodium oxide than that contained in the glass having the formula $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{P}_2\text{O}_5$.

Similarly, glasses containing other coating metals than calcium may be used in place of the phosphate glasses containing calcium.

When phosphate glasses containing calcium or other coating metal are employed, the concentrations of calcium or other coating metal and molecularly dehydrated phosphate radical, the weight ratios of the P₂O₅ content of the molecularly dehydrated phosphate to coating metal and the pH values of the treating solution are preferably maintained within the ranges given in connection with the formation of the treating

solution by the separate use of calcium or other metal compound and molecularly dehydrated phosphate not containing coating metal.

Any of the molecularly dehydrated phosphates may contain potassium or ammonium in place of sodium whether they do or do not contain coating metal.

The following method is one which may be employed in forming the corrosion resistant amorphous film on a mild carbon steel strip. The strip is cleaned with an alkaline detergent, followed by a 15-second pickle in 5 to 10% sulphuric acid. The pickling is not an essential step and it is to be understood that any method which provides a clean grease-free surface is a satisfactory preparation of the metal for the corrosion resisting treatment. The strip is immersed in the treating solution at a temperature and for a time dependent upon the particular corrosion conditions to which the strip is to be subjected. Where the treating solution contains 300 P. P. M. calcium, 1500 P. P. M. phosphate glass having a molar ratio of Na₂O to P₂O₅ of 1.1:1 and has a pH of 5, the strip may be immersed in the solution maintained at a temperature of about 65° C. for a period of the order of one minute. After this treatment, the strip may be allowed to dry without rinsing or it may be rinsed in cold or hot water. Such treatment provides an amorphous film on the strip which renders the strip corrosion-resistant when exposed to air during the time and under conditions normally encountered between the end of the rolling of the strip and the time that it is given an enamelling or lithographing treatment.

The invention is not limited to the preferred materials or practice, which have been given merely for illustrative purposes, but may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. The process of treating base metal articles of the group consisting of ferrous metals, copper,

zinc, and their alloys, for improving their resistance to atmospheric corrosion, preparatory to applying a nonferrous finish which comprises treating the articles to render substantially grease-free an exterior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one hundred parts per million by weight of at least one coating metal selected from the group consisting of calcium, strontium, barium, zinc, cadmium, nickel, cobalt, and manganese, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate, the weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate to the coating metal being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous coating metal phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the articles so as to provide a dry finish-receptive exterior surface having a substantially amorphous film thereover, the film being characterized by a good quality of bondability with nonferrous finishes.

2. The process of treating base metal articles of the group consisting of ferrous metals, copper, zinc, and their alloys for improving their resistance to atmospheric corrosion, preparatory to applying a nonferrous finish which comprises treating the articles to render substantially grease-free an exterior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one hundred parts per million by weight of calcium, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate, the weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate to the calcium being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous calcium phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the articles so as to provide a dry finish-receptive exterior surface having a substantially continuous amorphous film thereover, the film being characterized by a good quality of bondability with nonferrous finishes.

3. The process of treating ferrous metal articles for improving their resistance to atmospheric corrosion, preparatory to applying a nonferrous finish which comprises treating the articles to render substantially grease-free an exterior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one hundred parts per million by weight of at least one coating metal selected from the group consisting of calcium, strontium, barium, zinc, cadmium, nickel, cobalt, and manganese, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate, the weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate to the coating metal being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous coating metal phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the articles so as to provide a dry finish-receptive exterior surface having a substantially continuous amorphous film thereover, the film being characterized by a good quality of bondability with nonferrous finishes.

4. The process of treating ferrous metal articles

for improving their resistance to atmospheric corrosion, preparatory to applying a nonferrous finish which comprises treating the articles to render substantially grease-free an exterior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one hundred parts per million by weight of calcium, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate, the weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate to the calcium being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous calcium phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the articles so as to provide a dry finish-receptive exterior surface having a substantially continuous amorphous film thereover, the film being characterized by a good quality of bondability with nonferrous finishes.

5. The process of treating articles of zinc and its alloys for improving their resistance to atmospheric corrosion, preparatory to applying a nonferrous finish which comprises treating the articles to render substantially grease-free an exterior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one hundred parts per million by weight of at least one coating metal selected from the group consisting of calcium, strontium, barium, zinc, cadmium, nickel, cobalt, and manganese, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate, the weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate to the coating metal being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous coating metal phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the articles so as to provide a dry finish-receptive exterior surface having a substantially continuous amorphous film thereover, the film being characterized by a good quality of bondability with nonferrous finishes.

6. The process of treating articles of zinc and its alloys for improving their resistance to atmospheric corrosion, preparatory to applying a nonferrous finish which comprises treating the articles to render substantially grease-free an exterior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one hundred parts per million by weight of calcium, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate, the weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate to the calcium being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous calcium phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the articles so as to provide a dry finish-receptive exterior surface having a substantially continuous amorphous film thereover, the film being characterized by a good quality of bondability with nonferrous finishes.

7. The process of treating articles of copper and its alloys for improving their resistance to atmospheric corrosion, preparatory to applying a nonferrous finish which comprises treating the articles to render substantially grease-free an ex-

terior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one hundred parts per million by weight of at least one coating metal selected from the group consisting of calcium, strontium, barium, zinc, cadmium, nickel, cobalt, and manganese, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate, the weight ratio of P_2O_5 content of the molecularly dehydrated phosphate to the coating metal being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous coating metal phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the articles so as to provide a dry finish-receptive exterior surface having a substantially continuous amorphous film thereover, the film being characterized by a good quality of bondability with nonferrous finishes.

8. The process of treating articles of copper and its alloys for improving their resistance to atmospheric corrosion, preparatory to applying a nonferrous finish which comprises treating the articles to render substantially grease-free an exterior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one hundred parts per million by weight of calcium, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate, the weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate to the calcium being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous calcium phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the articles so as to provide a dry finish receptive exterior surface having a substantially continuous amorphous film thereover, the film being characterized by a good quality of bondability with nonferrous finishes.

9. The process of treating base metal articles of the group consisting of ferrous metals, copper, zinc, and their alloys, for improving their resistance to atmospheric corrosion, preparatory to applying a nonferrous finish which comprises treating the articles to render substantially grease-free an exterior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one hundred parts

per million by weight of at least one coating metal selected from the group consisting of calcium, strontium, barium, zinc, cadmium, nickel, cobalt, and manganese, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate glass, the weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate glass to the coating metal being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous coating metal phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the articles so as to provide a dry finish-receptive exterior surface having a substantially amorphous film thereover, the film being characterized by a good quality of bondability with non-ferrous finishes.

10. The process of treating base metal articles of the group consisting of ferrous metals, copper, zinc, and their alloys, for improving their resistance to atmospheric corrosion, which comprises treating the articles to render substantially grease-free an exterior surface to be protected, applying to the grease-free surface an aqueous solution containing at least one coating metal selected from the group consisting of calcium, strontium, barium, zinc, cadmium, nickel, cobalt and manganese, the metal being present in the form of a water-soluble salt, and at least one molecularly dehydrated phosphate, the weight ratio of the P_2O_5 content of the molecularly dehydrated phosphate to the coating metal being between 0.03:1 and 7:1, the pH value of the solution being between 3 and 9 and such that an amorphous coating metal phosphate film is deposited on the base metal without visible attack on the base metal surface, and thereafter drying the article so as to provide a dry exterior surface having a substantially continuous amorphous film thereover.

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The following references are of record in the file of this patent:

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