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3,444,007

PROCESS OF FORMING PAINT-BASE COATINGS ON ZINC AND ZINC ALLOY SURFACES

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9 Claims

ABSTRACT OF THE DISCLOSURE

A process for coating zinc and zinc alloy surfaces, wherein the surface is contacted with an aqueous alkaline solution which contains at least one metal ion other than an alkali metal ion, which ion is selected from the group consisting of silver, magnesium, cadmium, aluminum, tin, titanium, antimony, molybdenum, chromium, cerium, tungsten, manganese, cobalt, ferrous and ferric iron, and nickel, and a complexing agent which is present in the solution in a sufficient quantity to hold the other metal ions in the solution. The solution is maintained in contact with the surface for a period sufficient to form on the surface a paint-based coating. The metal ion selected from the indicated group is present in the solution in an amount which is sufficient to produce a coating quality which enables the thus-produced coating to function as a base for paint. In the most preferred embodiment, in addition to the metal ion from the indicated group, the solution also contains at least one alkali metal ion.

This application is a continuation of our copending application Ser. No. 310,877 filed Sept. 23, 1963, now abandoned.

This invention relates to the art of forming protective coatings on the surfaces of zinc and zinc alloys from aqueous alkaline solutions.

Heretofore, it has been well known and widely commercially practiced to prepare the surfaces of zinc and zinc alloys for the reception of paint or other siccative coatings by using aqueous acidic solutions, particularly phosphate solutions. A number of commercially satisfactory phosphate coating processes and systems are known and for a certain type of product manufacture are entirely satisfactory. In other types of zinc or zinc alloy products, however, such as those which require deformation of the painted metal surfaces subsequent to painting certain defects have been encountered, including loss of paint adhesion, decreased corrosion resistance to both humidity and salt spray or its equivalent.

This invention is based on the discovery that corrosion resistant coatings can be formed on the surfaces of zinc or zinc alloys from certain aqueous alkaline solutions and that these coatings provide bases for paint which are unexpectedly superior in adhesion to any of the heretofore known coatings produced from conventional aqueous acidic solutions including the best known phosphates.

In accordance with this invention it has been found that adherent corrosion resistance coatings are formed on the surface of zinc and zinc alloys by contacting the surfaces for a short time with an aqueous alkaline solution which contains at least one metal ion other than an alkali metal ion and a complexing agent capable of complexing the metal ions which are presented and causing them to remain in the solution. In a preferred form of the invention the aqueous alkaline solution contains at least two metal ions other than, and/

or in addition to, alkali metal ions and a sufficient quantity of complexing agent to maintain these ions in solution. It has been found that useful coatings are produced from the aqueous alkaline solutions of this invention when those solutions contain a wide range of variation of alkali strength, metallic ion concentration, complexing agent concentration, temperature and time of processing as well as type of application of the coating solution to the surface, each of which component and variations in operating conditions will be discussed in greater detail hereinafter.

The alkalinity of the solution may be developed by using any of the commonly available alkaline compounds and alkaline salts, such as triethanolamine and the alkali metal hydroxides, carbonates, phosphates, borates, silicates, polyphosphates, and pyrophosphates, or mixtures thereof as needed to give the desired pH. It has been found that the preferred operating conditions for the use of the solutions of this invention include the use of a solution which has a pH numerically greater than about 11, and that better results are obtained from solutions having a pH in the range of 12.6 and 13.3. However, some improvement is obtained from aqueous alkaline solutions having less alkali strength and lower pH values but the operation conditions for such solutions including time to produce the desired coating and temperature necessary to form the same are less advantageous commercially than those which are satisfactorily employed when using solutions of the greater alkali strength. Using any of the above described solutions, adherent coatings have been produced which vary in color from colorless to light yellow, to tan-yellow, to brown and finally to blue-black, depending upon the particular application conditions and solution constituency which is being used. The above described coatings are obtained from solutions which contain extremely small quantities of metal ions other than the alkali metal ions and, in general, the color of the coating increases in intensity toward brown as the time of treatment is increased and as the concentration of metallic ion therein is increased, as the temperature of treatment is increased and as the alkali strength is increased.

It has been found that the solution should contain at least one metal ion other than an alkali metal ion, which is normally introduced with the alkaline salts, in order to produce a rate of coating formation and/or quality of coating which enables such coatings to function as superior bases for paint or other siccative coating. It has also been found that such other metal ion is incapable of functioning to increase the coating rate or coating formation mechanism unless it is sufficiently complexed by a complexing agent to dissolve that metal ion in the coating solution. Based on the experimental evidence on hand, it is believed that any metal ion, other than an alkali metal ion which is complexed and in solution functions to improve the formation of the desired coating since metals falling within each of the groups of the periodic system and including the rare earth metals have been found to be satisfactory for this purpose. Satisfactory results have been obtained from the use of solutions containing the sodium ion and at least one other ion from the group comprising silver, magnesium, cadmium, aluminum, tin, titanium, antimony, molybdenum, chromium, cerium, tungsten, manganese, cobalt, ferrous and ferric iron and nickel. As above indicated, extremely minor quantities of such metal ion provide improvement. Good results have been obtained from solutions containing as low as about 0.002% iron in addition to the sodium ion introduced into the solution as sodium hydroxide to form a solution having a pH above about 12. Good results have also been obtained from high concentrations of

the metal ion or ions and although there appears to be no particular advantage gained from large quantities of the metal ions such excess quantities do not appear to be detrimental and any quantity of metal ion up to the limit of solubility thereof can be used satisfactorily. Somewhat better results have been obtained from the use of solutions which contain at least two metal ions other than the alkali metal ion, e.g., iron and cobalt, iron and silver, cobalt and cerium, etc.

The complexing, chelating or sequestering agent functions to complex the metal ion other than the alkali metal ion and maintain the same dissolved in the coating solution. For this purpose a wide variety of complexing, chelating and sequestering agents have been found to be satisfactory. It is suitable to use the inorganic complexing agents such as cyanides, condensed phosphates, ammonia and the like; the organic chelating agents including the dicarboxylic acids such as malonic acid, fumaric acid, etc.; the amino acids, such as glycine; the hydroxycarboxylic acids such as citric, gluconic, lactic, etc.; the hydroxyaldehydes such as acetylacetone; the polyhydroxyaliphatic compounds such as sorbitol, 1,2-ethanediol; the phenolic carboxylic acids such as salicylic acid, phthalic acid; the amine carboxylic acids such as ethylene dimine tetraacetic acid; the polyamino acids such as diethanolaminomethane phosphate; the salts of lower molecular weight lignosulfonic acids such as derived from wood pulping processes such as sodium lignosulfonate. The proportion of complexing agent which should be present is an amount at least sufficient to completely complex the metal ion, other than alkali metal ion, which is present. It will be apparent that as the concentration of metallic ion other than alkali metal ion increases the concentration of the complexing agent will also increase and since increasing quantities of certain of the complexing agent which are acidic in nature tends to reduce the effective alkali strength of the solution, it is preferred to employ the complexing agent in the form of neutral salts, particularly the alkali metal salts. Moreover, no advantage has been observed from the presence of concentrations of complexing agent in excess of that required to maintain the metal ion dissolved in the coating solution. Particularly good results have been obtained from the use of sodium hexahydroxyheptotatate, sodium gluconate and the sodium salt of ethylenediaminetetraacetic acid.

The solutions of this invention may optionally include a compatible surface active agent and the presence of such a surface active agent is particularly advantageous when the surface to be coated is soiled with grease, oil, or the like. For this purpose, the only requirement for the surface active agent is that it be compatible with the other ingredients of the solution, both under normal storage conditions and under the elevated temperature application conditions, that is, the surface active agent should not cause precipitation or agglomeration of the metal ions which are present, cause gelling or itself precipitate or gel in the solutions. It has been found that there are non-ionic, anionic and cationic wetting agents which are compatible in the solutions of this invention, and when included up to about 5% of the solution, w./v., can be used.

In general, the process of this invention comprises the step of contacting the zinc or zinc alloy surface to be coated by spraying, dipping, brushing, or the like, at a temperature between ordinary room temperature and the boiling point of the solution and for a time period sufficient to produce the desired total coating. The preferred method of application in the formation of coatings adapted for use as a base for paint is spraying. Preferred conditions for continuous production which enables the formation of the desired coating in the least time involves the use of the solution at a temperature between about 90° F. and 200° F. for a time between about 2 seconds and about 60 seconds. Commercially satisfactory coatings have been obtained in about 10 to 15 seconds at about 100° F.-160° F. and may be obtained in even shorter periods of

time with solutions containing relatively high concentrations of alkali and other metal ion and/or at the higher temperatures. Slightly longer contact periods are required for immersion application, but a satisfactory quality of coating is obtained from immersion contact times between about 30-90 seconds with solutions having a temperature of about 130° F. - 180° F.

The complete process of this invention also includes the use of a subsequent dilute aqueous chromic acid rinse on the preliminarily formed coating of this invention. A suitable solution for this purpose is one which contains about 0.01% to 0.5% CrO_3 , w./v. or percent by weight per unit volume. When the chromic acid solution is relatively concentrated, it is preferred to remove the excess by squeezing the excess off with rolls. A preferred dilute rinse solution for the purpose of this invention is one which is disclosed and described in detail in copending application Ser. No. 230,729, filed Oct. 15, 1962, now U.S. Patent 3,279,958, and assigned to the assignee of this application, namely, one which includes a hexavalent chromium and chromium complex ion which contains at least about 0.001% w./v. of the trivalent chromium ion and has a pH within the range of about 3.8 to 6.0, preferably about 4.5. After rinsing, the coating may be water rinsed or dried without rinsing as desired and after drying the coating is in condition for the reception of paint or other siccative coating.

The process of this invention has been found to be useful in forming coatings on the surfaces of pure zinc, electroplated zinc, hot-dipped zinc surfaces including hot-dipped zinc containing small quantities of alloying ingredients such as aluminum, etc., and zinc alloys per se or electrodeposited zinc alloy surfaces. Where the surface to be coated includes iron or steel in addition to zinc or zinc alloy, such as a partially galvanized steel or iron base or a composite article which includes assembled steel or iron portions and zinc or zinc alloy portions, it has been found that the solutions of this invention are uniquely useful. For such surfaces the solutions of this invention are first applied by the procedures and temperature application conditions above specified to first clean the steel or iron portion of the article and clean and form a coating on the zinc or zinc alloy portion of the article, and this step is advantageously combined with a subsequent conventional phosphate coating step. It has been found that the coating formed on the zinc or zinc alloy portion of such surface is not removed by an aqueous acidic zinc phosphate or aqueous acidic alkali metal phosphate coating solution of any conventional constitution, and the cleaned steel or iron portion of the surface receives an adherent protective phosphate coating having at least equal corrosion resistance and utility as a base for paint as conventionally cleaned iron or steel surfaces. For the purposes of such modified process use it is satisfactory to employ aqueous acidic zinc phosphate solutions or aqueous acidic alkali metal phosphate solutions having any of the present-day conventional constitution, which are now well known to those skilled in this art. Such a process is of unusual commercial significance because relatively little success has been heretofore attained in the formation of integral chemical coatings on composite surfaces including steel or iron, and zinc or zinc alloys or composite articles having steel or iron portions and zinc or alloy portions.

The following examples will illustrate in somewhat greater detail the specific varying conditions and typical coating solutions of this invention but it is to be understood that they are presented for purposes of illustration only and do not represent the definitive limits of the invention which have been hereinabove set forth.

EXAMPLE I

An aqueous alkaline solution was prepared to contain 0.76% NaOH , 0.1% sodium hexahydroxyheptotatate (CaFeMg crystalline sequestrant, Pfister Chemical Co.),

0.0037% iron added as ferric nitrate nonahydrate, and 0.0024% cobalt added as cobalt nitrate hexahydrate.

A first series of hot-dip zinc coated steel panels sold commercially under the trademark "Zincgrip" and reportedly manufactured by the process of U.S. Patent 2,197,622 were sprayed with the above solution at 160° F. to produce a contact time of about one minute with the solution, the panels withdrawn and rinsed in clean hot water for about 30 seconds and thereafter rinsed for about 30 seconds in a dilute aqueous rinse containing about 0.1% hexavalent chromium ion and about 0.04% trivalent chromium ion at an adjusted pH of about 4.5. The panels were then dried in a circulating air oven at 375° F. and thereafter painted with the conventional Dulux 707-6741 painting system. The representative painted panels were scribed diagonally from corner to corner and then subjected to the standard 5% salt spray test, the panels being rated on a numerical basis from 10 to 0, with 10 representing no creepage of the corrosion from the cross scribe; where corrosion occurs the degree of corrosion is rated in terms of sixteenths of an inch of creepage from the scribed line, with a rating representing the variation of migration of the creepage along the entire length of the cross scribed lines and where localized spots of corrosion occur, the width of the spot is reported in sixteenths of an inch. Other panels were tested for humidity resistance at 100° F. and 100% relative humidity, while other panels were tested for adhesion by the knife test, and for resistance to deformation. The deformation test employed was designed to comparatively measure paint adhesion to metal surfaces formed after painting and is a commercial test performed on a formability jig. In this test, a painted panel is placed in the jig which is equipped with a die which depresses an approximately 3/4" wide strip across the panel from a maximum de-

The knife adhesion test comprises manually drawing a knife blade across the surface of the coating and comparing the resistance to dislodgement of the coating, from piece to piece. The difficulty of dislodgment is rated in numerical values, from 10 to 0, with 10 representing excellent, 8 good, 6 fair, 4 poor, 2 very poor and 0 representing complete loss of adhesion.

A second series of hot-dip zinc coated steel panels, described as above, were sprayed with a solution containing 0.76% sodium hydroxide at 160° F. for about one minute. The panels were withdrawn and rinsed in clean, hot water for about 30 seconds and thereafter rinsed for about 30 seconds in the dilute aqueous chromium containing rinse described in Series I. The panels were then dried by a circulating air oven at 375° F., painted as described above, and thereafter subjected to each of the standard tests described above.

An aqueous alkaline solution was prepared to contain 0.76% sodium hydroxide, 0.1% sodium hexahydroxyheptate and 0.0037% iron added as

ferric nitrate·9H₂O

A third series of the hot-dipped zinc coated steel panels, described as above, were sprayed with the above solution at 160° F. to produce a contact time of about one minute with the solution. The panels were withdrawn and rinsed in clear, clean hot water for about 30 seconds and thereafter rinsed for about 30 seconds in the dilute aqueous chromic acid rinse described above. The panels were then dried in a circulating air oven at 375° F. and thereafter painted as described above. Representative painted panels were subjected to the standard tests described above.

The results of the standard tests are tabulated in Table I.

TABLE I

Panel Series No.	Bath	Salt Spray 408 hrs.	Humidity	Forming	Adhesion
1.....	0.76% NaOH+0.1% Sequestrant+0.0037% Fe ³⁺ +0.0024% Co ⁺⁺	1-3.....	F 9-9.5.....	2% Peelage, 70% Fracture...	10
2.....	0.76% NaOH alone.....	50% P.....	MD 9-9.5.....	12.5% P, 67.5% F.....	10-9
3.....	0.76% NaOH+0.1% Sequestrant+0.0037% Fe ³⁺	2-3.....	VF 9-9.5.....	15% P, 62.5% F.....	9

pression of about 0.3" tapering gradually to no depression over a length of 3", the depression being truncated in cross section and having a flat central depressed portion 3/8" wide and side portions sloping downwardly to the 3/4" width at the level of the plate. The corners between the sloping sides and the flat central depressed area are fairly sharp and thus provide a gradually varying degree of intensity of deformation. The degree of paint adhesion, after deformation, is measured by pressing over the external surface of the depressed strip regular pressure sensitive cellophane tape so that it covers the central portion and extends downwardly over the side portions to the base, care being taken to insure freedom from bubbles under the tape. Within 10 minutes after application of the tape it is removed by pulling at a right angle to the surface and the area exposed by paint removal or paint fracture is evaluated in terms of percentage of the total deformed area which is peeled and the percentage of the total deformed area which is covered with fractured paint.

The degree of blistering in the humidity test was rated in accordance with the standard method of ASTM D714-56, in which the size and frequency of blisters is evaluated on a numerical scale from 10 to 0, in which 10 represents no blistering and the size of the blisters increases as the numbers decrease. The frequency of the blisters is evaluated by letters in which D represents dense, MD medium dense, M represents medium, FM represents few medium, F represents few and VF represents very few, and a spread in the size of the blisters is represented by a spread in the numbers reported.

Panels of Series I after 408 hours' exposure in salt spray show creepage from 1/16" to 3/16" from the cross scribe and 7/16" spot creepage. Those treated in Series II show 50% peelage of the paint and those treated in Series III show 2/16" to 3/16" peelage from the scribed line and 8/16" spot creepage. Panels treated in Series I upon exposure to humidity of 528 hours exposure in the humidity cabinet showed a few blisters. Those treated in Series II have blisters, the frequency of which is from medium to dense, and those in Series III have very few blisters.

Panels treated in Series I show 2% peelage and 70% fracture in the forming test described above. Those treated in Series II show 12.5% peelage and 67.5% fracture and those processed in Series III show 15% peelage and 62.5% fracture. Panels treated in Series I show excellent knife adhesion. Those treated in Series II show slightly inferior adhesion and those treated in Series III show knife adhesion slightly inferior to those in Series II.

EXAMPLE II

An aqueous alkaline solution was prepared to contain 0.75% sodium hydroxide, 0.05% sodium hexahydroxyheptate, 0.011% cobalt added as cobalt nitrate·6H₂O, and 0.002% iron added as ferric nitrate·9H₂O. A series of hot-dip zinc steel coated panels of the above described type were cleaned in a conventional titanated cleaner and sprayed with the above solution at 160° F. to produce a contact time of about 15 seconds with the solution, the panels were withdrawn and rinsed in clean

hot water for about 10 seconds, and thereafter the metal is passed through squeegee rolls and then flooded with a final chromium rinse containing 0.1% hexavalent chromium and 0.04% trivalent chromium adjusted to a pH of about 4.5. Time of contact of the final rinse was about 2 to 3 seconds. The excess rinse was then squeezed off in the rolls, and the panels were then painted with the conventional one coat vinyl base paint.

A second solution was prepared to contain 0.75% NaOH and 0.05% of sodium hexahydroxyheptate. Another series of similarly cleaned panels were spray

vention. A solution was prepared to contain 3% sodium hydroxide and 0.2% sodium hexahydroxyheptate. To this solution varying quantities of the separate metal ions identified below in Table III were added to prepare treating solutions. Zinc panels of the type described above in Example I were spray-coated with each of these treating solutions under identical conditions to those specified in Example I, and then painted with the same paint system described in Example I. The painted panels were then subjected to the various tests described in Example I and the results of these tests are set forth below in Table III.

TABLE III

Bath	Salt Spray 504 Hrs.	Forming	Adhesion
Composition A*+0.042% Sn ⁺⁺ as SnCl ₄ ·6H ₂ O.....	0-2.....	7.5% F....	10
Composition A+0.042% Ag as AgNO ₃	0-4.....	17.5% F....	10-9
Composition A+0.042% Mn as Manganese Nitrate.....	0-2 Spot 1/16".....	2.5% F....	10
Composition A+0.042% Cd as Cd(NO ₃) ₂ ·4H ₂ O.....	0-1 Spot 1/16".....	2.5% F....	10
Composition A+0.042% Ti as TiO ₂	0-1 Spot 1/16".....	2.5% F....	10
Composition A+0.042% Ce as Cerium Nitrate.....	0-1 Spot 1/16".....	2.5% F....	10
Composition A+0.042% Fe ⁺⁺ as FeCl ₃ ·4H ₂ O.....	0-1 Spot 1/16".....	10.....	10
Composition A+0.042% Mg or Mg(NO ₃) ₂ ·6H ₂ O.....	0-1 Spot 1/16".....	10.....	10
Composition A+0.042% V or V ₂ O ₅	0-1.....	5% F....	10

*Composition A—3% NaOH, 0.2% CaFeMg.

coated with this solution by following the procedures above set forth, and thereafter painted in a comparable fashion with the identical paint.

A series of compositions were then prepared containing 0.75% NaOH, 0.011% cobalt ion and 0.002% ferric ion and 0.05% of the various sequestering agents which are set forth below in the table under the Series III compositions. With each of these solutions similarly cleaned zinc panels were spray-coated and painted using the identical procedures above described.

Panels from each of the three above described series were subjected to salt spray corrosion tests, humidity tests, knife adhesion tests and the formability tests, and each test was carried out under conditions identical to those described above in Example I, except as noted in the table. The results of those tests are set forth below in Table II.

EXAMPLE IV

This example illustrates the effect of the presence of combinations of metallic ions in the solutions of this invention. A first solution was prepared to contain 3% sodium hydroxide, 0.2% sodium hexahydroxyheptate, 0.008% ferric ion and 0.042% cobalt ion.

A second solution was prepared to contain 3% sodium hydroxide, 0.2% sodium hexahydroxyheptate and 0.042% cobalt ion.

A third solution was prepared to contain 3% sodium hydroxide, 0.2% sodium hexahydroxyheptate and 0.008% ferric ion.

A fourth series of varying solutions was prepared by adding metal ions other than the ferric ion to the third solution and a fifth series of solutions was prepared by adding metal ions other than cobalt to the second solution.

In each case, zinc panels of the type described above in

TABLE II

Series	Bath	Salt Spray 336 Hrs.	Humidity Hrs. 504	Forming	Adhesion
I.....	0.75% NaOH, 0.05% CaFeMg Seq., 0.011% Cobalt, 0.002% Fe ⁺⁺	10.....	VF 9.5.....	10.....	10
II.....	0.75% NaOH, 0.05% CaFeMg Seq.....	0-2.....	VF 9-9.5.....	10.....	10
III.....	Composition same as in Series I except each contains 0.05% of the specified sequesterant.				
	Dicarboxylic Acids:				
	1. Maleic Acid.....	10.....	VF 9-9.5.....	2.5% F.....	10
	2. Tartaric Acid.....	10.....	10.....	5% F.....	10
	3. Fumaric Acid.....	10.....	VF 9-9.5.....	10.....	10-9
	Amino Acids:				
	4. Glycine.....	0-3.....	10.....	10.....	10
	Hydroxycarboxylic Acids:				
	5. Citric Acid.....	10 Spot 1/16".....	VF 9.5.....	10.....	10-9
	6. Gluconic Acid.....	10.....	VF 9.5.....	0.5% P.....	10-9
	7. Lactic Acid.....	10.....	VF 9.5.....	0.5% P.....	10-9
	Hydroxyaldehyde:				
	8. Acetyl Acetone.....	0-1 Spot 1/16".....	VF 9.5.....	10.....	9
	Hydroxyaliphatic:				
	9. 1,2-ethanediol.....	10.....	10.....	10.....	10
	10. Sorbitol.....	0-1.....	VF 9.5.....	0.05% P, 2.5% F.....	10-9
	Phenolic Carboxylic Acid:				
	11. Salicylic Acid.....	0-1 Spot 1/16".....	VF 9.5.....	10.....	9
	12. Phthalic Acid.....	0-2.....	VF 9.5.....	0.5% F.....	9-8
	Amino Carboxylic Acid:				
	13. Ethylene Diaminetetraacetic Acid (Dow Chemical).....	10.....	VF 9.5.....	10.....	10
	Polyamino Acids:				
	14. Diethanolaminomethane phosphonate (Quester PFW A. R. Hass Chemical Company).....	10.....	VF 9.5.....	10.....	10
	Miscellaneous:				
	Marcarb NC (Marathon div. of American Can Co.).....	10 Spot 1/16".....	10.....	10.....	10
	The above is a complex mixture of the salts of lower molecular weight lignosulfonic acids and carboxylic and hydroxycarboxylic acids salts derived from carbohydrates produced from wood pulping process.				

EXAMPLE III

This example illustrates the effect of the presence of various separate metallic ions in the solutions of this in-

Example I were spray-coated under identical conditions to those specified in Example I and then painted with the same paint system and the painted panels were subjected

to the various tests described above in Example I. The results of these tests are set forth below in Table IV.

9. A method for coating metal surfaces containing iron and zinc which comprises contacting said surface with an

TABLE IV

Series	Bath	Salt Spray 504 Hrs.	Forming	Adhesion
I.....	3% NaOH, 0.2% CaFeMg, 0.008% Fe ⁺ , 0.042% Co ²⁺	10 Spot 1/16"	10.....	10-9
II.....	3% NaOH, 0.2% CaFeMg, 0.042% Co ²⁺	0-1.....	10.....	
III.....	3% NaOH, 0.2% CaFeMg, 0.008% Fe ⁺	0-2.....	10.....	
IV.....	Bath III+0.042% Ag as Ag NO ₃	10 Spot 1/16"	10.....	10-9
	Bath III+0.042% Mg as Mg(NO ₃) ₂	0-2 Spot 1/16"	1% F.....	10
	Bath III+0.05% Cd as Cd(NO ₃) ₂	10 Spot 1/16"	10.....	10-9
	Bath III+0.042% Sn as SnCl ₄	10 Spot 1/16"	10.....	10
	Bath III+0.042% Ti as TiO ₂	10.....	10.....	10
	Bath III+0.042% Sb as Sb ₂ O ₃	10 Spot 1/16"	10.....	10
	Bath III+0.042% Bi as Bi(NO ₃) ₃	0-1.....	10.....	9
	Bath III+0.042% Mo as Na ₂ MoO ₄	10 Spot 1/16"	10.....	9
	Bath III+0.042% W as Na ₂ WO ₄	10.....	10% F.....	9
	Bath III+0.042% Mn as Mn(NO ₃) ₂	10 Spot 1/16"	10.....	10
V.....	Bath II+0.008% As as As ₂ O ₃	0-1.....	10.....	10
	Bath II+0.008% Ce as Cerium Nitrate	10.....	2.5% F.....	10

What is claimed is:

1. A method for coating zinc and zinc alloy surfaces which comprises contacting said surface with an aqueous alkaline solution having a pH of at least about 11, which solution contains at least one metal ion other than an alkali metal ion selected from the group consisting of silver, magnesium, cadmium, aluminum, tin, titanium, antimony, molybdenum, chromium, cerium, tungsten, manganese, cobalt, ferrous and ferric iron and nickel, and a complexing agent present in said solution in an amount sufficient to hold said other metal ions in said solution and effecting a reaction between said solution and said metal surface to form a complex oxide paint-base coating on the metal surface, said metal ion selected from the indicated group being present in the treating solution in an amount sufficient to produce a coating quality which enables the thus-produced complex oxide coating to function as a base for paint.

2. The method as claimed in claim 1 wherein the aqueous alkaline solution contains at least one alkali metal ion.

3. The method as claimed in claim 2 wherein said other metal ion, other than an alkali metal ion, is present in an amount of at least 0.002% by weight per unit volume.

4. The method as claimed in claim 3 wherein said other metal ion is iron.

5. The method as claimed in claim 3 wherein said other metal ion is a plurality of ions and includes cobalt.

6. The method as claimed in claim 3 wherein said other metal ion is a plurality of ions and includes iron.

7. The method as claimed in claim 3 wherein said complexing agent is selected from the group consisting of sodium hexahydroxyheptate, sodium gluconate, and ethylenediaminetetraacetate.

8. The method as claimed in claim 3 wherein said solution is sprayed on said surface at a temperature within the range of about 90 degrees F. to about 200 degrees F.

aqueous alkaline solution having a pH of at least about 11, which solution contains at least one metal ion other than an alkali metal ion selected from the group consisting of silver, magnesium, cadmium, aluminum, tin, titanium, antimony, molybdenum, chromium, cerium, tungsten, manganese, cobalt, ferrous and ferric iron and nickel, and a complexing agent in a sufficient quantity to hold said other metal ions in said solution, effecting a reaction between solution and said metal surface to form a complex oxide paint-base coating on the zinc portion of the metal surface, said metal ion selected from the indicated group being present in the solution in an amount sufficient to produce a coating quality which enables the thus-produced complex oxide coating to function as a base for paint, thereafter, contacting said surface with an aqueous acidic phosphate solution selected from the group consisting of zinc phosphate solutions and alkali metal phosphate solutions and maintaining said phosphating solution in contact with said surface for a period sufficient to form a paint-base coating on the iron portion of said surface.

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U.S. Cl. X.R.

148—6.2, 6.14, 6.16