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**PRETREATMENT OF A METAL SURFACE FOR
CONVERSION COATING**

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ABSTRACT OF THE DISCLOSURE

A metal surface is treated in a bath containing phosphoric acid and a chlorate maintained at a pH of less than 2.7. Surfaces treated in this manner are more receptive to a subsequently applied corrosion-resistant and siccative paint bonding coat. Finally, to this bonding coat there is applied an organic finish.

The present invention relates to a composition and process for the treatment of metal surfaces and more particularly relates to a composition for and a process of preparing or conditioning metal surfaces to receive a subsequent protective coating.

It is well known that bonding coatings are desirable on metallic surfaces to protect such surfaces from corrosion and to form a base to promote adherence to such surfaces of organic finishes, generally in the form of paints, enamels, lacquers, etc. In the commercial manufacturing of metallic sheets, strips or the like, it has become customary to subject the sheet or strip to a treatment usually at the mill to protect the surface and prevent the formation of corrosion products in the interim between production of the sheet and the ultimate finishing of its surface and its intended end use. A variety of processes are used for the purpose and many specifically different compositions have been proposed as satisfactory for use in such processes.

At the present time well over 90 percent of all bonding coats on metal are phosphate coats or chromic acid in combination with any of the other activator ingredients such as chlorides, sulfates, fluorides, phosphates, complex fluorides, borates, etc. to form a protective coating on the surface. They generally are applied in the following manner: the sheet metal or strip is first thoroughly cleaned in an alkaline solution, the adherent solution then being removed by a water rinse. The clean metal is next either immersed in a hot bath or sprayed with a solution containing the bonding coat material until a coating of desired thickness or weight is formed. Generally, the weight of the bond coating is in the range of about 30 to 200 or more milligrams per square foot, preferably about 50 to 150 milligrams per square foot. A water rinse follows to remove all coating solution and nonadherent sludge. Some of these processes produce colorless coatings while others produce gray-colored coatings, but all are considered to contain a metallic phosphate or chromate or their combination as one of the coating components. After the water rinse, the bonding coat is dried at any convenient temperature as by air drying, since there is nothing required beyond the removal of the moisture from the bonded surface.

When an attempt is made to apply an organic finish

to the bonding coat, it has been found that the use of conventional cleaning or conditioning procedures prior to the application of the siccative paint-bonding coat are ineffective to promote the desired degree of adherence of organic finishes to the bonding coat on the metallic surfaces. For example, the organic finishes are relatively easily chipped, flaked or peeled from the metal surface, when the metal is subjected to bending or mechanical shock, and such removal of the finish leaves portions of the surface exposed to sources of corrosion which may be in contact therewith.

In accordance with the present invention, it has now been found that metal surfaces pretreated with an oxidizing bath containing phosphoric acid and a chlorate as the sole oxidizing agent, while maintaining the acidity of the bath at a pH level of less than 2.7, are rendered much more receptive to an adherent corrosion-resistant and siccative paint-bonding coat than has previously been obtained by prior art methods. The pretreatment process of the present invention is of special importance where the siccative paints are applied to metal articles and the articles are thereafter exposed to bending stress which would ordinarily cause the organic finish, usually containing color or lacquer coatings, to crack or peel were it not for the pretreatment on the metal surface.

The use of a solution containing a phosphorus-containing compound and an oxidizing agent such as a chlorate has been previously proposed for the treatment of metal surfaces. However, the use of such phosphorus-containing solutions has been for the purpose of producing a passivating phosphorus-containing coating on the metal surface. Generally, the phosphorus-containing compound is added to the solution in the form of either an alkali metal phosphate or a Group II metal phosphate to form a substantially insoluble rust and corrosion-resistant phosphate coating on such surfaces. Thus, conventional phosphate coatings are formed by a process using a single bath which contains phosphates, an oxidizing agent and sometimes other ingredients. The metallic article to be coated is placed in such bath and the required reactive conditions are established and maintained until the desired coating is formed.

As distinguished from such conventional processes, the present invention utilizes a novel solution for, and a process of, preparing or conditioning metal surfaces to receive a bonding coat. In accordance with the present invention the properly cleaned metallic articles to be treated are immersed in or sprayed with an oxidizing bath containing about 0.5 to 10 percent, preferably about 1 to 3 percent, phosphoric acid by weight and 1 to 10 grams, preferably 1 to 5 grams, of chlorate ion per liter of bath solution and the balance water while maintaining the acidity of the bath at a pH level within the range of from 0.5 to 2.7, preferably 1 to 2.2 at a bath temperature of between about 50° to 212° F., preferably 70° to 180° F.

The time of reaction during which the articles to be treated are subjected to the action of the solution depends on the composition of the metal, the nature of the surface, and the purpose for which the treated working piece is intended to serve. As a general rule, the articles need only be immersed in or sprayed with the solution for a short time, for the reaction taking place at the surface of the metal to be completed. Generally, it is sufficient

when operating at temperatures of between 50° and 212° F. to treat the surface for a period of time up to about 30 minutes but generally varying from about 5 seconds to 5 minutes and preferably about 15 seconds to 2 minutes. As a general rule, an increase of the temperature does not require a substantial alteration of the treatment period, but it has been found that by increasing the temperature, the time during which the article to be treated is subjected to the action of the solution may be decreased. For instance, at temperatures of 70° F., it has been found that the pretreatment is effected after a period of about 2 minutes; at 140° F. after a period of 1 minute; and at 180° F. after a period of 15 seconds.

Before starting the treatment of the present invention it is, in most cases, advisable to remove foreign matter from the metal surfaces by thoroughly cleaning and de-greasing. The de-greasing may be accomplished with known agents, for instance, with agents containing sodium metasilicate, caustic soda, carbon tetrachloride, trichloroethylene, etc.

It is to be understood that the term phosphoric acid is intended to include meta-phosphoric, ortho-phosphoric, pyro-phosphoric, tripoly-phosphoric, tetra-poly-phosphoric acid and other polyphosphoric acids. The chlorate ions may be conveniently introduced into the bath solution in the form of a metallic salt and preferably as the sodium salt. However, other metal salts such as potassium, barium, or magnesium chlorates may also be used.

When repeatedly used, the aqueous solution shows a certain depletion of its ingredients since they have been consumed in the treating of the metal surface. For this reason, the ingredients of the solution are replenished at a rate corresponding to their consumption, by introducing solutions containing the desired ingredients to the original solution to maintain the pH level within a range of about 0.5 to 2.7. Also, to avoid the undesirable formation of sludge in the treating bath, and to allow continual operation, it has been found advantageous to add about 1 to 10 grams per liter of solution, preferably 1 to 5 grams per liter of solution, nitric acid.

In the preferred practice of the present invention, the metal surfaces may be after-treated by thoroughly rinsing them with water in order to remove adhering ingredients of the bath, and thereafter without permitting the article to be dried immersing the pretreated metal article into the coating bath described hereinbelow.

The siccative paint-bonding coat which may be applied to the pretreated metallic surface can include any of the bond coatings commercially used. For instance, Table I contains various formulations of chromate-phosphate solutions which may be used in forming the siccative paint-bonding coating.

TABLE I

I	
	Grams/liter
Chromic acid (CrO ₃)	40-200
Magnesium oxide	12-60
Phosphoric acid	15-75
Ethylene glycol	7-35
Nonionic wetting agent	0.2-0.3

(Equivalent amounts of ammonium bichromate may be substituted for the chromic acid.)

II	
	Grams/liter
Chromic acid (CrO ₃)	40-200
Calcium carbonate	20-100
Phosphoric acid	12-60
Ethylene glycol	7-35
Nonionic wetting agent	0.2-0.3

(Equivalent amounts of ammonium bichromate may be substituted for the chromic acid.)

		Grams/liter
5	Chromic acid ¹	40-200
	Calcium carbonate ²	1-5
	Phosphoric acid	12-60
	Zinc oxide ³	14-69
	Ethylene glycol	7-35
	Nonionic wetting agent	0.2-0.3

10 ¹ Ammonium bichromate may be substituted for the chromic acid.
² Calcium oxide may be substituted in equivalent amounts for the calcium carbonate.
³ Aluminum hydroxide, magnesium oxide or magnesium carbonate may be substituted in equivalent amounts for the zinc oxide.

IV

		Grams
15	Disodium dihydrogen pyrophosphate	20
	Sodium chlorate	5
	Ferric chloride (FeCl ₃ ·6H ₂ O)	0.5
20	Water, to make 1 liter.	

V

25	Dipotassium dihydrogen pyrophosphate	20
	Sodium nitrite	5
	Ferric nitrate (Fe(NO ₃) ₃ ·9H ₂ O)	1
	Lavapon WS-2 ¹	1
	Water, to make 1 liter.	

¹ An alkyl aryl polyether alcohol with 10 ethylene oxide groups.

VI

		Parts
30	Chromic acid (CrO ₃)	0.90
	Phosphoric acid	0.85
	Ethylene glycol	0.25
35	Water	98.00

VII

40	Ammonium bichromate	2.0
	Ammonium dihydrogen phosphate	1.0
	Hypophosphorus acid	0.5
	Water	96.5

VIII

45	Zinc dichromate	2.8
	Dow Latex 566 (butadiene-styrene copolymer dispersion—the percentage being based on copolymer solid weight)	2.0
	Sucrose	0.6
	Triton 102 ¹	0.04
	Water	94.56

¹ An alkyl aryl polyether alcohol made by condensing one mol of p-(n-octyl)phenol with three mols of ethylene oxide.

IX

		Grams
50	Zinc dichromate	6
55	Sucrose	2
	Aqueous dispersion of polytetrafluoroethylene having 50% resin solids content by weight, 4 cc.	
	P-octyl phenyl tri-oxyethylene ethanol.	0.05
	Water, to make 4 liters.	

X

		Parts
60	Chromic acid (CrO ₃)	3
	Triethanolamine	1
65	Water	96

XI

70	Chromic acid (CrO ₃)	3
	Acrysol A-1 (polyacrylic acid)	3
	Water	94

XII

75	Chromic acid (CrO ₃)	4
	Zinc oxide	1.42
	Sucrose	1.3
	Water	93.28

The bond-coating solution may be applied to the pretreated metal surface either by spraying or by dipping the article into the solution. The metal carrying film of coating solution may be heated to a temperature of from about 100° F. to about 400° F., at which temperature the oxidants and reducing agents are substantially completely destroyed in the coating film with reduction of hexavalent chromium and formation of a highly adherent, oxidation-resisting, chemically inert, bonding coat consisting chiefly of compounds of chromium and phosphorus, probably chromic phosphate.

The bonding coat which forms on the pretreated metal surface is continuous, thin, highly adherent, hard, smooth, and lustrous, and without nonadherent material. These features permit repeated flexing of the coated metal through 360 degrees, deep-drawing of the metal up to the point where the metal itself tears, and similar fabricating operations involving deforming techniques, without destruction of the coating. Thus, organic finishes when applied to siccative paint-bonding coatings on metal surfaces which have been pretreated according to the present invention, do not decompose at the interface and are very difficult if not impossible to remove from the pretreated metal surface containing the bonding coat, short of destruction of the metal surface itself. Thus, metal surfaces pretreated according to the method of the present invention may receive organic finishes having an end use as: automobile finishes, can coatings, appliance coatings, precoatings of strip metals, coatings on metal building panels (house siding, gutters, downspouts, etc.), mobile home exteriors, exterior trim, metal cabinets and tables, and the like.

Exemplary of organic finishes which may be applied to the bond coating include: epoxy resins, e.g. reaction product of epichlorohydrin and polyhydric phenols, oxidation of olefins with peracetic acid or phenol-formaldehyde condensate esterified with epichlorohydrin vinyl resins (homopolymers and copolymers), e.g. polyvinyl chloride, polyvinyl fluoride, polyvinyl acetate, polyvinyl butyral, etc.; acrylic ester resins, e.g. polymerized esters of acrylic and a-methacrylic acid and a copolymer of methyl acrylate and hydroxyethyl methacrylate; cellulose-based finishes, e.g. cellulose acetate, nitrocellulose and cellulose acetate butyrate; polyester resins, e.g. tetrahydrophthalic anhydride based polyesters, etc.; polyurethanes, e.g. reaction product of hydroxyl bearing resins and a diisocyanate; silicones; rubber resins; alkyds, e.g. reaction product of polybasic acids and polyhydric alcohols; amino resins, e.g. urea-formaldehyde and melamine-formaldehyde; and phenolic baking resins, e.g. phenol-formaldehyde resins. Organic finishes may be applied to the bonding coating up to a thickness of about 100 to 200 mils when used in corrosion type coatings; but, generally, they are applied in the range of about 0.2 to 20 mils. After applying the organic finish to the bond coating, the coated article is heated for a sufficient period of time to achieve essentially a dry organic finish. Temperatures in the range of about 70° to 600° F. are generally used for a period of time from a few minutes up to about 48 hours, usually from about 1 hour to about 24 hours.

Characteristics of the above-mentioned organic finishes and application methods for applying these finishes to surfaces are discussed more fully in the following publications: American Paint Journal, September 1963, p. 112A; American Finishing Guidebook, Directory for 1963, Plastics Publication, Inc. p. 537; and Finishing Handbook & Directory 1963, Product Finishing, Sawell Publications Ltd., London, p. 129, hereby incorporated by reference.

Metal surfaces which may be treated according to the practice of the present invention include the ferrous metals, zinc, aluminum, and their alloys.

In order that those skilled in the art may more completely understand this invention and the methods by

which the same may be carried into effect, the following specific examples are offered:

Example 1

This example is offered to show the effect of the pH level of the pretreatment bath on the adhesion of a subsequently applied organic finish.

Bath solutions, having varying pH levels, are made by mixing in water phosphoric acid (85% o-phosphoric) and sodium chlorate. Ammonium phosphate is also added to the bath solutions in varying amounts to regulate the pH level of each of the baths. The amount of each additive, the estimated pH level and the actual pH level are given in Table II below.

TABLE II

Sample	H ₃ PO ₄ , cc./l.	NaClO ₃ , g./l.	NH ₄ H ₂ PO ₄ , g./l.	Estimated, pH	Actual, pH
A-----	10	3	0	1	1.8
B-----	6 $\frac{2}{3}$	3 $\frac{2}{6}$	3 $\frac{2}{3}$	2	2.0
C-----	2 $\frac{2}{3}$	3	7 $\frac{2}{3}$	3	2.7
D-----	$\frac{3}{4}$	3	15	4	3.75
E-----	0	3	15	5	5.05
F-----	0	3	15	6	5.9

¹ 1 gram of NaOH is also added.

Seven steel panels (4" x 12") are cleaned with an aqueous solution containing 20 g./l. NaOH and 10 g./l. KMnO₄. Into each of the above-identified pretreatment bath solutions is dipped one of the six previously cleaned steel panels for 45 seconds at a temperature of 140° F. The steel panels are then removed from the bath solutions and rinsed with water. The water-rinsed pretreated steel panels are then dipped into a 10% bond-coating solution consisting of:

	Grams
CrO ₃ -----	400
ZnO -----	138.6
H ₃ PO ₄ (100%) -----	120
CaCO ₃ -----	10
Ethylene glycol -----	174.4
Water, diluted to 1 liter.	

¹ Sufficient to reduce all Cr⁺⁶ to Cr⁺³ (0.186 gram ethylene glycol/gram CrO₃).

The seventh previously cleaned steel panel (Sample G), not subjected to a pretreatment bath, is also dipped into the 10% bond-coating solution until a bond coating weight of 100 milligrams per square foot is formed. The seven steel panels are taken from the bond-coating solution and are baked at 350° F. for 3 minutes. The seven steel panels are then painted with an acrylic paint system and baked at 385° F. for 20 minutes.

The painted steel panels are subjected to a bend test conducted in accordance with the standard method of ASTM B-522-41, which generally involves bending a lengthwise portion of the panel through 180° around a conical mandrel (Gardener Laboratories Conical Mandrel), having a small diameter of $\frac{1}{8}$ inch, the diameter four inches from the small end being one inch, and a length of 8 inches. The results of the bending test are reported in terms of flaking or fracture (craze) of the paint system. Flaking indicates separation of the coating from the panel surface. After the steel panels are subjected to the bend test, they are subjected to the Scotch adhesion test using Scotch filament tape #880. The results of the bend and adhesion tests are given in Table III.

TABLE III

Sample	Actual pH of Pretreat- ment Bath	Bend Test	Adhesion Test
A-----	1.8	No flaking or fracture.	No peeling.
B-----	2.0	do	Do.
C-----	2.7	Flakes and fractures.	
D-----	3.75	do	
E-----	5.05	do	
F-----	5.9	do	
G-----		No flaking or fracture.	Paint removed by tape.

¹ No pretreatment of Sample G.

It can be seen from the test results that, when the pH of the pretreatment bath is at a level of 2.7 or above the paint system flakes and fractures when the painted panel is subject to the bend test; whereas when the pH level of the pretreatment bath is below 2.7, e.g. 1.8 and 2, respectively, no flaking or fracture occurs and the paint system is not removed by the Scotch adhesion test, indicating good adhesion to the metal surface. Although Sample G, the steel panel not subjected to a pretreatment bath, passes the bend test, the paint coating is easily removed from the metal surface by the Scotch filament tape.

Example 2

Three 4" x 12" steel panels (Samples H to L) are cleaned with an aqueous solution containing 20 g./l. NaOH and 10 g./l. KMnO₄. Each of these steel panels are then dipped into an aqueous pretreatment bath solution for 1 minute at a temperature of 140° F. The pretreatment bath contains 10 cc./l. of H₃PO₄ (85%) and 3 grams/l. NaClO₃, and has a pH of 1.8. The pretreated steel panels are removed from the pretreatment bath solution and rinsed with water. Each panel is then dipped in a bond-coating solution, removed and heated for 3 minutes at 350° F. The bond-coating solutions are identified in Table IV below.

The three steel panels are then painted with an acrylic paint system and baked at 385° F. for 20 minutes. The painted steel panels are then subjected to the bend and adhesion tests described in Example 1. These results are also reported in Table IV.

TABLE IV

	Bend Test	Adhesion Test
Sample H, Coating Bath:		
Chromic Acid (CrO ₃), 3%-----	No flaking or fracture	30% paint removal.
Triethanolamine, ¹ 1%-----	-----	-----
Water, 96%-----	-----	-----
Sample I, Coating Bath:		
Chromic Acid (CrO ₃), 4%-----	Slight fracturing of paint surface.	50% paint removed.
Zinc Oxide, 1.42%-----	-----	-----
Sucrose, ² -----	-----	-----
Water, 93.28%-----	-----	-----
Sample K, Coating Bath:		
Chromic Acid (CrO ₃), 3%-----	No flaking or fracture.	No peeling.
Acrysol A-1 (poly-acrylic acid), ³ 3%-----	-----	-----
Water, 94%-----	-----	-----

¹ Sufficient for reducing 60% of chromium from hexavalent state to trivalent state upon heating to 350° F.

² Sufficient for reducing 60% of chromium from hexavalent state to trivalent state upon heating to 350° F.

³ Sufficient for reducing 100% of chromium from hexavalent state to trivalent state upon heating to 350° F.

It can be seen from the above results, when chromic acid is the sole coating material in the bond coating bath, it is necessary to reduce 100% of the chromium from the hexavalent state to the trivalent state to achieve good paint adhesion to the pretreated metal surfaces.

Example 3

Samples M to R, (four 4" x 12" panels of each) are prepared using various treating and bond coating compositions. Samples P to R are commercially prepared metal panels containing zinc phosphate as the bond coating. Two panels of each sample are painted with an epoxy paint system and the remaining two panels of each sample are painted with an acrylic paint system. The treatment of the metal panels are described in Table V, below.

One panel of each sample, painted with the epoxy paint system; and one panel of each sample, painted with the acrylic paint system, are subject to an appliance detergent test which comprises immersing the painted samples in a 1% detergent solution, maintained at a temperature of 165° F.±3". The detergent solution contains:

	Grams
25 Na ₄ P ₂ O ₇ -----	53
Na ₂ SO ₄ -----	19
Naccanol NRSF ¹ -----	20
Na ₂ SiO ₃ -----	7
30 Na ₂ CO ₃ -----	1
Water, to 1 liter.	

¹ A surface active agent-sodium alkyl aryl sulfonate.

The remaining painted panels are subjected to the Gravelometer test which indicates adhesion of the paint system to the metal surface and comprises shooting 20 pounds of steel shot with 60 pounds of air pressure against the painted surfaces. The results of the appliance detergent test and the Gravelometer test are also reported in Table V.

As can be seen from the Table V results, Samples M and N, pretreated with the composition for conditioning metal surfaces, are equivalent to commercially prepared coated metal surfaces, Samples O to R.

Other painted panels treated with a phosphoric-acid chlorate bath (pH 1.8), prior to the application of the bonding coat, were subjected to the standard humidity test and after 140 hours the paint on the panels blistered. This test indicates good adhesion of the paint system to the bond coating.

TABLE V

	Detergent Test	Gravelometer Test
Sample M (Steel):		
I. 4 cleaned steel panels are pretreated with phosphoric acid-chlorate bath (pH 1.8) for 45 seconds at a temperature of 145° F.	No blistering of paint system (acrylic and epoxy) after 600 hours.	No chipping of paint system (acrylic and epoxy) observed.
II. Rinsed with water and dipped into the 10% bond coating bath of Ex. 1.		
III. Bond coated panels are heated for 3 minutes at 350° F.		
IV. Two of the steel panels are coated with an acrylic paint and the other two panels are coated with an epoxy paint.		
V. The painted steel panels are baked for 20 minutes at 385° F.		
Sample N (Galvanized Steel):		
I.-V. 4 cleaned galvanized steel panels are treated the same as Sample M.	-----do-----	Do.
Sample O (Galvanized Steel):		
I. 4 cleaned galvanized steel panels are pretreated with a bath solution containing 20 g./l. NaOH and 10 g/l. KMnO ₄ for 30 seconds at a temperature of 160° F.	-----do-----	No chipping of paint system (acrylic and epoxy) after 600 hours.
II.-V. Same treatment as Sample M.		
Sample P (Galvanized Steel):		
I. Previously prepared zinc phosphate bond coating on galvanized steel is treated according to Steps IV and V of Sample M.	-----do-----	No chipping of paint system (acrylic or epoxy) observed.
Sample Q (Steel):		
I. Previously prepared zinc phosphate bond coating on steel is treated according to Steps IV and V of Sample M.	-----do-----	Do.
Sample R (Galvanized Steel) ¹ :		
I. Previously prepared zinc phosphate bond coating on a particular galvanized steel is treated according to Steps IV and V of Sample M.	-----do-----	Do.

¹ Supplied by Weirton Steel Co.

It is to be understood that, although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

It is claimed:

1. A method for conditioning the surface of a metal selected from the group consisting of ferrous metal, zinc, aluminum, and alloys thereof to receive a bonding coating selected from the group consisting of chromate, phosphate and chromate-phosphate bonding coats which method comprises the steps of applying to said surface an aqueous solution maintained at a pH level less than 2.7, said solution consisting essentially of phosphoric acid and a metal chlorate as an oxidizing agent, said phosphoric acid being present in said solution from 0.5 to 10 percent by weight, and from 1 to 10 grams of chlorate ion per liter of solution.

2. The method of claim 1 wherein the aqueous solution is maintained at a pH from 1 to 2.2.

3. The method of claim 1 wherein said metal chlorate is selected from the group consisting of sodium, potassium, barium and magnesium chlorate.

4. The method of claim 1 wherein the phosphoric acid is present in an amount from 1 to 3 percent by weight of solution.

5. The method of claim 1 wherein the metal chlorate is sodium chlorate and the chlorate ion is present in the aqueous solution in an amount from 1 to 5 grams per liter of solution.

6. The method of claim 1 wherein the temperature of the aqueous solution is within the range of 50 to 212° F. and the contact time is for a period of time up to 30 minutes.

7. The method of claim 6 wherein the temperature of the aqueous solution is within the range of 70 to 180° F., and the contact time is from 10 seconds to 5 minutes.

8. The product produced by the method of claim 1.

9. A method of conditioning the surface of a metal selected from a group consisting of ferrous metal, zinc, aluminum, and alloys thereof, to receive a bonding coating selected from the group consisting of chromate, phosphate and chromate-phosphate bonding coats which method comprises the steps of applying to said surface an aqueous solution maintained at a pH from 0.5 to 2.7 in a temperature range from 50 to 212° F., and the contact time is from 10 seconds to 5 minutes, said solution consisting essentially of 1 to 10 percent by weight of phosphoric acid and from 1 to 5 grams per liter of solution of chlorate ion, said chlorate ion being supplied to said solution by sodium chlorate.

10. A method for producing an adherent bonding coat selected from the group consisting of chromate, phosphate and chromate-phosphate bonding coats on a metal base selected from the group consisting of ferrous metal, zinc, aluminum and alloys thereof which method comprises the steps of applying to said base an aqueous solution maintained at a pH level less than 2.7, at a tempera-

ture within the range of 50° to 212° F. for a period of time up to 30 minutes, said solution consisting essentially of phosphoric acid and a metal chlorate as an oxidizing agent, said phosphoric acid being present in said solution from 0.5 to 10 percent by weight, and from 1 to 10 grams of chlorate ion per liter of solution; removing the treated metal base from said solution, rinsing said treated metal base with water, applying to said treated metal base a bonding coat selected from the group consisting of chromate, phosphate and chromate-phosphate bonding coats having a bonding coat weight of 30 to 200 milligrams per square foot and heating said applied bonding coat to a temperature sufficient to substantially destroy the oxidants and reducing agents in said bonding coat.

11. The method of claim 10 wherein the applied bonding coat is heated to a temperature of 100 to 400° F.

12. The product produced by the method of claim 10.

13. A method of producing an adherent organic finish on a metal base selected from a group consisting of ferrous metal, zinc, aluminum and alloys thereof and having a bonding coating thereon selected from the group consisting of chromate, phosphate and chromate-phosphate bonding coats which method comprises the steps of applying to said base an aqueous solution maintained at a pH level less than 2.7, at a temperature within the range of 50° to 212° F. for a period of time up to 30 minutes, said solution consisting essentially of phosphoric acid and a metal chlorate as an oxidizing agent, said phosphoric acid being present in said solution from 0.5 to 10 percent by weight, and from 1 to 10 grams of chlorate ion per liter of solution; removing the treated metal base from said solution, rinsing said treated metal base with water, applying to said treated metal base a bonding coat selected from the group consisting of chromate, phosphate and chromate-phosphate bonding coats having a bonding coat weight of 30 to 200 milligrams per square foot, heating said applied bonding coat to a temperature sufficient to substantially destroy the oxidants and reducing agents in said bonding coat, and applying to said bonding coat an organic finish.

14. The method of claim 13 wherein the thickness of the applied organic finish is 0.2 to 20 mils.

15. The method of claim 13 wherein the organic finish is heated to a temperature in the range of 70° to 600° F. for a period of time sufficient to achieve an essentially dry organic finish.

16. The method of claim 13 wherein the applied bonding coat is heated to a temperature of 100° to 400° F.

17. The product produced by the method of claim 13.

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