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2,901,385

MICRO-CRYSTALLINE BONDING COATS FOR METAL

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This application is a continuation-in-part of my co-pending applications, Serial Number 499,510, filed April 5, 1955, now abandoned, and Serial Number 537,900, filed September 30, 1955, now Patent No. 2,846,432, issued Aug. 5, 1958.

This invention relates to oxidation-inhibiting and bonding coats on aluminum, zinc and ferrous metal surfaces and it comprises wetting a metal surface free from water-breaks with a solution containing a dichromate of a divalent metal at least as high as iron in the electromotive series, the solution also containing a reducing agent which is comparatively inert at atmospheric temperatures but which actively reduces chromate to the trivalent form at temperatures above 100° C., the solution also containing at least one phosphate of the class of dihydrogen phosphates of divalent metals at least as high as iron in the electromotive series and free phosphoric acid, the bonding coat being formed by destroying substantially completely the oxidants and reducing agents in the film of chromate solution adhering to the metal surface by heating said film to a temperature of at least 100° C., the residue remaining on the metal surface constituting a highly adherent, oxidation-resisting, chemically inert, micro-crystalline bonding coat; all as is more fully herein-after set forth and as claimed.

Rust-inhibiting and bonding coats formed on metal by means of an aqueous solution are of three types, principally: (a) phosphate coats, invented by Coslett, U.S.P. 870,937; (b) oxalate coats, invented by Gravell, U.S.P. 1,315,017; (c) chromate treatments, at least as old as Lang, U.S.P. 1,082,161. At present, the most important use of chromate in metal coating is as a 0.10 percent chromic acid solution, applied as a rinse over a previously formed phosphate coating. Also, chromate has been applied over an iron oxide surface previously developed on the metal by means of oxygen at high temperature or by means of a nitric acid or other oxidizing solution, U.S.P. 2,210,850, Curtin, describes the first of such processes.

At the present time, well over 90 percent of all bonding coats on metal are phosphate coats and these are, in nearly all cases, applied in the following manner. The sheet steel or other metal is first thoroughly cleaned in an alkaline solution, the adherent solution then being removed by a water rinse. The cleaned metal is next immersed in a hot phosphate coating bath and kept there until a coating of the desired thickness or weight is formed. Equivalent results are obtained by subjecting the metal to a continuous spray of hot phosphating solution until the desired coating is obtained. A water rinse follows to remove all coating solution and non-adherent sludge. The phosphate coating may then be given a rinse with a 0.10 percent solution of chromic acid, although this is not an essential part of the process. Drying may be done at any convenient temperature, as by air-drying, since there is nothing required beyond removal of the moisture from the phosphated surface. On the large

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scale, however, where speed is essential, drying is done at an elevated temperature.

The chemical composition of the phosphate coating baths is necessarily very carefully controlled by frequent chemical analyses and otherwise. Coating formation is only one of the chemical reactions which takes place. Other reactions produce highly objectionable sludge in the bath. It is necessary to have a certain formula for the makeup and a different formula for the replenishment of such baths. Sodium nitrite, the preferred oxidant, is carefully and continuously metered into the bath at a predetermined rate and the nitrite content of the bath also requires frequent checking.

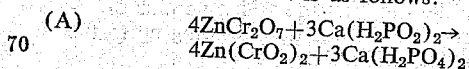
The process of the present invention is carried out in three steps: (1) freeing the surface of the metal from water-breaks, (2) wetting the surface with a chromate-phosphate solution and (3) destroying oxidants and reducing agents in the film of chromate-phosphate solution adhering to the metal by heating to above 100° C., the residue remaining on the metal surface constituting the desired bonding coat.

In regard to step (1), there are a number of means for reaching this objective. In some cases, metal may be freed from water-breaks by heating substantially above 100° C. Mechanical working of metal, as in the manufacture of steel strip or sheet by the cold-rolling process accomplishes the same result. By far the greatest amount of metal prepared for coating is treated with hot, alkaline solutions which remove dirt and grease and, if properly applied, leave a surface free from water-breaks. A solution containing about 2 percent of sodium metasilicate at 60 to 90° C. has been found to be unusually effective in connection with the present invention. This art is very well understood and is currently practiced on a very large scale. It will be evident that elimination of water-breaks in some fashion is an essential part of the present process as such areas would be wetted imperfectly or not at all by the chromate solution with consequent impairment of the coating.

In regard to step (2), various formulae are given for the chromate solution in the examples which follow. The chromate solution contains phosphate in the form of a divalent metal dihydrogen phosphate, or phosphoric acid, or both. The phosphate present forms part of the coating, usually as insoluble divalent metal phosphates although, in some cases, a little chromic phosphate, CrPO_4 , is formed, this substance being a desirable component of the coating.

The solution also contains a reducing agent for chromate which actively reduces hexavalent chromium to the trivalent form above 100° C. while being relatively inert at atmospheric temperatures. This last property is essential, otherwise, the chromate would be reduced immediately to the trivalent form, before being applied to metal. Since a solution of trivalent chromium has no coating properties, when applied to metal, the usefulness of the solution would be at once destroyed if the reducing agent reacted with chromate at the ordinary temperature. It is essential, therefore, that the chromate and reducing agent be capable of existing together in the same solution at ordinary temperatures, for a reasonable time, perhaps one to several weeks, with no particular impairment of the efficiency of the coating solution.

There are more than 100 reducing substances which might be used in the present invention. One of the best is hypophosphorous acid which works equally well in the form of its divalent metal salts or as ammonium hypophosphite. The reaction is as follows:



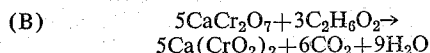
The zinc chromite formed is a coating component.

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The calcium dihydrogen phosphate reacts further with the under-lying metal or with substances present in the solution to form more basic phosphates which are also coating components.

Many organic compounds are desirable reducing agents for chromate, especially those which oxidize to carbon dioxide and water. Such substances as fumaric, maleic, citric, lactic, oxalic and hydroxyacetic acids are in this class. Formic acid is less desirable since it tends to vaporize before reducing chromate.

Polyhydroxy alcohols, as glycerol, propylene glycol, trimethylene glycol and ethylene glycol are most desirable, the last-named being particularly useful. The reaction using ethylene glycol is as follows:



The calcium chromite formed is a coating component. Similar reactions take place with many other organic reducing substances.

Fatty alcohols containing from about 12 to about 18 carbon atoms, for example, n-dodecyl alcohol, when made soluble by mono-esterification with a suitable polybasic acid, are able to function not only as a reducing agent but, in the form of the divalent metal salts of the resulting fatty acids, as zinc laurate, are capable of forming part of the coating and increasing its water-repellant properties. Compounds of the type of n-dodecyl phosphoric acid mono-ester are especially suitable since both the fatty acid and the free phosphoric acid resulting from oxidation produce coating components.

Certain other derivatives of the fatty alcohols function in similar fashion. For example, such substances as the myristamide of bis-diethanolamine and the polyethoxyethanol derivatives of stearic acid oxidize in the chromate solution with production of the free fatty acid which enters the coating in the manner described. Polyethoxy derivatives of fatty alcohols and amines function in analogous manner.

Because of the complexity of the various chemical reactions involved, which include a slight attack on the metal being coated by hydrogen-ion from the phosphates present, optimum results are often obtained by using the reactants in somewhat different proportions than shown by Reactions A and B.

In many cases, a small amount of free acid is needed to stabilize the solution against hydrolysis with precipitation of such substances as barium chromate and zinc monohydrogen phosphate. A small concentration of free phosphoric or chromic acid checks such tendencies. When the reducing agent present is a fairly strong acid, as maleic, such acid also inhibits hydrolysis. When the acid is destroyed in coating formation, the need for stabilizing the solution no longer exists.

In regard to step (3), the heating of the film of chromate solution adhering to the metal surface to destroy oxidants and reducing agents may be accomplished in many different ways. Perhaps the most convenient is to utilize a current of air or other gas preheated to 150, 200 or 300° C. Such a treatment produces the coating very quickly, the elimination of moisture being accomplished incidentally.

A competent chemist would probably expect that such a treatment of the film of chromate solution would leave a residue of powdery, non-adherent material which could be brushed off the metal surface, in fact, he would have no basis for any other expectation. Most surprisingly, the coating which is actually formed is perfectly continuous, thin, highly adherent, hard, smooth, lustrous and dust-free with no non-adherent material. The coating has a micro-crystalline to amorphous structure, also unpredictable, and it is this feature which permits of repeated flexing through 360° and deep-drawing up to the point where the metal itself tears.

The micro-crystalline structure is believed to result

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from the great rapidity of the coating formation, also, to the fact that the chromites and phosphates are forced to crystallize in the presence of each other.

It might also be expected that the coating, if formed, would have properties which are the sum of the phosphate and chromite components. Such, however, is not the case; the chromite-phosphate coatings of the present invention are definitely superior to ordinary phosphate coatings or to simple chromite or chromic hydroxide coatings in the matter of resistance to oxidation and greatly superior to such coatings with respect to deep-drawing and similar fabricating operations. Ordinary phosphate coatings are particularly inferior when subjected to drawing and other deforming operations. The phosphate coatings are relatively coarsely crystalline and, in deep-drawing, the hard brittle, crystals tear loose and scratch both the work and the die.

Coatings of the present invention take vinyl lacquer coatings perfectly, in fact, they act as stabilizers of the vinyl resins against thermal decomposition. The coatings containing calcium as the only divalent ion are particularly noteworthy in this respect. This important property, also unforeseen, is of great value in the baking of the vinyl resins on iron and other metals which catalytically decompose them.

The following examples show various formulations of the chromate-phosphate solution which is used in step (2). Usually, the chromate is made into a 25 percent solution and a second solution is made of the reducing agent and the phosphate components. These are combined in the proper proportions at the point of use. The substances other than water are on an anhydrous basis, and in parts by weight.

35	Example 1:	Parts
	Zinc dichromate	2.8
	Magnesium dihydrogen phosphate	0.4
	Phosphoric acid	0.1
	Hydroxyacetic acid	0.8
	Water	95.9

This is a general purpose formula, suitable for zinc, aluminum and steel.

40	Example 2:	Parts
	Zinc dichromate	11.2
45	Zinc dihydrogen phosphate	1.2
	Phosphoric acid	0.5
	Ethylene glycol	2.3
	Water	84.8

50 This concentrated formula is adapted to the spray treatment of preheated metal, especially sheet steel, where excess water is undesirable.

	Example 3:	Parts
55	Magnesium dichromate	2.4
	Magnesium dihydrogen phosphate	0.5
	Ethylene glycol	0.6
	Water	96.5

60 The formula of Example 3 is especially useful for zinc and aluminum.

	Example 4:	Parts
	Magnesium dichromate	2.4
	Barium dihydrogen phosphate	0.8
65	Phosphoric acid	0.5
	Fumaric acid	0.3
	Water	96.0

Example 4 shows a general purpose formula.

70	Example 5:	Parts
	Calcium dichromate	2.6
	Calcium dihydrogen phosphate	0.5
	Phosphoric acid	0.2
	Ethylene glycol	0.6
75	Water	96.1

Example 5 is particularly desirable for the coating of sheet steel to be made into food containers.

Example 6:	Parts
Calcium dichromate -----	2.6
Phosphoric acid -----	0.4
Ethylene glycol -----	0.6
Water -----	96.4

Example 6 is also adapted for food containers.

Example 7:	Parts
Calcium dichromate -----	2.6
Zinc dihydrogen phosphate -----	0.1
Phosphoric acid -----	0.2
Calcium hypophosphite -----	1.3
Water -----	95.8

Example 7 shows a general purpose formula giving coatings especially high in corrosion resistance.

Example 8:	Parts
Calcium dichromate -----	2.4
Chromic acid -----	0.2
Calcium dihydrogen phosphate -----	0.4
Ethylene glycol -----	0.6
Water -----	96.4

The formula of Example 8 is well adapted for the coating of metal to be lacquered and then stamped or drawn.

Example 9:	Parts
Calcium dichromate -----	13.0
Calcium dihydrogen phosphate -----	2.5
Phosphoric acid -----	1.0
Ethylene glycol -----	3.0
Water -----	80.5

Example 9 shows a concentrated formula for use on preheated steel sheet for food containers.

Example 10:	Parts
Barium dichromate -----	3.5
Chromic acid -----	0.2
Phosphoric acid -----	0.3
Maleic acid -----	0.3
Water -----	95.7

Example 10 is a general purpose formula for zinc, aluminum and iron.

Example 11:	Parts
Calcium dichromate -----	2.6
Calcium dihydrogen phosphate -----	0.4
Phosphoric acid -----	0.2
n-Dodecyl phosphoric acid mono-ester -----	0.2
Glycerol -----	0.4
Water -----	96.2

Example 11 shows a formula giving coatings in which the water repellency is increased by inclusion of calcium laurate derived from the dodecyl ester. This formula also is well adapted for coating aluminum surfaces and for sheet steel for food containers.

The coating formed on metal surfaces by means of the present invention usually weighs from about 1 ounce to about 4 ounces per one thousand square feet of coated surface. If much below 1 ounce, the coating might show discontinuous areas. 1½ ounces to 3 ounces is the general purpose range, especially when the metal is to be later subjected to deep-drawing. There does not seem to be much advantage, in most cases, in producing coatings heavier than 4 ounces per 1,000 square feet. The weight of the coating can be precisely controlled by means of the concentration of the chromate-phosphate solution, or by rollers, or by a regulated mist-like spray.

As a first specific embodiment of my invention, in the coating of sheet steel formed into automobile fenders, in step (1), the fender, suspended from a continuously moving conveyor, is subjected to a spray of a solution

containing 2 percent sodium metasilicate and 0.2 percent of dodecylbenzene sodium sulfonate at 80° C. until the metal surface is free from water-breaks, the time varying with the amount of dirt and grease on the surface. Before passing to step (2), the silicate solution adhering to the metal is removed by a water spray.

In step (2), the clean fender is sprayed for about five seconds with a chromate solution at atmospheric temperature formulated as in Example 8, then allowed to drain for 10 seconds. The drainage goes back to the chromate reservoir and is re-used.

The fender, with its adhering film of chromate-phosphate solution, then passes to step (3) where, in a suitable chamber, it encounters a stream of air pre-heated to 200° C. Coating formation takes place quickly and the dry, coated fender, after cooling, may be lacquered immediately.

In a second specific embodiment, corrugated, galvanized structural sheet is coated at the point of manufacture following the procedure of the first embodiment, above, except, in step (1), the aqueous solution is a 3 percent solution of trisodium phosphate at 70° C. and, in step (2), the formula of Example 1 is used.

In a third embodiment, sheets of freshly rolled aluminum are coated according to the procedure of the first embodiment except that, in step (1), the solution contains 0.5 percent sodium oleate, 1.0 percent free ammonia and 2.0 percent of diammonium phosphate and, in step (2), the chromate-phosphate solution is that of Example 11.

Embodiments 1, 2 and 3, above, may be carried out satisfactorily by dipping instead of spraying and the surplus chromate solution in step (2) may be quickly removed by an air blast.

In a fourth specific embodiment, in the coating of fairly clean, continuous strip sheet steel, in step (1), the moving strip is sprayed on both sides with an aqueous solution of 1.5 percent sodium metasilicate and 0.1 percent dodecyl benzene sodium sulfonate at 70° C. for 4 seconds per linear foot, the excess silicate solution being largely removed by corrugated rollers and the remainder by a jet of water.

The strip moves to step (2) where it is wetted, both sides, with a fine spray of chromate-phosphate solution at 20 to 40° C. for about 2 seconds per linear foot, the solution being formulated as in Example 5. The strip then passes under and over corrugated rollers which regulate the amount of solution left on the surface. The strip then passes to step (3) where the coating is quickly formed by a current of air, or cleaned flue gas, heated to 175° C. The coated sheet may be lacquered in the flat, then cut to the desired shapes and the individual pieces may be stamped or drawn into the final product.

In a fifth specific embodiment, wherein 30 gauge, cold-rolled, continuous strip steel is given the bonding coat at the time of rolling, step (1) is taken care of by the cold-rolling operation. The rapidly moving steel strip, still very hot from the rolling, is subjected, both sides, to a mist-like chromate-phosphate spray, with no run-off, using the formula of Example 9. Both the application of the chromate solution, step (2), and the formation of the coating, step (3), take place in less than 2 seconds per linear foot of strip, the residual heat of the strip being utilized to form the coating. The resulting coated strip may be coiled up, or cut into lengths, or lacquered in the flat.

Many other modifications of the operating details of the present coating process will be evident. Although there are an enormous number of items of zinc, aluminum and ferrous metal which require bonding coats, the process of the present invention can easily be adapted to coat all of them.

The present process for applying micro-crystalline,

chromite-phosphate coats to metal differs from known art in the following respects:

- (a) It is the fastest of all known processes;
- (b) It contains fewer steps than any known process, in fact, it contains only the minimum number of steps which are theoretically necessary;
- (c) The coatings are not formed at atmospheric temperatures;
- (d) The metal requires no preliminary oxidative step and no etching or other pre-treatment with acid;
- (e) There is no coating bath;
- (f) There is no formation of sludge;
- (g) The chromate-phosphate solution is quantitatively consumed in coating formation;
- (h) No chemical analyses are required to control the process.

The micro-crystalline chromite-phosphate bonding coats of the present invention are unequalled by any known bonding coat in oxidation resistance and capacity for withstanding flexing, deep-drawing and other deforming operations. They contain substantially no chromate or other soluble salts. The coatings are hydrophobic but are wetted with great ease by organic solvents, thus making a perfect bond between bonding coat and lacquer. They are compatible with, and stabilizers for, the highly important vinyl resin lacquers.

What I claim is:

1. Process for producing an adherent, micro-crystalline chromite-phosphate bonding coat on ferrous metal surfaces which comprises the following sequence of steps: (1) wetting the metal surface with a solution containing a dichromate selected from the class which consists of barium, calcium, magnesium and zinc dichromates, the solution also containing a reducing agent for said dichromate, said reducing agent being present in amount sufficient to reduce substantially completely the hexavalent chromium present, the solution also containing a phosphoric acid compound selected from the class which consists of barium, calcium, magnesium and zinc dihydrogen phosphates and free phosphoric acid, the phosphate being less in amount than the dichromate in the solution, and (2) destroying substantially completely hexavalent chromium compounds and reducing agents present in the film of said dichromate solution adhering to the metal surface by heating to a temperature above 100° C., the residue remaining on the metal surface constituting an adherent, micro-crystalline, chromite-phosphate bonding coat.

2. The process of claim 5 wherein the reducing agent comprises a polyhydroxy alcohol.

3. Process for producing an adherent, micro-crystalline chromite-phosphate bonding coat on ferrous metal surfaces which comprises the following sequence of steps: (1) freeing the metal surface from waterbreaks by preheating the metal to a temperature substantially above 100° C., (2) wetting the surface of the hot metal with a solution containing a dichromate selected from the class which consists of barium, calcium, magnesium and zinc dichromates, the solution also containing a reducing agent for said dichromate, said reducing agent being present in amount sufficient to reduce substantially completely the hexavalent chromium present, the solution also containing a phosphoric acid compound selected from the class which consists of barium, calcium, magnesium and zinc dihydrogen phosphates and free phosphoric acid, the phosphate being less in amount than the dichromate in the solution, and (3) destroying substantially completely hexavalent chromium compounds and reducing agents present in the film of dichromate solution adhering to the metal surface by heating to a temperature above 100° C., the necessary heat and temperature being supplied by the preheated metal, the residue remaining on the surface of the metal constituting an adherent, micro-crystalline chromite-phosphate bonding coat.

4. As a new product, a ferrous metal base carrying on the surface an adherent, micro-crystalline chromite-phosphate bonding coat containing up to 49 percent of divalent metal phosphates and 51 to 98 percent of divalent metal chromites, the divalent metal ions of the coating being selected from the class which consists of barium, calcium, magnesium and zinc ions, the coating being substantially free from hexavalent chromium, the coating being capable of withstanding deep-drawing and repeated flexing through 360°.

5. Process for producing an adherent, micro-crystalline chromite-phosphate bonding coat on a ferrous metal base which comprises the following sequence of steps: (1) wetting the metal surface with a solution containing a dichromate selected from the class consisting of barium, calcium, magnesium and zinc dichromates, the solution also containing an organic reducing agent for said dichromate, said reducing agent being present in amount sufficient to reduce substantially completely the hexavalent chromium present, the solution also containing a phosphoric acid compound selected from the class consisting of barium, calcium, magnesium and zinc dihydrogen phosphates and free phosphoric acid, the phosphate being less in amount than the dichromate in the solution, and (2) destroying substantially completely hexavalent chromium compounds and reducing agents present in the film of said dichromate solution adhering to the metal surface by heating to a temperature above 100° C., the residue remaining on the metal surface constituting an adherent, micro-crystalline chromite-phosphate bonding coat.

6. Process for producing an adherent, micro-crystalline chromite-phosphate bonding coat on a ferrous metal base which comprises the following sequence of steps: (1) wetting the metal surface with a solution containing a dichromate selected from the class consisting of barium, calcium, magnesium and zinc dichromates, the solution also containing a reducing agent for said dichromate which is a hypophosphorous acid compound, said reducing agent being present in amount sufficient to reduce substantially completely the hexavalent chromium present, the solution also containing a phosphoric acid compound selected from the class which consists of zinc dihydrogen phosphate and free phosphoric acid, the phosphate being less in amount than the dichromate in the solution, and (2) destroying substantially completely hexavalent chromium compounds and reducing agents present in the film of said dichromate solution adhering to the metal surface by heating to a temperature above 100° C., the residue remaining on the metal surface constituting an adherent, micro-crystalline chromite-phosphate bonding coat.

7. Process for producing an adherent, micro-crystalline water-repellant chromite-phosphate bonding coat on ferrous metal surfaces which comprises the following sequence of steps: (1) wetting the metal surface with a solution containing a dichromate selected from the class which consists of barium, calcium, magnesium and zinc dichromates, the dichromate solution also containing a reducing agent for said dichromate, said reducing agent being present in amount sufficient to reduce substantially completely the hexavalent chromium present, said reducing agent including up to 0.20 percent, based on the weight of the solution, of a phosphoric acid mono-ester of a straight-chain alcohol containing from about 12 to about 18 carbon atoms, said dichromate solution also containing a phosphoric acid compound selected from the class which consists of barium, calcium, magnesium and zinc dihydrogen phosphates, the phosphate being less in amount than the dichromate in the solution, and (2) destroying substantially completely hexavalent chromium compounds and reducing compounds present in the film of dichromate solution adhering to the metal surface by heating to a temperature above 100° C., the residue

remaining on the surface constituting an adherent, micro-crystalline water-repellant chromite-phosphate bonding coat.

8. The product of claim 4 wherein the chromite-phosphate bonding coat contains a substantial amount of water-repellant, insoluble organic substances produced by the oxidation by dichromate of a phosphoric mono-ester of a C₁₂ to C₁₈ open-chain alcohol.

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