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3,094,441 CHROMIC PHOSPHATE BONDING COATS FOR METAL

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This application is a continuation-in-part of my copending application, Serial Number 693,259, filed October 30, 1957, now Patent 2,901,385, issued Aug. 25, 1959.

The present invention relates to oxidation-inhibiting and bonding coats on aluminum, zinc and ferrous metal surfaces, said coats containing substantial amounts of chromic phosphate, and it comprises wetting the metal surface with a solution containing a chromic acid compound selected from the class consisting of free chromic acid and ammonium bichromate, the solution also containing a reducing agent which actively reduces hexavalent chromium to the trivalent state at temperatures in the neighborhood of 100° C. and above, the solution also containing a phosphoric acid compound selected from the class consisting of free phosphoric acid and ammonium phosphates, the phosphoric acid compound being present in amount of 0.51 mole to 2.90 mole for each mole of chromic acid or equivalent ammonium bichromate, the bonding coat being formed by heating the metal carrying the film of solution of chromic acid compound to a temperature of from about 100° C. to about 400° C., with reduction of hexavalent chromium and formation of a highly adherent, oxidation-resisting, bonding coat consisting chiefly of chromic phosphate; all as is more fully hereinafter set forth and as claimed.

I have found that, if aluminum, zinc or a ferrous metal is wetted with a solution containing chromic acid and phosphoric acid, with a suitable reducing agent for the former, and the metal is then heated to a temperature of 100° C., or higher, the hexavalent chromium is reduced to the trivalent form and precipitates on the metal surface as chromic phosphate.

Instead of forming a powdery, non-adherent deposit on the metal, as might be expected, the chromic salt forms a glassy, tenaciously adhering, continuous, dust-free film on the metal surface. I have also found that this chromic phosphate film has great value as a corrosion-inhibiting and bonding coat and is particularly valuable as a base upon which to apply lacquer and similar coats.

The formation of the chromic phosphate bonding coat may be illustrated as follows:

(A) $10CrO_3+10H_3PO_4+3C_2H_6O_2\rightarrow 10CrPO_4+6CO_2+24H_2O$

Ethylene glycol is the reducing agent and it is used in small excess to make certain that all of the chromic acid is reduced, also, because there is some loss of the glycol by vaporization. If the heating step is in the 125° C. to 225° C. range, the chromic phosphates formed are mainly of the ortho type. The chromic orthophosphate may be a hydrate when first formed, for example,

$$CrPO_4\cdot 6H_2O$$

At least two-thirds of the water of hydration is lost, usually, before a temperature of 150° C. is reached, the remainder being held more tenaciously. Most, or all, of this may be driven off at higher temperatures.

If the heating step is to be carried out at 350° C. to 400° C., it is possible to modify the reaction to produce chromic metaphosphate, instead of the orthophosphate of reaction (A).

(B) $10CrO_3+30H_3PO_4+3C_2H_6O_2\rightarrow 10Cr(PO_3)_3+6CO_2+54H_2O$

If the drying step is in the 325° C. to 375° C. range, a mixture of ortho and meta phosphates is formed with probably more or less of the intermediate pyrophosphate.

If there is more chromic acid present than that needed to combine with the phosphoric acid, some basic chromic phosphates may be expected to form. $(HOCr)_3(PO_4)_2$, basic chromic orthophosphate, and $(HO)_2CrOPO_2$, basic chromic metaphosphate, are typical of such compounds.

The chromic phosphate coats of the present invention may also be produced from chromic salts of acids which are capable of being displaced by phosphoric acid at fairly high temperatures, the acetate and formate being particularly convenient.

(C) $Cr(CH_3COO)_3+H_3PO_4\rightarrow CrPO_4+3CH_3COOH$

A heating step of 200–250° C. brings about coating formation with vaporization of acetic acid. This method is much more expensive than in cases where chromic acid is reduced in situ, since chromic acetate and formate cost much over one dollar per pound.

While there may be some uses for bonding coats containing a little free phosphoric acid, in most cases, this would be undesirable and the chromic acid is therefore present in at least a small excess to make certain that all of the phosphoric acid is converted to chromic phosphate.

Likewise, there may be some applications for bonding coats containing some unreduced hexavalent chromium. Ordinarily, it is preferred to have all of the chromium in the insoluble, trivalent form and the amount of reducing agent is adjusted to reduce all of the hexavalent chromium.

In carrying out the present process, it is not sufficient to heat the metal carrying the film of chromic acid solution to the point where it appears dry. The chemical reactions which produce the coat of chromic phosphate are not complete at this point and the heating must be continued for slightly longer to permit the reactions to go to completion.

The metal to be coated must be in condition to be wetted completely by the chromic acid solution, that is, the surface must be free from water-breaks, otherwise, a portion of the surface will not be wetted by the chromic acid solution and no coating will form on such areas. The present invention is not, however, concerned with methods for the elimination of water-breaks. They may be eliminated in any manner, for example, by electrochemical means in acid or alkaline solution, by acid pickling, by heat, by mechanical working and by the use of certain alkaline solutions. Working with bright, cold-rolled sheet steel, applicant has found that a solution of 2 percent anhydrous sodium metasilicate plus 0.2 percent of sodium dodecyl benzene sulfonate at 80° C., pressure-sprayed for 4 seconds, gives a surface which, after a cold water rinse, is perfectly wetted by the solutions of the present invention. Several hundred 14" x 20" steel sheets of different lots had their surfaces completely freed from water-breaks by this method.

In regard to reducing agents, there are at least 600 which could be used in the present invention. A very good inorganic reducer is hypophosphorous acid which reduces chromic acid quantitatively under the conditions of the process and has the advantage of being converted into orthophosphoric acid and thus entering the coating.

Organic compounds which are oxidized by chromic acid to carbon dioxide and water are particularly desirable. Such substances as maleic, fumaric, citric, lactic, oxalic and hydroxyacetic acids may be used. Especially desirable are the polyhydroxy alcohols, as glycerol, propylene glycol and ethylene glycol. The last two named have the advantage of a vapor pressure sufficiently high to allow

the escape of the surplus reducing agent when used in excess.

The heating step may be carried out by means of radiant heat, by infra-red heat, by heating in air or inert gas and in many other ways. It is believed that the most generally useful procedure is to heat in a current of air pre-heated to 125° C. to 250° C. until the chemical reactions for coating formation are complete. It is not possible to give exact information about the time required for the heating step since it varies with the thickness of the metal, the temperature and other factors. With continuous strip 30 gauge sheet steel, heated by air pre-heated to 200° C. and moving with fairly high relative velocity, the heating step can be completed in less than 2 minutes.

The coatings of the present invention are hydrophobic, the water-repellancy increasing with increasing temperature in the heating step. Conversely, they are wetted quickly and completely by the usual organic solvents.

The experiment now to be described gives a good idea of the properties of the bonding coats of the present invention.

A large sheet of bright, cold-rolled 30 gauge sheet steel was wetted with the solution of Example 1, below, then heat-processed at 220° C. The sheet now had a glassy, dark gray, dust-free, perfectly continuous coat. It was then placed in a horizontal position and a pool of 5 cc. of distilled water was placed in the center of the sheet.

The sheet was then manipulated to cause the pool of water to glide over most of the surface of the sheet, a path of 10 or 12 feet. The pool was then allowed to return to the center of the sheet and permitted to evaporate to dryness, requiring 30 hours. The water was tested for pH several times but no decrease in pH occurred, indicating no pickup of phosphoric acid. The water also remained perfectly colorless, showing the absence of hexavalent chromium. This is a very sensitive test, as even a trace of hexavalent chromium in the coat will give the water a noticeably yellow tint, usually, in a few seconds. After drying, the area whereon the pool of water had rested could not be distinguished from the remainder of the coated surface.

The following examples show various solutions which are useful in producing the bonding coats of the present invention. In all cases, the proportions are in parts by weight and the compounds, except for water, are on an anhydrous basis. Where a temperature is not given, it is assumed that the coating will be formed at 150° C. to 225° C.

Example 1

	Parts
Chromic acid	0.90
Phosphoric acid	0.85
Ethylene glycol	0.25
Water	98.0

This is a general purpose formula, good for use on aluminum, zinc, steel and iron.

Example 2

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

Because of its wetting characteristics, this solution is particularly useful on aluminum and zinc.

Example 3

	Parts
Chromic acetate	2.5
Phosphoric acid	1.0
Water	96.5

This is a relatively expensive general purpose formula.

Example 4

	Parts
Chromic acid	10.0
Phosphoric acid	9.0
Propylene glycol	3.0
Water	78.0

This formula is designed for application, as a fine mist, to preheated metal where a minimum of water is desirable. Much more concentrated solutions of this formula may be made.

Example 5

	Parts
Chromic acid	0.6
Phosphoric acid	0.5
Ethylene glycol	0.15
Water	98.75

This very dilute formula has applications in the metal container industry for the production of very thin bonding coats to sheet steel. This and Example 1 are the most generally useful formulae.

Example 6

	Parts
Chromic acid	1.0
Phosphoric acid	2.7
Hydroxyacetic acid	0.4
Water	95.9

With sheet steel coated with the solution of Example 6, the heating step is at a temperature of about 380° C. The chief coating product is chromic metaphosphate with probaly small amounts of chromic ortho and pyrophosphates.

Example 7

	Parts
Chromic acid	0.9
Phosphoric acid	0.5
Ethylene glycol	0.23
Water	98.37

The coating derived from this solution is mainly normal chromic orthophosphate and basic chromic orthophosphate with a lesser amount of chromic hydroxide.

As will be shown below, the chromic acid solutions of the present invention may be applied to pre-heated metal, for example, to sheet steel still very hot from the cold-rolling operation, in the form of a fine spray, or mist, the heat and temperature necessary for coating formation being supplied by the pre-heated metal.

As a first specific embodiment of my invention, in the coating of sheet steel formed into automobile fenders, the fender, suspended from a continuously moving conveyor, is completely wetted by spray means with the solution of Example 1 at the atmospheric temperature, this step taking about 5 seconds. The fender is allowed to drain for 10 seconds, the runoff going back for re-use. The fender is next exposed to a rapidly moving current of air, pre-heated to 200° C. Coating formation takes place quickly and the dry, coated fender, after slight cooling may be lacquered at once.

In a second specific embodiment, galvanized sheet is wetted with the solution of Example 2 and the coating developed as in the first embodiment.

In a third specific embodiment, sheets of freshly rolled aluminum are coated as in the first embodiment except that the chromic acid solution is that of Example 7.

In a fourth specific embodiment, wherein cold-rolled 30 gauge steel strip is given the bonding coat at the time of rolling, the strip, at a temperature of about 200° C. from the cold-rolling operation, is subjected, both sides, to a mist-like spray with no runoff, using the solution of Example 4. The coating is formed almost instantly, the residual heat of the strip supplying the necessary heat and temperature.

In a fifth specific embodiment, for the coating of continuous strip sheet steel, the moving strip is wetted on

both sides by sprays of chromic acid solution as in Example 5. The excess chromic acid solution is removed by rollers and flows back for re-use. The strip then passes to the heating step where it moves counter-current to air, or cleaned flue gas, at a temperature of 225° C. The coat is formed in about 1 minute. 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 desired product.

Some of the advantages of the hereindescribed process for applying bonding coats to metal are as follows:

(*a*) The process is limited to the two theoretically necessary steps;

(*b*) The process is very fast;

(*c*) The metal requires no preliminary oxidative step and no etching, pickling or other pre-treatment with acid;

(*d*) There is no coating bath;

(*e*) There is no sludge formation, the coating materials being quantitatively consumed in coating formation;

(*f*) No chemical analyses are required to control the process;

(*g*) The coating is of the highest quality.

Other advantages will be obvious.

What I claim is:

1. Process for producing an adherent, chromic phosphate bonding coat on a metal base selected from the class consisting of aluminum and ferrous metal which comprises, (1) wetting the metal surface with a solution containing a chromic acid compound selected from the class consisting of free chromic acid and ammonium bichromate, the solution also containing a reducing agent for said chromic 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 consisting of free phosphoric acid and ammonium dihydrogen phosphate, the phosphoric acid compound being present in amount of about 0.51 mole to 2.90 moles for each mole of chromic acid compound, as CrO_3, and (2) heating the metal carrying the film of chromic acid compound to a temperature of from about 100° C. to about 400° C. with reduction of hexavalent chromium to the trivalent state and formation of an adherent bonding coat which is chiefly phosphates of trivalent chromium.

2. Process for producing an adherent, chromic phosphate bonding coat on a metal base selected from the class consisting of aluminum and ferrous metals which comprises, (1) preheating the metal to a temperature substantially above 100° C., (2) wetting the surface of the hot metal with a solution containing chromic acid, the solution also containing a reducing agent for said chromic acid, said reducing agent being present in amount sufficient to reduce substantially completely the hexavalent chromium present, the solution also containing 0.51 to 0.99 mole of phosphoric acid for each mole of chromic acid, and (3) reducing substantially completely hexavalent chromium to the trivalent state 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 constituting an adherent, chromic phosphate bonding coat.

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