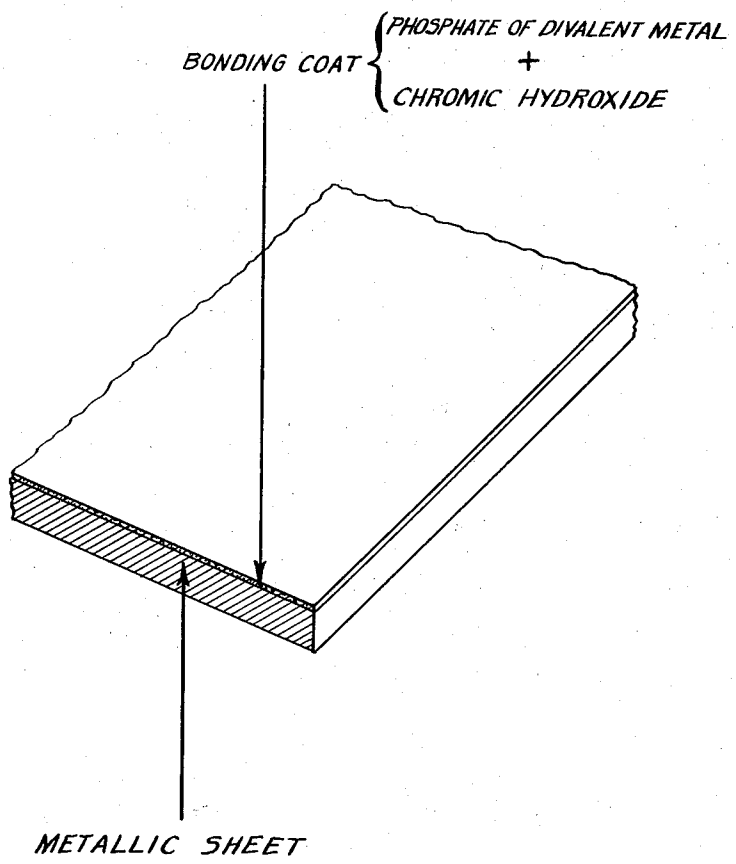
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BONDING COATS FOR METAL

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BONDING COATS FOR METAL

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This invention relates to bonding and oxidation-resisting coats on metal and it comprises wetting the metal surface with a solution containing hexavalent chromium, usually in the form of chromic anhydride or an ammonium salt thereof, said solution also containing a reducing agent for the hexavalent chromium, the bonding coat being formed on the metal surface by drying the metal at an elevated temperature with reduction of the hexavalent chromium principally to the trivalent state, said trivalent chromium then being present largely in the form of chromic hydroxide in various stages of hydration or dehydration, the bonding coat formed containing substantial amounts of said chromic hydroxide; all as is more fully hereinafter set forth and as claimed.

While the invention is most useful for coating ferrous metal and zinc, it can be used to coat any metal from copper to magnesium in the electromotive scale. This is in part because the metal being coated contributes only in a minor way to the coating. As steel is by far the most important metal, it will be used for purposes of illustration.

In my co-pending application, U. S. app. S. N. 499,510, there are described bonding coats on metal which are of the spinel type, these being produced by the reduction of dichromates of divalent metals present in solution on the surface of the metal, drying and reduction taking place at an elevated temperature.

The coatings of the present application differ in that they contain substantial amounts of chromic hydroxide, this substance, as defined below, being the characteristic and essential element of the coatings of the present invention.

Chromic hydroxide may be written as $Cr(OH)_3$ but, in actual practice, is seldom found or produced in exactly this form. If formed by precipitation at moderate temperatures, it may be in gel form. In practically all cases, the first product is a chromic hydroxide containing much more water than is shown in $Cr(OH)_3$ and this water is in part held tenaciously. For example, it may be heated to low red heat, briefly, without becoming more dehydrated than in the formula just given. For this reason, the chromic hydroxide of the coatings herein described are believed to range mostly from OCrOH to $Cr(OH)_3$ and various hydrates of the latter compound. In the description and claims the term, "chromic hydroxide" is intended to include all such compounds and mixtures thereof.

As to reducing agents for the hexavalent chromium, there are a great many which are suitable for use in the present invention. One important group consists of organic compounds which are oxidized by hexavalent chromium at elevated temperatures, especially those which oxidize to carbon dioxide.

Another unusually advantageous group of reducing agents consists of the oxy-acids of phosphorus in which the valence of the phosphorus is less than five, together with the corresponding ammonium and divalent metal salts. These acids are, hypophosphoric, phosphorous and hypophosphorous, the last-named being the most reactive

and efficient, quantitative reductions being easily attained. Calcium, magnesium and zinc hypophosphites are particularly desirable and have good water-solubility.

A large number of other substances will reduce hexavalent chromium under the conditions of the coating reaction, such as, sulfites and hyposulfites. Some of these have the disadvantage of leaving a water-soluble residue in the coating.

The use of the ammonium chromates permits of operating the bath at higher pH levels than when free chromic acid is used. In such cases, the ammonia is lost from the system by vaporization and the coating is much the same as if chromic anhydride had been used.

The following reactions are given to illustrate coating formation:

(A) $8CrO_3+3Ca(H_2PO_2)_2+12H_2O\rightarrow 8Cr(OH)_3+3Ca(H_2PO_4)_2$

In (A), chromic anhydride and calcium hypophosphite react to produce, principally, chromic hydroxide and calcium dihydrogen phosphate. The latter substance is capable of further reactions, forming insoluble substances, as tribasic phosphates. Metal coatings produced by reaction (A) might be expected to contain upwards of fifty percent of chromic hydroxide and a lesser amount of insoluble phosphates.

The number of organic compounds which can be used in the coating reaction is indefinitely large, some of the better ones being dextrose, glycerol, ethylene glycol, oxalic acid, citric acid, hydroxyacetic acid and maleic acid. Oxalic acid is the most reactive of the compounds named while ethylene glycol is one of the most convenient and inexpensive.

The coating reaction with ethylene glycol is illustrated as follows:

(B) $10CrO_3+3CH_2OH.CH_2OH+6H_2O\rightarrow 10Cr(OH)_3+6CO_2$

In (B), chromic anhydride and ethylene glycol interact to give a coating which is nearly all chromic hydroxide.

Part of the ethylene glycol, or other organic reducer, may be replaced by a hypophosphite and this will give a coating containing the corresponding proportion of phosphate. Or, the bath may contain an addition of zinc or other divalent dihydrogen phosphate. In such ways, the ratio of phosphate to chromic hydroxide in the coating may be varied over a wide range. Also, small amounts of hypophosphite and phosphite may sometimes be found in the coating.

In most or all of the coatings, there are small amounts of other compounds than those indicated, some of these arising from various secondary reactions. There is also usually a slight amount of ferrous iron in the coating, the iron being derived from the metal being coated.

The concentration of the chemicals in the coating bath is by no means critical. Good results are obtained with baths containing from about 0.5 to 3.0 percent of chromic anhydride, the other bath components being of course based on the chromic anhydride content. As will be shown below, there are special types of coating procedures with which the chromic acid concentration is decidedly higher than the values just indicated.

Following are a number of examples of typical coating baths, or solutions:

Example 1

	Parts by weight
Chromic anhydride	2.5
Ethylene glycol	0.5
Water	97.0
Total	100.0

The coating of Example 1 is principally chromic hydroxide.

Example 2

	Parts by weight
Chromic anhydride	2.0
Zinc hypophosphite	1.5
Water	96.5
Total	100.0

The coating of Example 2 is principally chromic hydroxide and zinc phosphate.

Example 3

	Parts by weight
Chromic anhydride	3.0
Ethylene glycol	0.5
Calcium hypophosphite	0.4
Water	96.1
Total	100.0

The coating of Example 3 is principally chromic hydroxide and calcium phosphate.

Example 4

	Parts by weight
Ammonium dichromate	3.0
Magnesium hypophosphite	1.4
Water	95.6
Total	100.0

The coating of Example 4 is principally chromic hydroxide and magnesium phosphate.

Example 5

	Parts by weight
Chromic anhydride	2.0
Ethylene glycol	0.5
Zinc dihydrogen phosphate	1.0
Water	96.5
Total	100.0

The coating is principally chromic hydroxide and zinc phosphate.

Example 6

	Parts by weight
Chromic anhydride	2.5
Calcium hypophosphite	1.6
Aluminum formate	0.5
Water	95.4
Total	100.0

The coating of Example 6 is principally chromic hydroxide, aluminum hydroxide, calcium phosphate and various products of secondary reactions.

Under commercial conditions, the materials for the coating solutions may advantageously be supplied in the form of concentrated solutions, one of which contains the hexavalent chromium compound and another solution for the reducing agent. The various materials for use in the baths have adequate water solubilities, some of them, as chromic anhydride and ethylene glycol, being extremely soluble. The solutions are sufficiently stable at room temperature after addition of the reducing agent to the diluted chromic anhydride solution. The solution of Example 1, for example, holds up well for a week or more, at the ordinary temperature.

Fatty alcohols, as n-dodecyl alcohol, when made soluble by mono-esterification with a suitable polybasic acid, as maleic or phosphoric, are able to act as reducing agents for chromic anhydride. Then, in the form of the corresponding lauryl or other fatty acid, insoluble salts of di- and trivalent metals are formed, these entering the coating and enhancing its water-repellant properties. If the ester is of the type of mono-lauryl phosphoric acid, the free phosphoric acid formed by the oxidation also enters the coating as an insoluble phosphate.

It should be pointed out that, in all of the examples above given, except Example 1, there is, in addition to chromic hydroxide, a minor formation of compounds of the spinel type in the coating, these being defined as chromites, ferrites and aluminates of zinc, magnesium, ferrous iron and divalent manganese, also the corresponding alkaline earth compounds, including the numerous complex compounds formed by the interchange of the various radicals. These substances are believed to be produced in small amount by secondary reactions.

The metal sheet, or other metal object, is first cleaned and degreased, as by a hot alkaline bath. It is essential that the surface to be coated be completely freed from water-breaks; otherwise, the coating solution will not wet the affected area and there will be no coating formation thereon. After rinsing off the alkaline wash, it is sometimes desirable to subject the surface, especially if of steel, to a very light pickle. This may be accomplished in a variety of ways, for example, by spraying with a 0.75% solution of ferric bisulfate at 20° to 50° C., for twenty to forty seconds. This pickling operation is generally quite unnecessary and the coating solution may be applied directly after the water rinse following the alkaline wash. The surface is sprayed or otherwise wetted with cold chromate coating solution, prepared as above described. This can be done, usually, in ten seconds, or less, as it is only necessary completely to wet the surface with the coating solution. After draining off the excess chromate coating solution, the metal is dried at an elevated temperature, for example, by heating it with a current of air or inert gas, preheated to 150° to 200° C., more or less, drying and coating formation proceeding simultaneously.

This brings about drying and coating formation very quickly, in the case of light sheet, often in less than one minute. The coated metal, after cooling somewhat, may be lacquered at once with no further processing since there is no dust nor non-adherent material formed.

The metal coatings herein described differ from phosphate and oxalate coatings produced by aqueous solutions in that there is little or no reaction in the coating bath or while the work is being sprayed, consequently, no sludge is produced in the bath. The coating is formed almost entirely during the hot drying operation, the coating being derived from the film of chromate coating solution adhering to the surface.

While the invention is most useful for coating iron and zinc, it can be used to coat any metal from copper to magnesium in the electromotive series. This is, in part, because the metal being coated contributes only to a very small extent to the coating.

The present invention can be used to coat sheet steel or strip at the time of rolling, with no previous degreasing or pickling. The chromate solution is sprayed on with as little excess as possible, this being removed by rollers. There is enough residual heat in the sheet metal, if done properly, to evaporate the solvent and produce the coating.

The coatings herein described may be used as a base for fused, vitreous enamels.

Another method for producing the coating is as follows:

The thoroughly cleaned sheet or other metal object is pre-heated to a fairly high temperature, for example, 250° to 300° C., depending somewhat on the thickness of the metal. The coating solution is then sprayed onto the hot surface in the form of a fine mist in an amount sufficient to cover completely the surface while providing little or no runoff. Coating formation is almost instantaneous, the residual heat of the metal providing the temperature for the chemical reactions and the drying of the surface.

This is a most convenient, rapid method of applying bonding coats and is particularly applicable to continuous

processing. In addition to the chromic hydroxide coatings of the present invention, it works remarkably well with the process for producing spinel types of coatings, referred to above. It may also be used in coatings which are principally phosphates or oxalates.

Sheet steel, coated in the flat with a chromic hydroxide coating as above described, may be lacquered in the flat and then stamped out into the desired shape. These stampings may be then subjected to extreme drawing and deforming operations with no impairment of the lacquer and bonding coats, in fact, in extreme cases, it is usually the case that the metal tears before impairment of the coats. It is of course necessary to select a suitable thermoplastic lacquer, many of the vinyl types being particularly well adapted.

The coatings herein described are very thin, of amorphous or microcrystalline structure, and adhere most tenaciously to the underlying metal. They usually withstand repeated flexes of 180 degrees.

In color, they are usually some shade from brownish gray to greenish gray. If produced in a hot, inert atmosphere, as flue gas, they may be grayish green, sage green or tea-green.

What I claim is:

1. Process for producing an adherent bonding coat on aluminum, zinc and ferrous metal surfaces which comprises the following sequence of steps: (1) freeing the metal surface from water-breaks, (2) wetting the metal surface with a solution containing chromate selected from the class which consists of chromic acid and ammonium dichromate, the solution also containing a hypophosphite reducing agent for said chromate selected from the class which consists of free hypophosphorous acid and calcium, magnesium and zinc hypophosphites and (3) destroying substantially completely oxidants and reducing substances present in the film of said chromate solution adhering to the metal surface by heating to a temperature above 100° C., the residue remaining on the metal surface constituting an adherent, chromic hydroxide-phosphate bonding coat.

2. Process for producing an adherent bonding coat on aluminum and ferrous metal surfaces which comprises the following sequence of steps: (1) freeing the metal surface from water-breaks, (2) wetting the metal surface with a

chromate solution, said chromate being selected from the class which consists of chromic acid and ammonium dichromate, the solution also containing an organic reducing agent for said chromate, the solution also containing a phosphate selected from the class which consists of free phosphoric acid and calcium, magnesium and zinc dihydrogen phosphates, the phosphate being less than the chromate in the solution, and (3) destroying substantially completely oxidants and reducing substances present in the film of said chromate solution adhering to the metal surface by heating to a temperature above 100° C., the residue remaining on the metal surface constituting an adherent, chromic hydroxide-phosphate bonding coat.

3. The process of claim 2 wherein the reducing agent is selected from the class which consists of polyhydroxy alcohols.

4. The process of claim 2 wherein a part of the reducing agent, about 0.1 to about 0.2 percent based on the weight of the solution, is a phosphoric acid mono-ester of a straight-chain alcohol containing from 10 to 18 carbon atoms.

5. The process of claim 2 wherein the chromate solution is applied to metal preheated to a temperature above 100° C., the heat and temperature necessary to bring about coating formation being supplied by the preheated metal.

6. An article of a metal selected from the group consisting of aluminum, zinc and ferrous metal carrying on the surface an adherent bonding coat containing up to 49 percent of phosphates of divalent metals selected from the class which consists of calcium, magnesium, zinc and iron, and from 51 to 98 percent of chromic hydroxide, the coating being substantially free from hexavalent chromium, the coating being capable of withstanding deep drawing and repeated flexing through 360°.

References Cited in the file of this patent

UNITED STATES PATENTS

1,145,186	Eberhard	July 6, 1915
2,210,850	Curtino	Aug. 6, 1940
2,272,216	Lodeeson	Feb. 10, 1942
2,383,663	Thomas	Jan. 29, 1946
2,505,734	Freud	Apr. 25, 1950