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3,578,509

# CONDITIONING FERROUS METAL SUBSTRATES

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## ABSTRACT OF THE DISCLOSURE

To prepare a ferrous metal surface for receiving a hexavalent-chromium-containing coating composition, the surface is first contacted with an aqueous solution having a pH of between about 2–6 and containing up to about 50 weight percent of ammonium dihydrogen phosphate and/or alkali metal dihydrogen phosphate. The resulting contacted surface is then rinsed and may be dried. The solution may also contain, for example, oxidizing ions and surface active agents. After this preparation and the establishment of the above-noted coating, substrates exhibit weldability and enhanced paint adhesion.

## BACKGROUND OF THE INVENTION

Phosphate coatings and hexavalent-chromium-containing coatings are two types of conditioning treatments for metal surfaces which provide corrosion protection and may offer augmented paint adhesion. Generally, the phosphate coatings are tightly adhering to the metal substrate and are porous coatings which provide a good base for paint. Usually, such phosphate coatings fail to provide enhanced corrosion protection and therefore often receive a very dilute rinse, for example, a chromic acid rinse, to increase the corrosion resistance of the finished product. These chrome rinses typically contain less than five grams per liter of hexavalent chromium, expressed as $CrO_3$. Such surface protection techniques have been shown, for example, in British Pat. 1,054,356.

On the other hand, hexavalent-chromium-containing coatings for metal substrates are applied to metal surfaces from liquid compositions containing hexavalent chromium, often supplied by chromic acid, to typically impart some corrosion resistance to the metal surface. Such coatings have been shown, for example, in British Pat. 1,033,-399 and in U.S. Pats. 2,768,104; 2,777,785; 2,846,342; 2,901,385; 2,902,390; 3,063,877; 3,346,522; and 3,382,-081. The coating compositions may contain some trivalent chromium, or the coatings can form trivalent chromium compounds during application and/or curing. Coatings thus prepared tend to be non-porous and somewhat amorphous in nature. They often provide good corrosion protection, but paint adhesion to such coatings is usually inferior to the like adhesion exhibited by the phosphate coatings. Moreover, if the hexavalent-chromium containing coatings are applied over conventional phosphate undercoatings, the paint adhesion properties of the phosphate coating is usually downgraded to that of the hexavalent-chromium-containing coating.

The process of the present invention overcomes such problems by first contacting a metallic ferrous substrate with a dihydrogen phosphate aqueous solution. The contacted surface is rinsed and may be permitted to dry. This surface resulting after contact with the dihydrogen phosphate solution is totally unsatisfactory as a basis for direct painting and offers no improvement in adhesion for directly applied paint or in corrosion resistance over conventional phosphate coatings.

However, it has been found that such a conditioning provides a superior surface treatment for subsequently applied hexavalent-chromium-containing coatings. Although not meaning to bound to any particular theory it appears that the conditioning prepares a ferrous-ferric phosphate substance on the substrate surface and, for convenience, such surfaces are sometimes referred to herein as "tertiary-iron-phosphated" surfaces. If the surface is permitted to dry, a loose powder is apparent at the surface, which powder can be readily removed by manual rubbing of the surface with a cloth. This loose powder, ostensibly, is at least partially autogenous in its formation, i.e., is formed by an interaction of the phosphate solution with the ferrous substrate.



After this initial surface treatment, whether the surface is dried or left wet, the conditioning appears to alter the manner in which the hexavalent-chromium-containing coating deposits, and the conditioning orients or induces the coating toward a crystalline film. Without the tertiary-iron-phosphated surface, the coating tends to be more amrophous, i.e., has retarded crystallinity. However, as a result of the surface treatment of this invention, and after curing of the subsequently applied coating, the coated surface provides a base for paint adhesion which is enhanced over conventional phosphate coatings. Moreover, the coated surface permits weldability of the ferrous substrate and additionally provides enhanced corrosion resistance superior to that obtained from conventional phosphate coatings with or without chromic acid rinses.

It has also been possible heretofore to approach the problem of protecting metal surfaces by first using merely a conventional phosphate pretreatment followed then by an unusually heavy chromic acid rinse, as for example the practice taught in U.S. Pat. No. 2,882,189. Although lacquer adhesion to such coatings is apparently acceptable, and thus these coatings have ostensibly found acceptance in the food container art, such coatings are achieved by sacrificing weldability and are thus distinguished from the coatings of the present invention, for example, not only by the conventional phosphate pretreatment, but also by their performance.

## SUMMARY OF THE INVENTION

Broadly, the present invention is directed to a method of treating a ferrous metal substrate for coating with a hexavalent-chromium-containing coating composition, wherein the resulting coated substrate exhibits weldability and enhanced paint adhesion, which method comprises contacting the surface of such substrate with an aqueous solution maintained at a pH level between about 2–6, which solution contains up to about 50 percent by weight of at least one compound selected from the group consisting of ammonium dihydrogen phosphate, alkali metal dihydrogen phosphates, and their mixtures, and rinsing the resulting contacted surface.

The invention is further directed to the method for producing a corrosion-resistant coating on a ferrous metal substrate by applying, to the resulting rinsed surface prepared by the method described immediately hereinabove, or by applying to such rinsed surface which has been subsequently dried, a hexavalent-chromium-containing coating composition and heating the substrate at a temperature, and for a period of time, sufficient to vaporize volatile substituents from the composition and deposit on the substrate a composition residue.

This invention is further directed to the products prepared by the methods described above.

Exemplary of "ferrous metal" substrates as the term is used herein include iron, stainless steel, and steel such as cold rolled steel. For convenience, the contacting solution is referred to herein sometimes as the "aqueous solution" or as the "dihydrogen phosphate solution" and where the resulting rinsed surface is dried the resulting powder on such surface is sometimes referred to herein as a "powdery residue." Also for convenience, the condi-

tion of the surface before application of the hexavalent-chromium-containing coating composition, i.e., after rinsing of the surface, or after rinsing the subsequent drying of the surface, may be referred to herein as a "first treated" surface. The hexavalent-chromium-containing coating compositions are often referred to herein merely as the "coating compositions" or, because of the adherency of resulting residues to the metal substrate after curing, are referred to as "bonding coating" compositions.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The aqueous solution can contain suspended substituents, but in its simplest form is merely prepared as a solution of the dihydrogen phosphate, e.g., ammonium dihydrogen phosphate or alkali metal dihydrogen phosphates such as lithium, sodium, cesium, and potassium, or their mixtures, in water. Such dihydrogen phosphate is provided in sufficient amount to maintain a pH level of the solution between about 2–6. Such solutions having a pH maintained at a level above about 6 can offer insignificant enhancement in the adhesion of subsequently applied paint. Such solutions maintained at a pH level below about two can produce an undesirable sludge on the metal surface and lead to coated surfaces of retarded paint adhesion. Preferably, for best subsequent paint adhesion as well as economy, sufficient dihydrogen phosphate compounds are present to provide a pH for the aqueous solution of between about 2–3. For economy, the aqueous solution suitably does not contain above about fifty percent by weight of the dihydrogen phosphate and also for economy advantageously contains below about 30 percent by weight of such compound. Preferably, for best economy the aqueous solution contains between about 0.5–15 weight percent of such dihydrogen phosphate compound.

In addition to the dihydrogen phosphate, this aqueous solution can contain from about 0.25 percent to about 10 percent by volume of a surface active agent. Such an agent augments the cleansing of the surface as the dihydrogen phosphate coating solution is contacting the ferrous substrate and further assists in achieving uniform contact. Usually, above about one-quarter percent by volume of such agent is required to provide for desirable contact uniformity. However, above about 10 percent by volume of such agent is uneconomical. Advantageously, for best economy and efficient cleaning, the agent is present in the aqueous solution in an amount of between about 0.5–3 percent by volume.

Suitable surface active agents are hydroxyl-containing hydrocarbon ethers which include the alkyl ethers of alkylene glycols, such as butyl ether of propylene glycol, the oxyalkyl ethers of alkylene glycols, e.g., 1-butoxy-ethoxy-2-propanol, fatty alcohol polyoxyalkylethers, alkylphenol polyoxyalkylethers such as polyoxyethylated nonylphenols, and polyalkylene glycols, e.g., tetraethylene glycol. Other suitable surface active agents which may be used include products from pine wood distillation, e.g., pine oil, as well as products preapred from waste sulfite liquors such as lignin sulfonic acids.

Moreover, the aqueous solution can contain between about 1 to 10 grams per liter of an oxidizing ion, e.g., chlorate, bromate, nitrate, and that from hydrogen peroxide. Such ions serve to reduce the contact time between the metallic substrate and the aqueous solution. Less than about one gram per liter of such ions, however, is usually insufficient for reducing such contact time, and above about 10 grams per liter of such ions is uneconomical and may inhibit subsequent weldability of the coated substrate. Preferably for efficiency and economy not above five grams per liter of such ions are present in the aqueous solution. Generally the ferrous substrate is contacted with the aqueous solution, for example by dipping the substrate into a bath of the solution, for a time of from about five seconds up to about one minute regardless of the presence of oxidizing ions in the solution. A contact



time of less than about five seconds may be insufficient to provide for a significant enhancement in the adhesion of subsequently applied paints. A contact time of greater than about one minute may retard the weldability of substrates containing the subsequently applied and cured coating composition. Preferably, for retaining desirable weldability as well as enhanced adhesion for subsequently applied paints, the contact time between the aqueous solution and the ferrous substrate is between about 5–15 seconds. Typically, for the preferred contact time the substrate will exhibit, if it were permitted to dry, between about 5–35 milligrams per square foot of powdery residue on the ferrous substrate which is a desirable amount of residue as explained in more detail hereinbelow.

Enhanced salt spray resistance for "final" coated articles, that is, those first treated surfaces to which a hexavalent-chromium containing coating composition is subsequently applied and cured, and thereafter to which a paint topcoating is provided, can often be achieved by supplying the dihydrogen phosphate coating solution with up to about 10 grams per liter of metallic ions. Above about 10 grams per liter of such ions often does not provide for sufficient enhancement of the salt spray resistance to make further ion concentration desirable. Typically, for improved salt spray resistance as well as economy, the aqueous dihydrogen phosphate solution contains between about 4–6 grams per liter of such ions.

Metallic ions which can or have been used for enhancing salt spray resistance include calcium, ferrous, cobaltous, manganous, nickelous ions and their mixtures. However, caution should be taken when introducing such ions into the aqueous solution to avoid the commensurate introduction of chloride and sulfate ions, since these ions can act to retard salt spray resistance.

After contacting the ferrous substrate with the aqueous solution, the surface of the substrate is rinsed with water in order to remove water soluble substituents, e.g., alkali metal substituents as well as any substances present on the contacted surface which might result from the presence of oxidizing ions in the solution. After rinsing of the contacted ferrous substrate, the resulting rinsed substrate is for economy, preferably left wet prior to coating with the hexavalent - chromium-containing coating composition. The substrate may be dried, e.g., simply air dried, which can be augmented by using warm water in the preceding rinse.

Sufficient dihydrogen phosphate is present in the solution and/or sufficient contact time between solution and substrate is permitted, with longer contact times usually being employed for weaker solutions, to provide on the substrate, if the contacted surface were permitted to dry, at least about 5 milligrams per square foot of powdery residue but generally not above about 100 milligrams per square foot of such residue. Less than about 5 milligrams per square foot can be insufficient to enhance the adhesion of paint topcoats, while above about 100 milligrams per square foot of the powder is uneconomical; and, advantageously for best economy, only up to about 50 milligrams per square foot of such residue, if the surface were permitted to dry, is established on the substrate. Preferably, for augmented paint adhesion and excellent corrosion resistance as well as ecoonmy, a loose powder of between about 5–35 milligrams per square foot would be achieved on the ferrous substrate if it were permitted to dry. Such preferred amounts are readily obtainable from solutions containing the preferred amount of about 0.5–15 weight percent of dihydrogen phosphate compound contacting the ferrous substrate for the preferred time of about 5–15 seconds.

The corrosion-resistant, hexavalent-chromium-containing coating compositions often contain chromic acid as the hexavalent-chromium-providing substance. But such chromium can be supplied by a salt such as ammonium dichromate, e.g., as taught in U.S. Pat. 2,846,342, or by sodium or potassium salts as shown in U.S. Pat. 2,559,812,

or by substances such as calcium, barium, magnesium, zinc, cadmium, and strontium dichromate as shown for example in U.S. Pat. 2,901,385, and/or British Pat. 1,033,339. Additionally, the hexavalent-chromium-providing substance might be a mixed chromium compound, i.e., include trivalent chromium compounds as shown in U.S. Pat. 3,185,596. Although the coating compositions might contain as little as about 0.25 weight percent of hexavalent chromium, expressed as $CrO_3$, and may contain as much as about 400 grams per liter of composition of hexavalent chromium, expressed as $CrO_3$, such compositions typically contain from several weight percent up to about 20–30 weight percent of hexavalent chromium, expressed as $CrO_3$.

In addition to a hexavalent-chromium-providing substance, these coating compositions contain a reducing compound which is typically a polyalcohol or organic acid and many of these useful reducing compounds have been shown for example in U.S. Pats. 2,559,812; 2,901,385; and 2,777,785. The reducing agent or component is usually present as a single compound which is often organic but can be an inorganic substance, such as potassium iodide, or a hypophosphite reducing agent as shown in U.S. Pat. 2,846,342. Organic reducing agents may be very low molecular weight agents such as formaldehyde, disclosed in U.S. Pat. 3,063,877 or such high molecular weight materials as polyacrylic acid compounds as taught in U.S. Pat. 3,185,596. The reducing agent can be the solution media of the coating composition, as shown in U.S. Pat. 2,927,046 and such reducing components may be preformed and stored prior to use, as taught for example in U.S. Pat. 3,346,522. The reducing agents may not be added to the coating composition directly, but rather supplied to a metal surface already containing an applied chromic acid solution, i.e., the agents are applied during drying of the chromic acid solution, on the metal surface as shown in U.S. Pat. 2,768,103. Combinations of reducing agents are disclosed, for example, in U.S. Pat. 3,382,081.

Additional substances which may be included in such coating compositions include phosphoric acid. These phosphate-containing coating compositions may, conveniently, be referred to as chromate-phosphate coating compositions. Other useful compounds often found in hexavalent-chromium-containing coating compositions are manganese compounds which are useful for extending the useful life of the coating bath, as disclosed in U.S. Pat. 2,777,785, or pigmentary substances as disclosed in British Pat. 1,033,399, as well as resinous materials which have been shown in U.S. Pat. 3,346,522. Additional useful coating composition components may include organic and inorganic acids to maintain composition acidity as taught in British Pat. 972,072 as well as surface active agents.

Substantially all of the hexavalent-chromium-containing coating compositions are water based but other liquid materials are used, and typically these are alcohols, e.g., tertiary butyl alcohol, and this particular alcohol has been used in conjunction with high boiling hydrocarbon solvents to prepare the liquid medium for the coating composition, as taught in U.S. Pat. 2,927,046. Often the coating compositions are solutions but may be dispersions which can contain dispersed pigments, or contain a water dispersible reducing agent such as water dispersible polyacrylic acid compounds.

The coating compositions are usually applied to a metal surface either by dipping the article into the coating composition or by spraying the composition onto the metal surface, which surface can be a preheated metal surface to assist in the curing of the coating, as taught in U.S. Pat. 2,846,342. However, the coating composition may be used as an electrolytic bath to coat a metal surface employed as a cathode in the bath, as shown in British Pat. 972,072. Although the first treated surface may exhibit a loose, powdery residue if dried, it may nevertheless be carefully placed into such a bath without deleterious removal of such residue. Moreover, such residue will not be significantly dissolved by such a bath even within greatly extended coating times of ten to fifteen minutes. The coating composition may be applied to the metal surface after an etch, e.g., a nitric acid etch, as taught in U.S. Pat. 2,768,103, or the reducing agent may be applied after the application of the hexavalent-chromium-containing solution and during drying of such solution on the metal surface, as mentioned hereinabove. The coating composition may be applied from a heated bath, for example one heated up to 200° F. as taught in U.S. Pat. 2,768,104. Moreover, after application and curing of the composition the heated metal may be desirably quenched in a solution of chromic acid in water as taught in U.S. Pat. 2,777,785.

After application of these coating compositions to a metal substrate, the preferred temperature range for the subsequent heating, which is also often referred to as curing and which may be preceded by drying such as air drying, is from about 200° F., as taught for example in U.S. Pat. 3,185,596, but more typically from about 212° F. at a pressure of 760 Hg, up to about 300° C., i.e., about 572° F., e.g., as taught in British Pat. 972,072. Such an elevated substrate temperature may be attained by preheating the metal prior to application of the coating composition as shown in U.S. Pat. 2,846,342. However, such curing temperatures do not often exceed a temperature within the range of about 450°–550° F., to avoid charring or other adverse coating effects as taught in U.S. Pat. 2,777,785. At the elevated curing temperatures the heating can be carried out in as rapidly as about 2 seconds or less but is generally conducted for several minutes at a reduced temperature to provide the most corrosion-resistant and adherent coatings. Resulting coating weights may be as low as about 1.5 to 3 milligrams per square foot, or be as heavy as about 200 milligrams per square foot, but are typically within the range from about 5 to about 100 milligrams per square foot.

Before starting the treatment of the present invention it is advisable to remove foreign matter from the metal surface by thoroughly cleaning and de-greasing. De-greasing may be accomplished with known agents, for instance, with agents containing sodium metasilicate, castic soda, carbon tetrachloride, trichloroethylene, and the like.

After baking the resulting coating on the ferrous substrate it can be topcoated with any suitable paint, i.e., a paint, primer, including electrocoating primers, enamel, varnish, or lacquer. Such paints can contain pigment in a binder or can be unpigmented, e.g., generally cellulose lacquers, rosin varnishes, and oleoresinous varnishes, as for example tung oil varnish. The paints can be solvent reduced or they can be water reduced, e.g., latex or water-soluble resins, including modified or soluble alkyds, or the paints can have reactive solvents such as in the polyesters or polyurethanes. Additional suitable paints which can be used include oil paints, including phenolic resin paints, solvent-reduced alkyds, epoxys, acrylics, vinyl, including polyvinyl butyral and oil-wax-type coatings such as linseed oil-paraffin wax paints. The paints can be applied as mill finishes.

The following example shows a way in which the invention has been practiced but should not be construed as limiting the invention. In the example the following procedures have been employed.

MANDREL TEST BENDING (ASTM–D 522)

The conical mandrel test is carried out by the procedure of ASTM test D–522. Briefly, the testing method consists in deforming a paint-coated metal panel by fastening the panel tangentially to the surface of a conical steel mandrel and forcing the sheet to conform to the shape of the mandrel by means of a roller bearing, rotatable about the long axis of the cone and disposed at the angle of the conical surface, the angle of deformation or arc travel of the roller bearing being approximately 180°. Following

the deformation, a strip of glass fiber tape coated with a pressure-sensitive adhesive is pressed against the painted surface on the deformed portion of the test panel and is then quickly removed. The coating is evaluated quantitatively according to the amount of paint removed by the adhesive on the tape, in comparison with the condition of a standard test panel.

## REVERSE IMPACT STRENGTH

In the reverse impact test, a metal ram of specified weight, in pounds, with a hemispherical contact surface is allowed to drop from a predetermined height in inches onto the test panel. Paint removal is measured quantitatively on the convex (reverse) surface. Quantitative measurements are expressed in inch-pounds and the figure presented is the maximum amount, from at least two determinations, withstood by the coating without any removal to bare metal.

## COIN ADHESION

A freshly minted, i.e., uncirculated, nickel coin is firmly secured in vise-grip pliers; the pliers are manually held in a position such that a portion of the rim of the nickel coin contacts the coated substrate at about a 45° angle. The nickel coin is then drawn down across the panel for about two inches. The type of coating flaking and/or chipping is evaluated qualitatively by visual observance, and panels are compared with the condition of a standard test panel.

## PAINT FILM

The paint film (topcoat) referred to in the example is a commercial white alkyd enamel topcoat typically applied by dip-coating panels into the enamel. This paint is prepared from a modified alkyd resin based upon a system of partially polymerized phthalic acid and glycerine. The paint contains 50 weight percent solids and has a viscosity of 50 seconds as measured on a No. 4 Ford cup at 70° F. After coating, panels with the enamel, the coating is cured by baking in a convection oven for 20 minutes at a temperature of 320–325° F.

## EXAMPLE

A cold rolled, low carbon steel coil four inches in width and 0.036 inch in thickness is employed for preparing treated test panels. The coil is run at 4.5 feet per minute through a potassium dihydrogen phosphate bath maintained at 170° F., having a pH of 3.9, and containing 15 points of total acid per liter of the bath. As the coil emerges from the bath it is rinsed and dried with infrared lamps at a substrate temperature of 250° F. maintained for less than about one minute. Panels cut from this coil for subsequent coating and testing are designated herein as "K-Phos" panels and exhibit a loose powder coating having an average weight of about 15 milligrams per square foot.

Additional comparative test panels, designated in the table below as "Bonded" test panels are commercial panels containing an average coating weight of about 40–50 milligrams per square foot of a tightly adhering, corrosion-inhibiting iron phosphate substrate coating and exhibit no loose powder. Such "Bonded" panels have met with general acceptance as a standard for performance when evaluating corrosion-inhibiting phosphate coatings in, for example, the automotive and household appliance industries.

Both "Bonded" and "K-Phos" panels are coated with the same hexavalent-chromium-containing coating composition prepared in accordance with the teachings of U.S. Pat. No. 3,382,081. This coating is applied to the panels by dipping same into a composition containing 40 g./l. (grams per liter) of $CrO_3$, 15 g./l. of succinic acid, 7.5 g./l. of succinimide, and 0.5 g./l. of polyoxyethylated nonylphenol. After dipping, the panels are removed, excess coating composition is drained from the panels, and the panels are air dried at room temperature until the coatings are dry to the touch. Subsequently, the panels are cured under infrared lamps for about one minute to a substrate temperature of 450° F. This treatment provides a coating residue on the panels of about 50 milligrams per square foot.

All "Bonded" and "K-Phos" panels which have been coated with the chromium-containing bonding coat residue are topcoated with the white alkyd enamel topcoat mentioned hereinabove, and are tested for coin adhesion in the manner described hereinbefore. The results of this test are set forth in the table below.

TABLE

| Panel: | Coin adhesion |
|---|---|
| Bonded | Fair-poor |
| K-Phos | Excellent |

Additional testing of K-Phos pretreated panels by the conical mandrel test shows a coating retention of 99 percent to the metal substrate, thereby further demonstrating the excellent adhesion for the paint to the substrate. Further, such panels tested in the reverse impact test show no paint failure on the impacted surface at 16 inch-pounds.

Further, K-phos treated panels containing the residue for a chromium-containing bonding coat composition are subjected to electrical resistance spot welding. This is performed with copper electrodes at an electrode pressure of 550 lbs. using a weld time of 9 cycles based on a 60 cycle frequency and at a weld heat of 12,500 amp-seconds. During such welding, no metal expulsion is observed and only very slight sticking of the coating to electrode is visually apparent.

Additionally, the welded substrate pulls a good "button" in the peel test. In this test, two coupons (panels) which have been welded together by at least one spot weld are peeled apart past the weld, thereby tearing the welded spot from one of the coupons. Hence, one coupon has a hole at the place of the spot weld and the other coupon has a "button" of metal, at the place of the spot weld. The electrodes for the welding are circular and have a diameter of 0.250 inch. The button pulled from the test coupon, measured across its narrowest apparent diameter with a micrometer caliper calibrated for measuring to the nearest 0.001 inch, must be about 0.240–0.250 inch across at the beginning of, and at the end of, a series of 2,000 spot welds to pull a good button. In view of the above, these K-Phos treated panels are considered to be highly suitable for such electrical resistance spot welding.

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.

What is claimed is:

1. The method of producing a corrosion-resistant coating on a ferrous metal substrate, wherein the resulting coated substrate exhibits weldability and enhanced paint adhesion, which method comprises:

(1) contacting the surface of said substrate with an aqueous solution maintained at a pH level of between about 2–6, said contacting providing sufficient aqueous solution for said substrate to establish thereon, when in dry condition after said contacting and subsequent rinsing, an amount of at least about five milligrams, and not substantially above about 100 milligrams, per square foot of surface, of a partially autogenous, dry powdery residue, with said solution comprising up to about 50 percent by weight of at least one compound selected from the group consisting of ammonium dihydrogen phosphate, alkali metal dihydrogen phosphates, and their mixtures;

(2) rinsing the resulting contacted surface thereby preparing a first treated surface;

(3) applying to said first treated surface a hexavalent-chromium-containing coating composition for metal substrates containing hexavalent-chromium-providing substance and reducing compound therefor; and,

(4) heating said substrate at a temperature, and for a period of time, sufficient to vaporize volatile substituents from said coating composition and deposit on the substrate a composition residue.

**2.** The method of claim **1** wherein said aqueous solution contains between about 0.25–10 percent by volume of a surface active agent selected from the group consisting of hydroxyl-containing hydrocarbon ethers, products from pine wood distillation, and products prepared from waste sulfite liquor, and up to about 10 grams per liter of metallic ions selected from the group consisting of calcium, ferrous, cobaltous, manganous, nickelous, and their mixtures.

**3.** The method of claim **1** wherein said aqueous solution contains between about 1–10 grams per liter of chlorate ion and between about 05–30 weight percent of dihydrogen phosphate compounds, and said alkali metal dihydrogen phosphate is selected from the group consisting of sodium dihydrogen phosphate, potassium dihydrogen phosphate, and their mixtures.

**4.** The method of claim **1** wherein said coating composition residue is the residue remaining after heating an applied hexavalent-chromium-containing coating composition, containing between about 0.25–400 weight percent of hexavalent chromium expressed as $CrO_3$, at a temperature not substantially above about 300° C. and for a time of surface, and said coating composition residue is present on said substrate surface in an amount not substantially in excess of about 200 milligrams per square foot.

**5.** A coated, corrosion-resistant ferrous metal substrate exhibiting weldability and enhanced paint adhesion at the surface thereof, which coated substrate comprises:

(1) a first, partially autogenous residue providing when in dry condition after rinsing not substantially above about 100 milligrams per square foot of surface of said residue, and,

(2) a coating composition residue obtained upon heating an applied corrosion-resistant, hexavalent-chromium-containing coating composition containing hexavalent-chromium-providing substance and reducing compound therefor, at a temperature, and for a period of time, sufficient to vaporize volatile substituents from said coating composition and deposit a coating composition residue;

wherein said first treated surface is the surface obtained by contacting the metallic surface of said ferrous substrate with an aqueous solution maintained at a pH level between about 2–6, which solution comprises up to about 50 percent by weight of at least one compound selected from the group consisting of ammonium dihydrogen phosphate, alkali metal dihydrogen phosphate, and their mixture, and rinsing the resulting contacted surface.

**6.** The coated metal substrate of claim **5** wherein said coating composition is applied over a moist surface remaining after rinsing of said resulting contacted surface.

**7.** The coated, corrosion-resistant ferrous metal substrate of claim **5** wherein sufficient aqueous solution is provided for the metallic surface of said ferrous substrate to establish thereon said partially autogenous residue in an amount of at least about 5 milligrams, and not substantially above about 100 milligrams, per square foot of surafce, and said coating composition residue is present in an amount not substantially in excess of about 200 milligrams per square foot of substrate surface.




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RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

148—6.15, 6.2, 31.5

# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,578,509 Dated May 11, 1971

Inventor(s) Bert E. Palm & William Wayne Warner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

**In the Specification:**

Col. 5, line 4, change "1,033,339" to -- 1,033,399 --.

Col. 6, line 23, after "760" add -- mm. --.

**In the Claims:**

Claim 3, Col. 9, line 20, change "05-30" to -- 0.5-30 --.

Claim 4, Col. 9, line 31, delete "surface," and add -- at least about two seconds --.

Claim 4, Col. 9, line 31, delete "coating composition".

Signed and sealed this 9th day of November 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
U.S. GOVERNMENT PRINTING OFFICE 1969 O-366-334