

PATENT SPECIFICATION

(11)

1 273 413

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NO DRAWINGS

- (21) Application No. 24927/69 (22) Filed 15 May 1969
 (31) Convention Application Nos. 729 918 (32) Filed 17 May 1968
 729 932 17 May 1968
 788 324 31 Dec. 1968
 788 334 31 Dec. 1968 in

- (33) United States of America (US)
 (45) Complete Specification published 10 May 1972
 (51) International Classification B44D 1/34
 (52) Index at acceptance

B2E 19Y 209 20Y 248 327 32Y 349 360 361 378 381 38X
 38Y 397 401 40X 40Y 41X 41Y 438 498 518 532
 568 579 588 591 59X 59Y 607 611 61X 61Y 628
 62X 62Y 630 64Y 65Y 679 708 728 742 768 778
 789 80Y

C7U 4C 4K 4M1 4Q 7B 7C 7E 7G 7K 7L

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(54) IMPROVEMENTS IN OR RELATING TO COATED METALS

(71) We, DIAMOND SHAMROCK CORPORATION, of 300 Union Commerce Building, Cleveland, Ohio, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

Hexavalent-chromium-containing liquid compositions, for example, chromic acid, are applied to metal surfaces in order to impart some corrosion resistance to metal surfaces. For example, chromic acid and *t*-butanol have heretofore been mixed together and applied to metal substrates followed by baking to attain a corrosion-resistant coating, as disclosed in U.S. Patent 2,927,046. Such compositions may also include additions of water plus hydrocarbon solvents to the chromic acid/*t*-butanol composition, as disclosed in U.S. Patent 2,762,732.

Other hexavalent-chromium-containing liquid compositions for imparting corrosion resistance to metal surfaces are ones which contain a specified reducing compound. Some of these have been described in British Patent 1,033,399 and in U.S. Patents 2,559,812, 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. These coating compositions may contain some trivalent chromium, or

the coatings can form trivalent chromium compounds during application and/or heating. Coatings thus prepared tend to be non-porous and somewhat amorphous in nature. They can provide initial, limited corrosion protection for the surfaces of the metal substrate they are applied to, but under rigorous conditions or extended exposure to corrosive atmospheres, such protection is of undesirably short duration.

It has now been found that hexavalent-chromium-containing liquid compositions for metal substrates can offer enhanced corrosion protection when the residue obtained on the substrate by heating such compositions is in intimate mixture with pulverulent metal which is less noble, as determined on the electromotive force series, than the preponderant metal of the metal substrate. Additionally, such a residue can augment adhesion of a paint or other form of topcoating subsequently applied over, and dried on, the residue. Moreover, where such a topcoating comprises an additional coating of hexavalent-chromium-containing liquid composition or is a "welding primer" containing an electrically-conductive pigment, such a protected substrate demonstrates outstanding corrosion protection. The corrosion protection afforded by the present invention can be outstanding, even for subsequently bent or deformed substrates. Moreover, where the substrate is a weldable metal, the coatings of the present invention can be selected to retain the weldability of the

[Price 25p]

metal in the coated substrate.

According to the present invention, a metal substrate has on a surface thereof an adherent, corrosion-resistant coating which comprises the residue from a hexavalent-chromium-containing liquid composition in intimate mixture with pulverulent zinc, manganese, aluminium, magnesium or mixtures or alloys thereof, the pulverulent metal being less noble on the electromotive force series than the predominant metal of the metal substrate, wherein the residue is resin-free and is obtained by applying to the metal surface a hexavalent-chromium-containing liquid composition and then heating the substrate carrying the pulverulent metal and applied liquid composition at a temperature, and for a period of time, sufficient to vaporize volatile components from the coating composition and deposit the residue on the surface.

Additionally, the present invention relates to a method of providing a metal substrate with an adherent, corrosion-resistant, resin-free coating, comprising:

- (1) applying to the surface a hexavalent-chromium-containing liquid composition;
- (2) applying to the surface pulverulent metal selected from zinc, manganese, aluminium, magnesium and mixtures and alloys thereof, the pulverulent metal being less noble on the electromotive force series than the predominant metal of the metal substrate; and
- (3) heating the substrate at a temperature and for a period of time sufficient to vaporize volatile components from the liquid composition and deposit on the surface a resin-free residue in intimate mixture with the pulverulent metal.

For convenience, the hexavalent-chromium-containing liquid compositions are often referred to herein as the "coating" or "liquid" compositions or as the "pretreatment" or "treating" compositions. The material obtained on the substrate after application of such a coating or liquid composition to the metal substrate and the heating of such a substrate to bond the composition thereto is often referred to herein for convenience as a "residue". Also, when the provision of a topcoating is contemplated, the coated substrate resulting from the formation of the residue is often referred to herein for convenience as the "intermediate coated substrate". Such additional coating composition over the residue, that is, the composition applied to the surface of an intermediate coated substrate to form a topcoating, is often referred to herein for convenience simply as the "composition topcoating". The intermediate coated substrate provided in carrying out the invention is characterised in one particular respect, as compared with coated substrates

prepared according to certain prior art teachings, in that the residue, as already indicated, is resin-free. Coating compositions are disclosed in, for instance, Patent Specifications Nos. 1033399 and 1019202 which, in addition to various chromium compounds contain polytetrafluoroethylene and other resinous polymeric materials which become incorporated in the subsequent coated products. The liquid coating compositions of the invention produce coatings which are devoid of such resinous polymeric materials and thus are described herein as being "resin-free"; in the main, the liquid coating compositions are themselves resin-free or, in order to ensure that the residue when produced is resin-free as required, are at least free from any resinous polymeric material or precursor thereof which would not in effect disappear on formation of the residue by virtue of being vaporized with the volatile components of the coating composition during the heating of the substrate carrying the pulverulent metal and the applied liquid composition as illustrated by Example II below.

The liquid compositions which are free from reducing compound and which contain chromic acid or its equivalent as hexavalent-chromium-providing substance can have a minor amount, e.g., 20 percent or less, of such chromium supplied by a salt such as ammonium dichromate, or by sodium or potassium salts, or by substances such as calcium, barium, magnesium, zinc, cadmium, and strontium dichromate. Additionally, a minor amount such as 20 percent or less of the hexavalent-chromium-providing substance might be a mixed chromium compound, i.e., it may include trivalent chromium compounds. Although the liquid composition might contain as little as 0.25 weight percent of hexavalent chromium, expressed as CrO_3 , and may contain as much as 500 grams per litre of composition of hexavalent chromium, expressed as CrO_3 , such composition typically contains from 2 up to 5 weight percent of hexavalent chromium, expressed as CrO_3 .

A preferred embodiment of the invention contemplates the provision of a coated metal substrate, wherein the liquid composition applied comprises a hexavalent-chromium-providing material, at least 80 weight percent of which is supplied by chromic acid, 0.98 parts by weight, based on the total weight of the composition, of pulverulent metal, and a volatile liquid medium. If desired all the hexavalent-chromium-providing material in the liquid composition may be supplied in the form of chromic acid; the pulverulent metal may be absent from the liquid composition, i.e. when it is provided separately, or it may

constitute as much as 98 parts by weight of the liquid composition.

- Although water and *t*-butanol are miscible in all proportions, in order to enhance corrosion resistance of the final coated substrates, *t*-butanol preferably forms the preponderant amount of the liquid medium and only a very minor amount of the medium is water or water plus other liquid material.
- Thus, liquid mediums which are preponderantly *t*-butanol advantageously contain less than 10 percent of water and preferably are virtually to completely water free, as well as containing less than 10 percent of other alcohols, hydrocarbons, or their mixtures. For economy, where water supplies the preponderant amount of the liquid medium, the balance of the medium advantageously contains less than 25 percent of other liquids such as *t*-butanol, or hydrocarbons, and preferably, for enhanced economy, these liquids are present in an amount of less than 15 percent by volume, or may be completely absent. The above-mentioned hydrocarbons which may be in admixture with alcohols or water can be aliphatic or aromatic and may also be chlorinated hydrocarbons or cyclic hydrocarbons. Such suitable hydrocarbons have been more extensively discussed in U.S. Patent 2,762,732. The liquid medium is typically a solution but may be a dispersion and also can contain dispersed pigments as well as such materials as surface active agents.
- The hexavalent - chromium - containing liquid compositions containing one or more reducing compounds often contain chromic acid as the hexavalent-chromium-providing substance. However, such chromium can be supplied instead by a salt such as ammonium dichromate, e.g., as described in U.S. Patent 2,559,812, or by substances such as calcium, barium, magnesium, zinc, cadmium and strontium dichromates, as shown for example in U.S. Patent 2,901,385 and British Patent 1,033,399. Additionally, the hexavalent-chromium-providing substance might be a mixed chromium compound, i.e., it may include trivalent chromium compounds, as shown in U.S. Patent 3,185,596. Although the coating compositions may contain as little as 0.25 weight percent of hexavalent chromium, expressed as CrO_3 , and may contain as much as 500 grams per litre of hexavalent chromium, expressed as CrO_3 , these compositions typically contain from several weight percent up to 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 an organic acid; many of these useful reducing compounds have been described for example in

U.S. Patents 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. Patent 2,846,342. Organic reducing agents may be very low molecular weight agents such as formaldehyde, disclosed in U.S. Patent 3,063,877, or such high molecular weight materials as polyacrylic acid compounds, as disclosed in U.S. Patent 3,185,596. The reducing agent can be the solution medium of the coating composition, as shown in U.S. Patent 2,927,046, and such reducing components may be preformed and stored prior to use, as described for example in U.S. Patent 3,346,522. The reducing agents need not be added to the coating composition directly, but may be supplied to a metal surface already coated with 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. Patent 2,768,103. Combinations of reducing agents are disclosed, for example in U.S. Patent 3,382,081.

Additional substances which may be included in such coating compositions include phosphoric acid or a compound of phosphorous, such as a metal dihydrogen phosphate, and the phosphate can form part of the coating, as disclosed in U.S. Patent 2,901,385. These phosphate-containing coating compositions may, conveniently, be referred to as chromate-phosphate coating compositions. Other useful compounds which may be included in these hexavalent-chromium-containing coating compositions are manganese compounds which assist in extending the useful life of the coating bath, as disclosed in U.S. Patent 2,777,785. Additional useful coating composition components include organic and inorganic acids, to maintain composition acidity as disclosed in British Patent 972,072, as well as surface active agents.

Substantially all of the hexavalent-chromium-containing liquid compositions containing one or more reducing compounds are water based, but other liquid materials may be used and, typically, these are alcohols, e.g., tertiary butyl alcohol; this particular alcohol has been used in conjunction with high boiling hydrocarbon solvents to constitute the liquid medium of the coating composition, as has been mentioned hereinabove. Often the coating compositions are solutions, but they may be dispersions which can contain dispersed pigments or which contain a water-dispersible reducing agent, such as water-dispersible polyacrylic acid compounds.

All these liquid coating compositions are

usually applied to a metal surface either by dipping the metal substrate into the coating composition or by spraying the composition on to the metal surface, which can be pre-heated to assist in vaporizing volatile components from the coating, as disclosed in U.S. Patent 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 Patent 972,072. The coating composition may be applied to the metal surface after an etch, e.g., a nitric acid etch, as disclosed in U.S. Patent 2,768,103, or when a reducing agent is used with the composition, such agent may be applied after the application of the hexavalent-chromium-containing liquid composition minus the reducing agent and during drying of such composition 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 disclosed in U.S. Patent 2,768,104. Moreover, after application and heating of the composition, the heated metal may be desirably quenched in a solution of chromic acid in water, as described in U.S. Patent 2,777,785.

After application to the metal substrate of a liquid coating composition of the kind containing a reducing compound, the preferred temperature range for the subsequent heating, which may be preceded by drying such as air drying, is from 200°F., as disclosed for example in U.S. Patent 3,185,596, but more typically from 212°F. at a pressure of 760 mm. Hg, up to 300°C., i.e., about 572°F., e.g., as described in British Patent 972,072. In a particular preferred embodiment of the method of the invention, wherein the liquid coating composition is of this kind, i.e. it contains a reducing compound, the substrate is heated at a temperature not substantially above 300°C. for a time of at least 2 seconds. Such an elevated substrate temperature may be attained by preheating the metal prior to application of the coating composition as shown in U.S. Patent 2,846,342. However, in order to avoid charring and other adverse coating effects, as described in U.S. Patent 2,777,785, the temperature used does not often exceed the range of 450°-550°F. At the most elevated heating temperatures, the heating step can be carried out in as rapidly as 2 seconds, but this step is generally conducted for several minutes at a reduced temperature to provide the most corrosion-resistant and adherent coatings. Resulting residue weight may be as low as 1.5 to 3 milligrams per square foot, or be as heavy as 200 milligrams per square foot, but are typically within the range from 5 to 100 milligrams per square foot.

Where the invention is performed by

applying to the metal substrate a liquid composition free from reducing compound, the temperature for heating is typically as discussed hereinabove except that the heating can be and preferably is conducted at a temperature up to 900°F. At such elevated temperatures, the heating can be carried out in as rapidly as 0.2 second, but is typically conducted for several minutes at a reduced temperature. Resulting residue weights are the same as discussed hereinabove, except that they may be as heavy as 500 milligrams per square foot.

The pulverulent metal should preferably be present on the surface of the metal substrate in an amount from 10-2000 milligrams per square foot of such surface. Less than 10 milligrams per square foot of such pulverulent metal can be insufficient to impart significant enhancement of corrosion resistance. Greater than 2,000 milligrams per square foot of such surface can lead to coated substrates wherein a portion of the pulverulent metal is insufficiently bonded to the substrate, i.e., "cemented" to the substrate by the residue from the liquid composition, and such portion may therefore be readily removed during subsequent handling and/or treatment of the substrate. Advantageously, for augmenting paint adhesion, the pulverulent metal is present on the substrate surface in an amount above 20 milligrams per square foot. Typically, the pulverulent metal is present on the substrate surface in an amount from 50-400 milligrams per square foot.

The pulverulent metal should preferably have a particle size range such that all particles pass 100 mesh and a major amount pass 325 mesh ("mesh" as used herein is U.S. Standard Sieve Series). Advantageously, for preparing a coated substrate having augmented uniformity in the distribution of the pulverulent metal, as well as enhanced cementing of metal to the substrate, the pulverulent metal employed is one where essentially all particles, e.g., 80 weight percent or more, pass 325 mesh. The desired amount of pulverulent metal present on the substrate surface may be a function of the average particle size of such metal. Thus, for best paint adhesion, the more coarse powders, those having an average particle size approaching 5 microns and more, are employed in greater amounts than pulverulent metals having an average particle size approaching one micron.

The metals employed for the pulverulent metal should be less noble on the electromotive force series than the predominant metal in the metal substrate. As the term is used herein, the "predominant" or "preponderant" metal of the metal substrate is the metal supplying the major amount of the

metallic substance of the substrate. However, when there is no such metal supplying a major amount, e.g., in an alloy which might contain about 42-45 weight percent of two metals, as in the alloy Chromel C wherein such metals would be nickel and iron, the predominant metal for such an alloy is iron, i.e., the less noble metal, as determined on the electromotive force series. The pulverulent metals are the less noble metals, i.e., magnesium, aluminium, manganese and zinc, as well as their alloys, e.g., zinciferous and aluminiferous metals, and additionally include mixtures of any such metals. Moreover, for most readily achieving enhanced corrosion protection by the less noble pulverulent metals, the metals of the substrate are advantageously metals from copper to zinc, inclusive, on the electromotive force series, as well as alloys of such metals wherein such metals are present in major amount, but virtually always these metals are copper, lead, tin, nickel, cobalt and chromium when other than a ferrous metal substrate is being treated. Preferably, for weldability, as well as economy, the substrate is a ferrous metal substrate such as iron, stainless steel, or steel such as cold rolled steel or hot rolled and pickled steel.

The pulverulent metal can be applied dry to the metal substrate, for example by simply brushing or blasting the metal on to the substrate, or by electrostatic spraying. It can be applied as a dispersion of such metal in the liquid composition, but preferably for enhanced dispersion stability when the liquid composition is substantially water based, the pulverulent metal is applied to the metal substrate separately from the hexavalent-chromium-containing liquid composition. When the pulverulent metal is applied separately, it can be applied dry or as a dispersion in a volatile liquid, for example, water or a readily volatile alcohol, or other volatile organic liquids such as benzene, with water usually being preferred for economy. For economy, such dispersions advantageously contain at least 5 grams per litre of dispersed metal to avoid subsequent uneconomical evaporation of large amounts of volatile liquid. However, the dispersions may contain above 90 weight percent of pulverulent metal in the case of a dense metal such as zinc, i.e., above 65 volume percent of such metal. Typically though, where the metal is dispersed in the hexavalent-chromium-containing liquid composition, for example, the weight percent of such powder in such composition is within the range from about 10-50 percent, though in general (as already indicated) the pulverulent metal can constitute up to 98 parts by weight, based on the total weight of the composition.

Such dispersions may be applied to the metal substrate by any conventional method for coating a substrate with a liquid, for example, dip coating, roller coating, or reverse roller coating, curtain coating, airless spray, rotary brush coating, pressure spray, or combinations of such techniques as for example, spray and brush techniques. However, for usual spray application, the concentration of pulverulent metal in the dispersion for a dense metal such as zinc does not exceed 500 grams per litre.

When applied in dry form or as a dispersion in a volatile liquid, the pulverulent metal may be applied before or after the application of the coating composition, so long as such composition has not been subjected to the heating step which forms the residue on the substrate. When the coating composition is applied electrolytically, the pulverulent metal is preferably applied thereafter to avoid loss of such metal in the electrolytic bath. Often, the pulverulent metal can be incorporated into the coating composition and thus applied to the metal substrate simultaneously with such composition. Where the pulverulent metal is dispersed in a volatile liquid and it is desired to dry such dispersion on the substrate surface during or after application thereto, it is preferably forced dried, for example at an attained metal substrate temperature up to 200°F. Also, as has been disclosed in U.S. Patent 2,846,342, mentioned hereinbefore, an elevated substrate temperature to obtain fast residue formation may be achieved prior to, and maintained during, application of the coating composition. Temperatures conducive to fast residue formation can be employed during application of the coating composition, so long as the pulverulent metal is present on the substrate surface before, or is applied in admixture with, or simultaneously with, the liquid coating composition.

When employing a volatile liquid for applying the pulverulent metal, the dispersion can contain up to, for example, 10 percent by volume of a surface active agent. Such agent may typically be a hydroxyl-containing hydrocarbon ether which includes the alkyl ethers of alkylene glycols, such as butyl ether or propylene glycol, the oxyalkyl ethers of alkylene glycols, e.g., 1-butoxyethoxy-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 prepared from waste sulfite liquors, such as lignin sulfonic acids, and products from pine wood distillation, e.g. pine oil. In order to further augment salt spray resistance of the coated substrate, such dispersions can

contain up to 10 grams per litre of metallic ions, and typically from 1-4 grams per liter of such ions. These metallic ions include calcium, ferrous, cobaltous, cupric, manganous and nickelous ions and mixtures thereof. However, care should be taken, when introducing such ions into the dispersion, to avoid the introduction of chloride and sulfate ions, since they can act to retard salt spray resistance.

Before subjecting a substrate to the method of the present invention, it is in most cases advisable to remove foreign matter from the metal surface by thoroughly cleaning and de-greasing it. De-greasing may be accomplished with known agents, for instance, with agents containing sodium metasilicate, caustic soda, carbon tetrachloride or trichloroethylene. A commercial alkaline cleaning composition which combines washing and mild abrasive treatments can be employed for cleaning, e.g., an aqueous trisodium phosphate-sodium hydroxide cleaning solution. Instead of cleaning only, the substrate can undergo cleaning plus etching, for example, by being treated with a hydrofluoric acid etching agent. To accomplish etching of the substrate, instead of only applying the hexavalent-chromium-containing liquid composition, in some cases a mixture may be applied which incorporates the etching agent in such composition.

To augment corrosion resistance of a coated substrate made using a liquid composition free from reducing compounds, the liquid composition can, if desired, contain up to 5 weight percent of further ingredients, i.e., in addition to those discussed hereinabove, often employed in the metal coating art for imparting some corrosion resistance or enhancement in corrosion resistance for metal surfaces. These include zinc chloride, magnesium chloride, molybdates, fluoridic acid and zinc nitrate. Such augmentation of corrosion resistance may also be obtained by quenching the coated metal substrate, following heating of the substrate with the applied liquid composition, in a bath which contains a minor amount, e.g., 5 weight percent or less and, for economy, advantageously only a few weight percent or less, of an acid of phosphorus, such as phosphoric acid. With phosphoric acid in the quenching bath, highly desirable resistance to corrosion has been obtained with metal substrates quenched in such baths containing as little as 0.1 weight percent of the acid.

After the liquid composition is converted to the residue and the substrate cooled, a further coating composition may be applied to the substrate. For enhanced corrosion resistance, this coating composition preferably also contains a reducing compound or, alternatively, is a "welding primer", so that an additional coating is formed which

either is the same as the residue already present or is a "welding primer" coat. In accordance with a preferred embodiment of this feature of the method of the invention, this further coating composition is formed in substantially the same way as is preferably used for the first coating according to the above-described preferred embodiment using a liquid composition containing a reducing compound, the substrate being heated at a temperature not substantially above 300°C. for a time of at least 2 seconds. The welding primers, which can alternatively be used to provide a further coating for affording enhanced corrosion resistance, contain a particulate, electrically-conductive pigment of aluminium, copper, cadmium, steel, carbon, zinc, or magnetite, i.e., the magnetic oxide of iron, including mixtures thereof such as aluminium flake and zinc powder. Generally, the carbon pigments, e.g., channel blacks or furnace blacks, are the most finely divided of these electrically-conductive pigments, often having particle sizes of 0.01 micron for the intensely black pigments. Comparatively, the finely divided aluminium powders have flake thicknesses for the finest grades of 0.25 micron. These aluminium pigments can be typically produced by stamping, generally of small pieces of aluminium foil, or by ball milling atomized aluminium formed by air blasting a molten aluminium spray. Typically a finely-divided zinc pigment is a distilled zinc dust or particles prepared by atomizing molten zinc in an air stream. Particle sizes for distilled zinc powders often average from 2 to 6 microns with generally 99 weight percent or better passing a 240 mesh U.S. Standard Sieve.

Since these primers generally are applied preparatory to subsequent welding of the substrate, they must contain a substantial amount of the electrically-conductive pigment, e.g., at least 30 volume percent pigment for the zinc-rich primers and often more than 65 volume percent of particulate pigment, but on a weight basis, because of the density of the zinc, these primers can contain up to 98 weight percent of such pigment.

In formulating the weldable primers, the binder component can be made up of resins specially selected to afford particular characteristics to the applied coating. Thus the binder components for the zinc-rich primer having the greatest adhesion are polyamide resins combined with epoxy resins, although other binder materials have been found to be compatible with particulate zinc pigment, e.g., polystyrene, chlorinated or isomerized rubber, polyvinyl acetate and polyvinyl chloride-polyvinyl acetate copolymers, alkyd/melamine, and epoxy esters including epoxy ester medium oil content linseed oil.

Additionally the formulations can contain flow control agents, as for example urea formaldehyde resins, thixotroping agents such as silica and organic derivatives of magnesium montmorillonite, and anti-settling agents particularly for the aluminium and zinc primers, which agents include hydrogenated castor oil and aluminium stearate. Also for the aluminium and zinc primers where gassing can be a problem, a gas inhibiting substance such as lime or calcium oxide is generally included in the formulation. Also, these primers usually contain, and/or are cut back, thinned or diluted after formulation but before application with, petroleum-derived hydrocarbon liquids such as toluene, benzene, xylene and synthetically prepared aromatic solvent blends from petroleum. Zinc-rich weldable primers have been more extensively reviewed in an article entitled "Zinc-Rich Paints" in *Paint and Varnish Production*, April, 1964, p. 35 f.; May, '64, p. 87 f.; and June, 64, p. 47 f.

The final make-up of the primer can be dependent upon the method of application of the primer to the treated metal substrate. Typically for primers containing zinc dust or combinations of zinc dust with aluminium flake, or zinc flake with aluminium flake and the like, where such primers are spray applied to the metal substrate, they may contain from 50-80 weight percent of the pulverulent metal and 10-30 weight percent of binder. Also such primers generally are formulated with a few weight percent or less of a thixotroping agent, and often with a half weight percent or less of a metallic drier, e.g., a lead, manganese, cobalt, or other metallic salt of an organic acid, and typically 10-30 weight percent of petroleum-derived hydrocarbon liquid.

However, for such primers which are electrically deposited, they typically contain, based on the weight of the total paint solids, 40-65 weight percent of electrically-conductive pigment, e.g. zinc flake or combinations of zinc and aluminium flake, as well as 20-40 weight percent of binder plus 5-25 weight percent of one or more extender pigments. However, on a basis of the overall coating bath, such electrodeposited primers can typically contain greater than 80 weight percent of water medium supplied by deionized water to avoid any reactions between the electrically conductive pigment and water. Additionally, in the overall coating bath, there is usually present in very minor amounts, e.g., a half percent or less, a pigment dispersing agent, such as a metallic stearate, a comparable amount of surfactant, as well as slightly greater amounts of organic solvent, supplied for example by a petroleum distillate.

For these electrically deposited primers, an extender pigment, e.g., rutile or anatase titanium dioxide, zinc oxide or leaded zinc oxide, is included to enhance the uniformity of the deposited primer film. Also, the binders used for such electrodeposited primers are preferably high resistance type resins, thereby permitting the presence of enhanced amounts of extender pigment in the primer formulation. For electrodeposition, such primers are typically coated on to copper, cupriferous, zinciferous, or ferrous metal substrates.

The primer can also be applied to the treated substrate by various other methods, e.g., any of those methods which have been mentioned hereinbefore regarding application of the hexavalent-chromium-containing liquid composition to the substrate. Generally to achieve a significant enhancement in corrosion resistance, the applied primer has a film thickness in excess of 0.05 mil, but for economy, has a film thickness not substantially in excess of 6 mils. However, where the substrate is to be subsequently welded, the primer film thickness will typically be 1 mil or less to provide rapid welding. The primer is preferably applied to a treated substrate which has first been cooled to a temperature below 200°F. after heating to convert the applied liquid composition to the residue, since substrate temperatures above 200°F. may cause excessively rapid evaporation of the volatile components in the primer composition which can result in a discontinuous, applied film.

After application the primer is dried, which can often be accomplished simply by air drying at room temperature or by accelerated air drying at an elevated temperature such as 200°F. or higher. Additionally, such drying can be enhanced by catalytic action, for example with a metallic drier including lead, manganese, and cobalt or other metallic salts of organic acids, e.g., cobalt acetate. Such primers as are dried at room temperature by air drying can be ostensibly dry to the touch in as little as 10-12 minutes. Many of the weldable primers, e.g., those based on epoxy resin or epoxy/melamine resins for the binder component, are dried by baking at an elevated temperature and for a period of time sufficient to vaporize volatile components of the composition, the baking temperature being dependent upon the applied film thickness as well as on the particular binder present in the formulation.

For baking, a simple convection oven is preferred as opposed to infrared baking, since the capacity of the zinc and aluminium primers to reflect infrared radiation can lead to inefficient operation. Advantageously, for primers dried at elevated temperatures, they are baked at a temperature

- within the range of 350°-1000°F. for a time of 0.5-10 minutes. Temperatures below 350°F. and times of less than 0.5 minutes can provide incomplete baking which, especially on mill finished coils, may lead to deleterious film removal, e.g. during coiling. Temperatures above 1000°F. can lead to film degradation, e.g., charring of the binder solids, and baking times greater than 10 minutes are usually uneconomical. Typically, a zinc-rich primer having an applied film thickness of 0.1-3 mils is baked in an oven having an ambient air temperature of 400°-700°F. and for a time of 0.5-5 minutes.
- After heating, the resulting coated substrate of the present invention can be further topcoated with any suitable paint, i.e., a paint, primer, including electro-coating primers, enamel, varnish or lacquer. Such paints may 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 may 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 may be applied as mill finishes.

When reference is made herein to the application of a coating prior to welding of the substrate, it is to be understood that the subsequent welding under consideration can be spot welding, i.e., localized electrical resistance welding, or seam welding such as with roller electrodes. Typically spot welding may be performed with copper electrodes at electrode pressures from 100 to 5,000 pounds, and at 4-5 volts and 10,000-17,000 amps operating conditions, with a weld time, in cycles, from 4 to 400 based on a 60-cycle frequency. When the weldable substrate can be coated on more than one surface, e.g., a sheet or strip of ferruginous material, the undercoat composition can be applied to and heated on all surfaces, and the topcoat composition may be applied only to those surfaces which will be in close proximity or direct contact with the welding electrodes.

The following examples show ways in which the invention has been practised, but should not be construed as limiting the invention. In the examples, the following procedures have been employed.

Preparation of Test Panels

Steel test panels (4" × 12" unless otherwise specified, and all being cold rolled, low carbon steel panels) are prepared for

subsequent treatment by dipping into water, or by spraying with water which has incorporated therein 2-5 ounces of cleaning solution per gallon of water. The cleaning solution is 25% by weight of tetrasodium pyrophosphate, 25% by weight of disodium phosphate, and the balance sodium hydroxide, or such a cleaning solution as 25 weight percent tripotassium phosphate and 75 weight percent potassium hydroxide. The bath is maintained at a temperature of 150°-180°F. After this cleaning, the panels can be scrubbed with a brush or a dry cleaning pad which is a porous, fibrous pad of synthetic fibre impregnated with abrasive. Following the cleaning, or cleaning plus scrubbing, the panels are rinsed with warm water.

Corrosion Resistance Test (ASTM B117-64)

Corrosion resistance of coated panels is measured by means of the standard salt spray (fog) test for paints and varnishes, ASTM B-117-64. In this test, the panels are placed in a chamber kept at constant temperature where they are exposed to a fine spray (fog) of a 5% salt solution for specified periods of time, rinsed in water and dried. The extent of corrosion on the test panels is then compared one with the other by visual inspection. Where test panels are scribed, the scribing is performed before testing the panel by cutting an "X" configuration on the face of the panel, the scribe lines being made through the coatings to expose the underlying metal. The extent of corrosion along the scribe lines is also measured by visual inspection and through comparison among test panels.

Condensing Humidity Test

In this test, water is heated in the bottom of a cabinet to produce a condition of 100 percent humidity in the cabinet and a temperature for the ambient steam within the cabinet of 120°F. Panels are placed in the cabinet at a 15° angle to the water surface; the bottom edge of the panel is 8 inches above the water surface, and the top edge 10 inches above the water surface. To terminate the test, panels are simply removed from the cabinet. Upon removal, panels are air dried and visually inspected for rust on the face of the panel, that, is not around the panel edges. Results are reported as that portion of the total panel face, in percent, which exhibits red rust and blister coating failure. Where panels have been scribed before testing, in the manner described hereinbefore in connection with the corrosion resistance test ("salt spray"), results are reported for that portion of the scribe lines showing corrosion as determined by visual inspection of these lines.

Coin Adhesion

A freshly minted, i.e., uncirculated, United States nickel coin is firmly held in

- vice-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 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.

Panel Bending

90° Bend

- Unless otherwise specified in the examples, the panel bending, where corrosion resistance of coated panels is tested at a bend, is a 90° bend. This bend is obtained by manually grasping a test panel at the opposing edges of shortest dimension and then manually bending the panel over the edge of a flat surface, such as the edge of a table, with the panel being positioned at such edge to obtain the bend at approximately the mid-section of the panel. The bending is continued until the panel, by visual inspection, is viewed to have a bend of approximately 90°.

Bearing Bend

- Where bearing bending is specified in the examples, such bending is attained by placing a hollow metal cylinder in an upright position and then centering the panel on the uppermost hollow end of the cylinder. The cylinder has a 1 1/4-inch inside diameter and its upper annular surface on which the panel is placed is beveled inwardly. After the panel is thus centered, a one-inch diameter, chromed steel bearing is placed on the panel approximately over the centre of the hollow core of the cylinder. A die is then gradually pressed downwardly on to the bearing up to a pressure of 2000 psi. Upon removal of the die and the bearing, the panel exhibits a dimple conforming to the roundness of the bearing and having a depth of about 1/4-inch.

Mandrel Bending

- When mandrel test bending is specified in the examples such bending has been carried out by the procedure of ASTM D-522. Briefly, the testing method consists in deforming the 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 100°.

Weather Rack Testing

Corrosion protection under weathering conditions is obtained by mounting test panels on an outdoor rack to expose the panels to weathering conditions prevailing in the North Central Region of the United States. The test panels are mounted for such exposure as is obtained during late autumn.

Paint Film

The paint film referred to in the examples is a commercial white alkyd enamel top-coat 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 1

Test panels are prepared as described hereinbefore and are coated by dipping in the coating composition, removing the panels and draining excess composition therefrom and then immediately baking or air drying at room temperature until the coating is dry to the touch and then baking. Baking proceeds under infrared lamps at a substrate temperature of up to 450°F. for a time up to 1 minute. The panels are then bent to a 90° bend in accordance with the procedure described hereinabove. Coating baths for the panel contain 40 grams per litre CrO₃ and 200 grams per litre of zinc dust having an average particle size of 2.9 microns, as well as 0.5 gram per litre of a surface active agent, typically a lignosulfonate, in a *t*-butanol medium. Where baths contain additional ingredients, these have been shown in the table below as weight percents of such ingredients.

In the table below, results are reported for the salt spray test both for the face of the panel and the bent portion of the panel face. Panels which have not been bent before testing are shown as "not tested" for the bend. Duration of exposure of the panels to the test is also reported in the table below.

Table 1

	Additional Ingredient Wt. Percent	Panel	Hours In Test	Percent Corrosion In Salt Spray	
				Bend	Face
5	None	1	64	0	<1
		2	64	0	0
		3-4	65 each	both 0	both 0
		5	531	N.T.	0
		6	792	N.T.	0
10	0.7% ZnCl ₂	7*	161	0	0
		8*	161	<1	0
		1	113	0	<1
		2	113	0	<1
		3-7+	258 each	all 0	all 1
15	0.7% MgCl ₂ ·6H ₂ O	1-4	235 each	all 0	all 1
		5	235	0	<1
	1.2% ZnNO ₃	1-2	160 each	both 0	both 0
		3	160	0	1
	1% H ₃ PO ₄	1-2	112 each	both 0	both 1

20 N.T. = Not Tested.

* = Panels dipped in 48-hour old bath.

+ = Bath for one panel also contained 0.50 weight percent H₃PO₄.

30 The above results thus show the excellent corrosion protection attained by the chromic acid/zinc powder/*t*-butanol baked coating as well as for such coatings from a bath containing minor amounts of phosphoric acid or an inorganic salt. Corrosion protection with such compositions is not only obtained on unworked faces of the panels but also on portions of the panels which have been subjected to 90° bending before exposure to salt spray testing. Additionally such protection can be achieved even with greatly extended exposure, one panel retained in the bath for nearly 800 continuous hours of salt spray testing showing no visual corrosion and hence excellent protection for the coating composition.

45 Example 2

50 Panels are prepared and coated as described hereinabove with coating baths as described in Example 1. Where the coating baths contain additional ingredients, such substances have been shown in the table below in weight percent of the bath unless otherwise specified. The polyacrylic acid additional ingredient is a water solution of

polyacrylic acid, ammonium polyacrylate 65 and sodium polyacrylate; this polyacrylic acid additional ingredient represents only a small part of the coating bath composition and does not behave as a barrier coating resin, but functions as a reducing compound 70 for the hexavalent chromium, as described in the aforementioned U.S. Patent 3185596. The solution has a total solids content of 25 weight percent, a pH of 2-3, a specific gravity of 1.09, and a viscosity at 25°C. as 75 measured at 25 r.p.m. on a Brookfield viscosimeter of 500-1500 centipoise.

Also, as shown in the table below, some panels are coated with the Example 1 chromic acid/zinc powder/*t*-butanol com- 80 position and after baking in the manner described hereinbefore are quenched in a dilute bath of phosphoric acid. In the table, results are reported for the condensing humidity test for the face of test panels, 85 and, where tested, for corrosion along scribed lines of panels as such testing and scribing has been described hereinbefore. Duration of such testing for each panel is 90 also reported in the table.

Table 2

	Additional Ingredient, Wt. Percent	Panel	Hours In Test	Percent Corrosion In Condensing Humidity	
				Scribe	Face
5	None	1	27	0	0
	2.5% Polyacrylic Acid	1-2	24 each	both 0	both 0
	0.5% H ₃ PO ₄	1	27	0	0
10		1	64	0	0
		2	90	0	0
	0.7% ZnCl ₂	1-3	23 each	all 0	all 0
		4-5	72 each	both 0	both 1
	0.7% MgCl ₂ ·6H ₂ O	1-3	64 each	N.S.	all 0
		4-5	67 each	both 0	both 0
15	0.25 Vol. Percent H ₃ PO ₄ Quench	1	136	N.S.	0
		2-3	160 each	N.S.	both 0
		4-5	184 each	N.S.	both 0
		6	208	N.S.	0
20		7	360	N.S.	0

N.S. = No Scribe.

These results demonstrate the excellent condensing humidity corrosion resistance for panels containing even minor amounts of phosphoric acid or inorganic chloride salts, as well as for coated panels quenched in phosphoric acid. Such excellent corrosion resistance is not only demonstrated on panel faces but also along scribe lines cut through to the substrate metal. Moreover, such resistance on faces of panels include no ostensible corrosion after 360 hours of continuous testing, thereby demonstrating the desirable extended corrosion protection afforded by a phosphoric acid quench.

Example 3

Panels are prepared and coated in the manner described hereinbefore with the composition of Example 1. The coated panels are quenched in a weak phosphoric acid bath containing the acid in amounts shown in the table below. Also as shown in the table below, one panel is quenched in water in place of an acid quench. All acid quenched panels are then scribed in the manner above described and then bent as as described hereinbefore. In the table results are reported for such panels subjected to the salt spray test.

Table 3

	Ingredient In Quench, Vol. Percent	Panel	Hours In Test	Face	Percent Corrosion In Salt Spray	
					Scribe	90° Bend
50	None, water only	1	1,616	0	N.T.	N.T.
55	0.1% H ₃ PO ₄	1	170	2	0	0
		2	170	0	0	0
	0.2% H ₃ PO ₄	1-2	170 each	both 0	both 0	both 0
	0.25% H ₃ PO ₄	1-7	360 each	all 0	all 0	all 0

N.T. = Not Tested.

From Table 3 it can be seen that quenched panels, including the first panel subjected to quenching with water only, display excellent corrosion resistance in salt spray testing even for panels which have been scribed through to the substrate metal and additionally bent before subjecting to the test.

Example 4

Test panels are prepared as described above and coated in the manner described above with a coating composition containing 150 grams per litre powdered zinc having an average particle size of 2.9 microns, in a *t*-butanol medium. One bath also contains 30 grams per litre CrO₃ and the panels dipped therein are designated A and B. The other bath contains 40 grams per litre CrO₃ and the panels dipped therein are designated panels C and D. After baking in the above-

mentioned manner, all panels are quenched in a bath of 0.2 volume percent phosphoric acid.

Panels A and C are each scribed and subjected for 25 hours to the condensing humidity test described hereinbefore. Panels B and D are bent in the above-mentioned manner and are subjected to the salt spray test for 25 hours.

Results of such testing for all panels show freedom from corrosion on panel faces, scribes and bends after both tests, thereby demonstrating the desirable protection achieved for substrates coated with compositions of the present invention.

Example 5

Four high tensile steel rods for prestressed concrete which each measure 12 inches long by 0.25 inch in diameter are cleaned

by rubbing with a dry cleaning pad. The pad is a porous, fibrous pad of synthetic fiber and is impregnated with abrasive. Two rods are dipped in a *t*-butanol bath containing 200 grams per litre of powdered zinc having an average particle size of 2.9 microns, 40 grams per litre CrO_3 , and 0.5 volume percent of phosphoric acid.

Two additional cleaned rods are coated 10 by dipping in a *t*-butanol bath containing

200 grams per litre of the above-mentioned zinc, 40 grams per litre CrO_3 , and 1 weight percent of ZnCl_2 . All four rods are heated in a muffle furnace for a time, and up to a temperature, as shown in the table below. 15 The rods are then subjected either to condensing humidity or to salt spray testing as described hereinabove. Results of such testing are shown in the table below.

20

Table 4

		<i>Cure</i>		<i>Condensing</i>	<i>Humidity</i>		<i>Salt</i>	<i>Spray</i>
	<i>Rod</i>	<i>Time</i>	<i>Cure Temp.,</i>	<i>Test</i>	<i>Percent</i>		<i>Test</i>	<i>Percent</i>
		<i>Secs.</i>	<i>°F.</i>	<i>Hrs.</i>	<i>Corrosion</i>		<i>Hrs.</i>	<i>Corrosion</i>
25	1	105	490°-520°	48	<1	—	—	—
	2	105	490°-520°	—	—	90	—	0
	3	45	800°	65	0	—	—	—
	4	45	800°	—	—	65	—	0

The above results thus demonstrate the 30 rods coated with formulations of the present invention exhibit excellent corrosion resistance from both the condensing humidity and salt spray test even for very high temperature cured coating compositions. 35 Such compositions and elevated temperature curing thus are deemed to be highly suitable for protecting the rods against corrosion.

Example 6

40 Test panels are prepared as described above and coated in the manner described above with a coating composition containing 300 grams per litre powdered zinc having an average particle size of 2.9 microns, 45 40 grams per litre of CrO_3 , and 0.4 weight percent succinimide, in a *t*-butanol medium. Another test panel is prepared as above described and coated in the aforementioned manner in the above bath containing 300 50 grams per litre powdered zinc; however, the bath additionally contains one weight percent of MgCl_2 .

After heating both panels in the above-mentioned manner, each panel is scribed and 55 subjected for 24 hours to the condensing humidity test. After such testing the panels are visually inspected and found to be free from corrosion on both panel surfaces and along scribe lines thus demonstrating the 60 desirable corrosion resistance achieved for such compositions of the present invention.

Example 7

Test panels are prepared as described above and coated initially by dipping in a 65 water medium containing 40 grams per litre of CrO_3 and 0.2 grams per litre of polyoxyethylated nonylphenol. After the panels are removed and excess coating medium drained from the panels, they are sprayed 70 with a composition containing 150 grams per litre of zinc powder having an average particle size of 2.9 microns to prepare

panels having about 200 milligrams per square foot of panel surface of zinc dust. These panels are then baked in the manner described hereinbefore and after baking 75 panels are bent 25° and 45°.

After bending, the panels are subjected to the salt spray test for a total of 47 hours, following removal from the salt spray 80 test the panels are inspected both at the bend and on the face of the panels for corrosion and are found to be completely free over the entire panel surface from corrosion both for panels bent 25° and 45°. 85 These results thereby demonstrate the desirable corrosion protection achieved by compositions of chromic acid and water which compositions receive, after application to a metal surface, a deposition of 90 pulverulent zinc.

Example 8

Test panels are prepared as described above and coated in the manner described above. Three panels are coated with composition containing 35 grams per litre of 95 CrO_3 and 200 grams per litre of powdered zinc having an average particle size of 2.9 microns. Three panels are coated with a composition containing 200 grams per litre of the same powdered zinc and 45 grams per litre of CrO_3 . Three additional panels are coated in a composition containing 300 100 grams per litre of the powdered zinc and 45 grams per litre of CrO_3 . All of the coating compositions are in a *t*-butanol medium. 105

After heating all nine panels in the above-mentioned manner, one panel from each coating bath is bent through 90° and subjected to salt spray. Additionally, one panel 110 from each bath is scribed and subjected to the above-described condensing humidity test. Further, one panel resulting from each bath is scribed and subjected to the weather rack test. In the 115 table below results of such testing are

shown along with durations of the test. Additionally, for panels from each bath, there is shown in the table below the coating weight in milligrams per square foot, as well as the weight of zinc dust and the weight of chromium in the coating, both also in milligrams per square foot.

TABLE 5

Bath Concentrations Gms. CrO ₃ /gms. Zn Dust	Coating Weight Mgms./ft ²	Cr Wt. Mgms./ft. ²	Zn Dust Wt. Mgms./ft. ²	Salt Spray				Percent Corrosion				Weather Rack	
				Hrs.	Face	Bend	Hrs.	Face	Scribe	Humidity	Days	Face*	Scribe
35/200	403	34	335	120	2	0	150	0	0	0	23	0/2	0
45/200	415	41	333	120	0	0	48	<1	1	1	23	0/3	0
45/300	603	41	521	120	0	0	48	0	<1	23	0/>1	0	0

* The notation 0/2, for example, represents front/back faces, respectively.

The above results thus demonstrate the excellent corrosion protection achieved with coatings obtained from baths containing varying concentrations of powdered zinc and CrO₃ in each of the salt spray, condensing humidity, and weather rack tests.

Example 9

Two test panels are prepared as described above and coated in the manner described above with a coating composition containing 5 75 grams per litre of CrO_3 and 500 grams per litre of powdered zinc, having an average particle size of 2.9 microns, in a *t*-butanol medium. After the panels are coated and excess composition drained therefrom, the 10 panels are subjected to baking under infrared lamps for 35 seconds at a substrate temperature up to about 460°F.

After baking, each panel is quenched in a bath of 0.2 volume percent phosphoric acid. 15 Subsequently, each panel is scribed, bent through 90°, and subjected for 936 hours to the above-described salt spray test. After such extended corrosion resistance testing each panel is visually inspected, and both 20 panels are found to be free from corrosion

on panel surfaces, along scribe lines, and at the bend, thus demonstrating the excellent corrosion resistance achieved for such compositions of the present invention.

Example 10

Panels are prepared and coated as described hereinabove with a *t*-butanol coating composition containing 35 grams per litre CrO_3 and 200 grams per litre of pulverulent zinc having an average particle size of 2.9 30 microns. The panels are baked in the manner discussed hereinbefore and after baking are quenched in a bath of 0.2 volume percent phosphoric acid.

As shown in the table below some panels 35 are then scribed and all panels are bent in a manner also as shown in the table below. Thereafter, each panel is subjected to the salt spray test and the results of such testing are shown hereinbelow in the table. 40

Table 6

	Number of Panels	Hours	Percent Corrosion, Face	Corrosion, Bend	Salt Spray Scribe
	3	304 each	all 0	all 0*	all 0
45	4	240 each	all 0	all 0+	N.T.
	2	184 each	both 0	both 0**	both 0

N.T. = Not Tested.

* 90° Bend.

+ Bearing Bend.

50 ** Conical mandrel bend.

The above results thus show the highly desirable corrosion protection achieved in salt spray testing not only on scribed panel surfaces but on panel surfaces under 55 extended testing which surfaces have been subjected either to the 90° bend, the bearing bend, or the conical mandrel bend which have been described hereinbefore.

Example 11

60 Four test panels, measuring 2" × 6", are prepared as described above and coated as described hereinabove in a *t*-butanol bath containing 35 grams per litre CrO_3 , 50 grams per litre of pulverulent aluminium flake, and 200 grams per litre of powdered 65 zinc having an average particle size of 2.9 microns. Three of the panels are heated in

the manner described above; one of these (panel A) is quenched in a water bath and the remaining two (panels B and C) are 70 are quenched in a bath of 0.2 volume percent phosphoric acid. The fourth panel (D) is coated by dipping for 5 seconds in a bath of molten lead and after removal therefrom is quenched in a bath of 0.2 volume 75 percent phosphoric acid. The first two panels, i.e., A and B, are scribed and subjected to the salt spray test, and the remaining two panels, C and D, are subjected to the condensing humidity test. Duration of 80 the tests as well as the result of such testing are shown for these panels in the table below.

Table 7

	Panel	Hours	Salt Spray	Percent Corrosion Hours	Condensing Humidity
	A	163	0% face & scribe	—	N.T.
90	B	163	0% face & scribe	—	N.T.
	C	—	N.T.	22.5	0
	D	—	N.T.	22.5	0

N.T. = Not Tested.

The above results thus show the desirable corrosion protection achieved for coated panels prepared from baths containing mixtures of aluminium and zinc powders.

5 Example 12

Two test panels are prepared as described above and are dipped into a bath containing 40 grams per litre of CrO_3 supplied by chromic acid as well as 0.5 grams per litre of polyoxyethylated nonylphenol, with the balance distilled water. After dipping, the panels are removed from the bath, excess composition drained from the panels, and immediately dried in an air-circulating oven, for a time shown in the table below, to a substrate temperature of 450°F.

After cooling, these two panels are coated with a zinc-rich primer having at first a weight per gallon of 23.1 lbs., an initial solids volume of 50 percent, and containing initially 84.5 weight percent of non-volatiles. Prior to use, this primer is reduced to

a viscosity of 45 seconds as measured on a No. 4 Ford cup with an aromatic solvent prepared synthetically from petroleum and having a flash point of 145°-150°F. Primer coated panels, which panels include two panels prepared, i.e., scrubbed and cleaned, as described hereinbefore but without the chromic acid treatment, are all dried for 3 minutes in an air-circulating oven to a metal substrate temperature of 425°F. Primer coating thickness measures 0.5 mil for each panel.

All four panels, that is, the two primer coated panels which have been first treated and the two primer coated panels that have been just scrubbed and cleaned, are subjected to the same corrosion resistance test, after scrubbing, as described hereinbefore. The results of such testing as well as the duration of the test are shown in the table below as "salt spray" data. Rust in the field is rust over the face of the panel surface.

Table 8

45 Panel No.	Pretreatment	Pretreatment Cure Time In Minutes	Primer Cure Time In Minutes	168 Hrs. Salt Spray Resistance	
				% Red Rust at Scribe	% Red Rust in Field
1	No	—	3	70	50
2	No	—	3	70	40
3	Yes	3	3	30	Tr
4	Yes	3	3	10	Tr

50 Tr = Trace

The results from the above table thus demonstrate the desirable enhancement in corrosion protection obtained by the combination of the weldable primer applied over the chromic acid liquid composition. Although corrosion protection can be provided by the primer alone, when the pretreatment is used in combination with the weldable primer, all panels achieve excellent corrosion resistance not only along scribe lines but also across the panel face.

Example 13

Test panels are prepared as described above and four panels, referred to herein as "bare steel panels" are selected for testing or treatment plus testing. Two of the bare steel panels are coated with chromic acid by dipping and drying in the manner described in Example 12. One of these treated panels plus an additional bare steel panel are then coated with the zinc-rich primer described in Example 12. This primer coating is likewise applied to these two panels and treated in the manner described in Example 12.

The panels thus prepared for testing are one bare steel panel, one panel with only the initial surface treatment, one panel with only the primer, and lastly, a panel with the initial surface treatment plus the primer coating over such treatment. All panels are

subjected to the salt spray testing in the manner described hereinbefore. For each panel the test is determined to be ended when the panel, by visual inspection, exhibits first red rust on the face of the panel. The results of such testings are shown in the table below.

Table 9

Panel*	First Red Rust In Salt Spray	
Bare Steel	<1 hour	
Bare Steel plus Pretreatment	<1 hour	
Bare Steel plus Primer	48 hours	
Bare Steel plus Pretreatment plus Primer	168 hours	95

*The primer coated panels have 0.5 mill paint thickness.

In addition to the above tabulated results, the panel containing the initial surface treatment plus the subsequent primer coating is maintained in the salt spray test for 216 hours at which time such panel is noted to have only about 3 percent red rust on the face of the panel. The results from the above table and the subsequent extended testing of the one panel thus clearly demonstrate the desirable enhancement in corrosion protection obtained by the combination of the chromic acid pretreatment when used in conjunction with the weldable primer.

Corrosion protection for the bare steel

panels or the bare steel panels with the initial surface treatment is comparably very poor. The protection for the primer alone over the bare steel although much greater than for the initial surface treatment nevertheless lasts only about two days to first rust. However, when the initial surface treatment is used in combination with the primer the corrosion protection to first rust for the panel is extended to greater than three times beyond that of the panel with the primer coating only, even though the initial surface treatment alone will provide less than an hour of protection to first red rust on the face of the panel.

Example 14

Ten panels are prepared as described above for testing. Six panels are dipped into a *t*-butanol bath containing 35 grams per litre of CrO_3 and 200 grams per litre of powdered zinc metal having average particle size of 2.9 microns. After dipping, the six panels are removed from the bath, ex-

cess composition drained from the panels and they are then immediately dried in a circulating oven for a time of six minutes up to a substrate temperature of 475°F.

Three of the resulting panels as well as three initial panels which have not received a pretreatment are coated with a zinc-rich primer based on an epoxy resin binder, having initially a weight per gallon of 20 lbs., and a solids value of 50 percent. The primer is cut back (i.e. thinned) before use to a viscosity of 50 seconds as measured on a No. 4 Ford cup with the aromatic solvent described in Example 12. The six primer coated panels are dried by placing for 4 minutes in an air circulating oven and thereby obtaining a substrate temperature up to 425°F. Primer coating thickness on the six panels measure 0.5 mil for each panel. All panels are then subjected to the salt spray corrosion resistance test as described hereinabove. The results of such testing are shown in the table below.

Table 10

Panel	Pretreatment	Primer	Corrosion Resistance in Salt Spray	
			Coating Failure	Test Hours To Failure
1	No	No	Red Rust	>1
2	Yes	No	Red Rust	310
3	Yes	No	Red Rust	310
4	Yes	No	Red Rust	320
5	No	Yes	Blister	65+
6	No	Yes	Blister	80+
7	No	Yes	Blister	80+
8	Yes	Yes	Red Rust	445
9	Yes	Yes	Red Rust	480
10	Yes	Yes	Red Rust	480

+ All red rust by 110-120 hours but blistering so badly before then that coating considered failed by 65, 80, and 80 hours, respectively.

The above results thus demonstrate the desirable enhanced corrosion protection for panels containing a pulverulent metal. Bare steel panels, that is, panel No. 1 in the above table, offer virtually no corrosion resistance in salt spray whatsoever. Panels receiving the pretreatment alone exhibit a desirable 310-320 hours protection. But since panels, with the zinc-rich primer alone exhibit deleterious blistering failure in 65-80 hours, these additive test hours, i.e., 375 to 400 hours, demonstrate that the 445-480 hours for the combination treatment can provide a highly desirable enhancement in corrosion resistance.

Example 15

Test panels are prepared as described above and are coated with a coating composition containing 40 g./l. (grams per litre) of CrO_3 , 15 g./l. of succinic acid, 7.5 g./l.

of succinimide, and 0.5 g./l. of polyoxyethylated nonylphenol which composition is referred to hereinafter as the "C/S" composition. The panels are coated by dipping into this coating composition, removing and draining excess composition from the panel, and air drying at room temperature until the coating is dry to the touch, unless otherwise noted in the table below.

Three zinc dust spray dispersions are prepared each containing 0.3 g./l. of lignin sulfonic acid dispersing agent, and either 50 g./l., or 75 g./l., or 200 g./l. of zinc dust, as shown in the table below. These dispersions are sprayed onto coated panels with a "Devilbiss" (Reg. Trademark) paint spray gun (Type JGC 502) calibrated to deliver 1-3 milliliters of water in 5 seconds at 35 lbs. air pressure per square inch. Achieved coating weights for the zinc, in

(28)

- milligrams per square foot of panel surface, are also shown in the table, along with the average particle size of the zinc. After application of this pulverulent zinc all
- 5 panels, containing dry or moist coating composition, as shown in the table below, plus zinc dust, are baked under infrared lamps at a substrate temperature of up to 450°F. for a time up to one minute.
- 10 In the table below, results are also reported for panels coated only with the C/S composition, and hence free from zinc dust, which panels are identified in the table as the "Standard A" panels. Also, compara-
- 15 tive panels are coated only with a chromic acid/adipic acid/succinimide composition having these substituents in the following amounts respectively, in g./l., 40:20:10.
- These panels are also free from zinc dust and are identified in the table below as the "Standard B" panels. These pulverulent-metal-free panels are included as a basis for comparison with the pulverulent-zinc-containing panels and are coated and the coatings cured in the manner described herein-
- 20 above. As indicated in the table below, some of these comparative panels and some of the zinc-containing panels are coated with the alkyd enamel described above, and the resulting coatings cured, as described
- 25 hereinbelow.
- In the table results are reported for the condensing humidity test as well as for the coin adhesion test and the corrosion resistance (salt spray) test, each of which has
- 30 been described hereinbefore.
- 35

TABLE II

Zinc Dust		Weight on Panel; mg./sq. ft.		Topcoating	Coin Adhesion	Condensing Humidity	Salt Spray
Average Particle Size—microns	Spray Conc., g./l.	Standard A Panel	Standard B Panel				
	None	—	—	Alkyd None Alkyd None	Fair — Fair —	24 hrs., 2-3% — 3 hrs., incipient trace failure —	— — 91.5 hrs.-5% —
1.63	50	60	60	Alkyd	Good	—	—
2.9	200	50*	50*	Alkyd	Good-Excellent	—	—
2.9	200	50	50	Alkyd	Good-Excellent	—	—
2.9	200	120	120	Alkyd	Excellent	—	—
2.9	200	240	240	Alkyd	Excellent	—	—
1.63	50	100	100	None	—	80 hrs.-1% 504 hrs.-10-12%	— —
2.9	200	50*	50*	None	—	112 hrs.-2%	—
2.9	200	50	50	None	—	112 hrs., less than 1%	—
1.63	175	50	50	None	—	—	65 hrs.-3%
2.9	200	80	80	None	—	—	112 hrs., less than 1%
2.9	200	150	150	None	—	—	112 hrs.-0%
2.9	200	220	220	None	—	690 hrs., 2%	—

* Zinc dust applied while coating composition still moist.

The above results clearly show the superior topcoat adhesion obtained for the pulverulent-metal containing coating compositions. Additionally, such compositions readily achieve excellent corrosion resistance as determined by the condensing humi-

dity test even for pulverulent metal weights on test panels of as little as 50 milligrams per square foot. Such a small amount of the pulverulent zinc can also provide good corrosion resistance as determined by the salt spray test whereas slightly greater

amounts, e.g., 80 milligrams per square foot of panel surface, achieves excellent corrosion resistance as determined by such test, even when compared with the alkyd-top-coated, chromic acid/adipic acid/succinimide composition which affords desirable corrosion protection in salt spray testing.

Example 16

Test panels are prepared as described above and are coated by dipping into the "C/S" composition described in Example 15. Two zinc dust spray dispersions are prepared each containing 0.3 g./l. of lignin sulfonic acid dispersing agent and one containing 200 g./l. of zinc dust and the other 500 g./l. zinc dust. One panel containing air-dried coating composition is set aside and each of the remaining panels are sprayed, while wet, with one of the spray dispersions as shown in the table below, from a paint spray gun as described in Example 15. Achieved coating weights for the zinc (in milligrams per square foot of panel surface) are shown in the table below along with the average particle size of the zinc. After application of this pulverulent zinc, all panels containing coating composition including the zinc-free panels which have been set aside during spraying, are baked under infrared lamps at a substrate temperature of up to 450°F. for a time up to 1 minute.

One pulverulent-zinc-containing panel is then set aside, as indicated in the table below, and the balance of the panels including the zinc-free panel containing only the residue from the above-described coating composition, are coated again by dipping

the panels into the coating composition described hereinbefore, removing and draining excess composition from the panels, and air drying the panels at room temperature until the coating is dry to the touch. All of these subsequently coated panels are then baked under infrared lamps in the manner described hereinbefore. For convenience, the zinc-free panel containing the coating composition residue undercoating as well as the coating composition residue topcoating is identified in the table below as the "Standard C" panel.

In the table below, results are also reported for a panel containing first the residue from only one coating of C/S composition. Also, a comparative panel is coated first with a chromic acid/adipic acid/succinimide composition containing these substituents in the following amounts, respectively in g./l., 40:20:10. Both panels, free from zinc dust, are coated and the coatings cured in the manner described hereinabove.

These two panels, as well as some zinc-containing panels, as indicated in the table below, are coated with the alkyd enamel and the resulting coatings cured, as described hereinbefore. The first above-described panel is identified in the table below as the "Standard A" panel, and the other is identified as the "Standard B" panel. These standard panels are included as a basis for comparison with the pulverulent-zinc-containing panels. In the table, results are reported for the coin adhesion and the corrosion resistance (salt spray) test, each of which has been described hereinbefore.

TABLE 12

Average Particle Size Microns	Zinc Dust Spray Conc., g./l.	Weight on Panel, mg./sq. ft.	Paint Topcoating	Coin Adhesion	Salt Spray
None	Standard A Panel	30	Alkyd	Fair	91.5 hrs. - 5%
None	Standard B Panel	130	Alkyd	Fair	16 hrs. - first rust
None	Standard C Panel		None	—	184 hrs. - 11%
2.9	200		Alkyd	Fair-Good	—
1.63	200		Alkyd	Excellent	1,036 hrs - 0%
2.9	200	240	None	—	—
2.9	200	80	Alkyd	Good-Excellent	112 hrs., less than 1%
2.9	200	150	None	—	112 hrs. - 0%
2.9	500	480*	None	—	329 hrs., more than 2%
2.9	500	480	None	—	690 hrs., 0%

* No coating composition topcoating.

The above results clearly show the desirably enhanced paint adhesion obtained for the pulverulent-metal-containing coating compositions. Such compositions readily provide excellent corrosion resistance as determined by the salt spray test, even by comparison with a painted panel, i.e., the Standard B panel.

The Standard C panel, containing both a first coating and a second coating of the above-described coating composition, but which is zinc-free, exhibits red rust corrosion over 11 percent of the panel surface area in 184 hours. The zinc-containing panel having 480 milligrams per square foot of the pulverulent zinc and a first coating of the coating composition exhibits, in 329 hours, a desirable suppression of red rust to only 2 percent of the panel surface area, and the like panel having both a first coating and a second coating of the coating composition exhibits no corrosion on the panel face in 690 hours of salt spray testing.

Moreover, such panels containing lesser metal powder weights, e.g., 130 milligrams per square foot and higher, can be virtually free from red rust corrosion for up to more than 1,000 hours, thus far surpassing the corrosion protection obtainable from pulverulent-metal-free coatings.

Example 17

Additional panels, prepared as described in Example 16 with the C/S composition are, while still wet, coated in the manner described in Example 16 to contain 200 milligrams per square foot of zinc dust having an average particle size of 2.9 microns. Some of these panels are then cured in the manner of Example 16 and designated as (A) panels; the balance of the panels, designated hereinbelow as (B) panels, are cured as described above, re-coated with additional C/S composition, and cured in the manner shown hereinbefore.

Other test panels, designated hereinbelow as (C) panels, are prepared as described in Example 12 to contain 20 milligrams per square foot of the pretreatment coating composition as well as containing a primer coating as described in such example having a cured film thickness of 0.5 mil. Further test panels designated hereinbelow as (D) panels are prepared in the manner described in Example 1, that is, coated by dipping in a *t*-butanol medium containing 40 grams per litre CrO_3 and 200 grams per litre of pulverulent zinc. These panels, after curing by the above described method, are coated with a zinc-rich primer having a weight per gallon of 22 pounds, a viscosity of 80 seconds as measured on a No. 4 Ford cup after first mixing with 8 volume percent of an aromatic solvent prepared synthetically from petroleum and having a flash point of 145°-150°F., which primer cures to a coating containing 50 percent zinc, by volume. The primer coated panels are then cured for 90 seconds in an oven heated at 580°F. The panels display a cured film thickness of 0.5 mil.

Additional test panels, designated herein-

below as (E) panels, are tested for comparative weldability. These panels are commercial panels containing an average weight of about 40-50 milligrams per square foot of a tightly adhering, corrosion inhibiting iron phosphate substrate coating. Such panels have met with general acceptance as a standard for performance when evaluating corrosion inhibiting coatings, in, for example, the automotive and household appliance industries. These panels are primer coated with the zinc-rich primer described in Example 12 and after drying have a primer film thickness of 0.5 mil.

All of these panels, i.e., the (A) through (E) panels, are then subjected to electrical resistance spot welding, performed with copper electrodes at an electrode gap of $3/8$ inch using a slow closure rate, an electrode pressure of 550 pounds, and using a weld time of 24 half cycles based on a 60 cycle frequency and at a weld heat of 12,000-12,500 amp-secs. During such welding, the comparative (E) panels after merely 6 continuous spot welds are not further weldable. Such showing constitutes complete failure for electrical resistance spot welding for such panels.

During such welding, the welded substrates for all the (A) through (D) panels pull an acceptable "button" in the peel test. In this peel 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 buttons pulled from the initial test coupons, measured across their narrowest apparent diameter with a micrometer calliper calibrated for measuring to the nearest 0.001 inch, were virtually 0.250 inch across. Additionally, buttons measured in the same manner as the test approaches 2,000 spot welds measured at least 0.220 inch across. In view of the pulling of acceptable buttons through 2,000 spot welds, all such (A) through (D) panels are considered to be highly suitable for electrical resistance spot welding.

Example 18

In this example, test panels are prepared and tested with compositions which are not compositions of the present invention. Nine test panels are prepared as described above and four panels are coated by dipping in a *t*-butyl alcohol medium containing 35 grams per litre of CrO_3 (standard bath). Four panels are coated by dipping in a *t*-butyl alcohol bath containing 35 grams per litre CrO_3 plus 0.2 grams per litre of nonyl phenyl polyethylene glycol ether (modified bath). The remaining panel is coated by dipping in a *t*-butyl alcohol bath containing 40 grams per litre CrO_3 (heavy bath). After all panels are thus coated they are treated as described hereinbefore.

One of the panels from each of the standard bath and the modified bath, as well as the panel from the heavy bath, are scribed. Following this, panels are subjected to condensing humidity and salt spray testing as described hereinabove. Results of such testings are shown in the table below.

Table 13

80	Part A — Condensing Humidity			
	Percent Corrosion in Condensing Humidity			
	Panel	Test Hours	Face	Scribe
	Std.	17	5	N.S.
	Std.	17	>5	20
85	Mod.	17	5	N.S.
	Mod.	17	>5	20
	Hvy.	6.5	1-2	50
	Part B — Salt Spray			
90	Panel	Test Hours	Salt Spray % Corrosion	
	Std.	16.5	>70	
	Std.	16.5	>60	
	Mod.	16.5	>75	
	Mod.	16.5	>50	
95	Std. = Standard bath.			
	Mod. = Modified bath.			
	Hvy. = Heavy bath.			
	N.S. = Not Scribed.			

These results thus demonstrate that panels coated with compositions which are not of the present invention, that is, which do not contain pulverulent metal, offer only transitory corrosion resistance in either the condensing humidity or salt spray test. This limited protection is particularly undesirable in the salt spray test and along scribe lines in the condensing humidity test. Hence, such compositions, even with the elevated temperature treatment, are deemed to be unsuitable for protecting panels against corrosion.

WHAT WE CLAIM IS:

1. A metal substrate having on a surface thereof an adherent, corrosion-resistant coating which comprises the residue from a hexavalent - chromium - containing liquid composition in intimate mixture with pulverulent zinc, manganese, aluminium, magnesium or mixtures or alloys thereof, the pulverulent metal being less noble on the electromotive force series than the predominant metal of the metal substrate, wherein the residue is resin-free and is obtained by applying to the metal surface a hexavalent-chromium-containing liquid coating composition and then heating the substrate carrying the pulverulent metal and applied liquid composition at a temperature, and for a period of time, sufficient to vaporize volatile components from the coating composition and deposit the residue on the surface.
2. A coated metal substrate according to claim 1, wherein the liquid composition applied comprises a hexavalent-chromium-providing material, at least 80 weight percent of which is supplied by chromic acid, 0-98 parts by weight, based on the total weight of the composition, of pulverulent metal, and a volatile liquid medium.
3. A coated metal substrate according to claim 1 or 2, wherein the coated metal surface has a top coating thereon which is the residue obtained by drying a composition comprising a vehicle containing a particulate, electrically - conductive pigment selected from aluminium, copper, cadmium, steel, magnetite, carbon and zinc.
4. A coated metal substrate according to claim 1 or 2, wherein the coated metal surface has a topcoating thereon comprising the residue from a hexavalent-chromium-containing coating liquid composition containing a reducing compound.
5. A coated metal substrate according to any preceding claim, wherein the pulverulent metal has an average particle size not greater than 100 mesh and is present on the surface in an amount not greater than 2000 milligrams per square foot.
6. A coated metal substrate according to any preceding claim, wherein the residue from the liquid composition is obtained after heating an applied hexavalent - chromium-containing liquid composition containing from 0.25 weight percent to 500 grams per litre of hexavalent chromium expressed as CrO_3 , and the residue, exclusive of the pulverulent metal, is present on the substrate surface in an amount not in excess of 500 milligrams per square foot.
7. A coated metal substrate according to any preceding claim, wherein the metal of the substrate is selected from copper to zinc, inclusive, on the electromotive force series, and alloys thereof.
8. A coated metal substrate according to claim 1, substantially as hereinbefore described.
9. A method of providing a metal substrate with an adherent, corrosion-resistant, resin-free coating comprising:
 - (1) applying to the surface a hexavalent-chromium-containing liquid composition;
 - (2) applying to the surface pulverulent metal selected from zinc, manganese, aluminium, magnesium and mixtures and alloys thereof, the pulverulent metal being less noble on the electromotive force series than the predominant metal of the metal substrate; and
 - (3) heating the substrate at a temperature and for a period of time sufficient to vaporize volatile components from the liquid composition and deposit on the surface a resin-free residue in intimate mixture with the pulverulent metal.
10. A method according to claim 9, wherein the liquid composition contains a hexavalent - chromium - providing material at least 80 weight percent of which is provided by chromic acid, and the substrate is heated at a temperature up to 900°F .
11. A method according to claim 10, wherein the substrate is heated at the selected temperature for a time of at least 0.2 second.
12. A method according to claim 9, wherein the liquid composition is a hexavalent-chromium-containing coating composition containing a reducing compound and the substrate is heated at a temperature not substantially above 300°C . for a time of at least 2 seconds.
13. A method according to any of claims 9 to 12, wherein the pulverulent metal is applied to the surface as a dispersion of the metal in volatile liquid, independently of the application of the liquid composition.
14. A method according to any of claims 9 to 12, wherein the pulverulent metal is applied to the surface as a dispersion of the metal in the liquid composition.
15. A method according to any of claims 9 to 14, wherein a hexavalent-chromium-containing coating composition containing a reducing compound is applied over the

These results thus demonstrate that panels coated with compositions which are not of the present invention, that is, which do not contain pulverulent metal, offer only 5 transitory corrosion resistance in either the condensing humidity or salt spray test. This limited protection is particularly undesirable in the salt spray test and along scribe lines in the condensing humidity test. Hence, 10 such compositions, even with the elevated temperature treatment, are deemed to be unsuitable for protecting panels against corrosion.

WHAT WE CLAIM IS:

15 1. A metal substrate having on a surface thereof an adherent, corrosion-resistant coating which comprises the residue from a hexavalent - chromium - containing liquid composition in intimate mixture with pulverulent zinc, manganese, aluminium, mag- 20 nesium or mixtures or alloys thereof, the pulverulent metal being less noble on the electromotive force series than the predominant metal of the metal substrate, wherein the residue is resin-free and is obtained by 25 applying to the metal surface a hexavalent-chromium-containing liquid coating composition and then heating the substrate carrying the pulverulent metal and applied 30 liquid composition at a temperature, and for a period of time, sufficient to vaporize volatile components from the coating composition and deposit the residue on the surface.

35 2. A coated metal substrate according to claim 1, wherein the liquid composition applied comprises a hexavalent-chromium-providing material, at least 80 weight percent of which is supplied by chromic acid, 40 0.98 parts by weight, based on the total weight of the composition, of pulverulent metal, and a volatile liquid medium.

45 3. A coated metal substrate according to claim 1 or 2, wherein the coated metal surface has a top coating thereon which is the residue obtained by drying a composition comprising a vehicle containing a particulate, electrically - conductive pigment 50 selected from aluminium, copper, cadmium, steel, magnetite, carbon and zinc.

55 4. A coated metal substrate according to claim 1 or 2, wherein the coated metal surface has a topcoating thereon comprising the residue from a hexavalent-chromium-containing coating liquid composition containing a reducing compound.

60 5. A coated metal substrate according to any preceding claim, wherein the pulverulent metal has an average particle size not greater than 100 mesh and is present on the surface in an amount not greater than 2000 milligrams per square foot.

65 6. A coated metal substrate according to any preceding claim, wherein the residue from the liquid composition is obtained

after heating an applied hexavalent - chromium-containing liquid composition containing from 0.25 weight percent to 500 grams per litre of hexavalent chromium expressed as CrO_3 , and the residue, exclusive 70 of the pulverulent metal, is present on the substrate surface in an amount not in excess of 500 milligrams per square foot.

7. A coated metal substrate according to any preceding claim, wherein the metal of 75 the substrate is selected from copper to zinc, inclusive, on the electromotive force series, and alloys thereof.

8. A coated metal substrate according to claim 1, substantially as hereinbefore described. 80

9. A method of providing a metal substrate with an adherent, corrosion-resistant, resin-free coating comprising:

(1) applying to the surface a hexavalent-chromium-containing liquid composition; 85

(2) applying to the surface pulverulent metal selected from zinc, manganese, aluminium, magnesium and mixtures and alloys thereof, the pulverulent metal being 90 less noble on the electromotive force series than the predominant metal of the metal substrate; and

(3) heating the substrate at a temperature and for a period of time sufficient to 95 vaporize volatile components from the liquid composition and deposit on the surface a resin-free residue in intimate mixture with the pulverulent metal.

10. A method according to claim 9, 100 wherein the liquid composition contains a hexavalent - chromium - providing material at least 80 weight percent of which is provided by chromic acid, and the substrate is heated at a temperature up to 900°F. 105

11. A method according to claim 10, wherein the substrate is heated at the selected temperature for a time of at least 0.2 second.

12. A method according to claim 9, 110 wherein the liquid composition is a hexavalent-chromium-containing coating composition containing a reducing compound and the substrate is heated at a temperature not substantially above 300°C, for a time of 115 at least 2 seconds.

13. A method according to any of claims 9 to 12, wherein the pulverulent metal is applied to the surface as a dispersion of the metal in volatile liquid, independently of the application of the liquid composition. 120

14. A method according to any of claims 9 to 12, wherein the pulverulent metal is applied to the surface as a dispersion of the 125 metal in the liquid composition.

15. A method according to any of claims 9 to 14, wherein a hexavalent-chromium-containing coating composition containing a reducing compound is applied over the 130



first coating and the substrate is heated at a temperature not substantially above 300°C. for a time of at least 2 seconds.

- 5 16. A method according to any of claims 9 to 14, wherein a topcoat comprising a vehicle containing a particulate, electrically conductive pigment selected from aluminium, copper, cadmium, steel, magnetite, carbon and zinc is applied over the

composition residue and is then dried.

10

17. A method according to claim 9, substantially as hereinbefore described with reference to the foregoing Examples 1-17.

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Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1972.
Published at the Patent Office, 25 Southampton Buildings, London WC2A 1AY from which copies may be obtained.



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