

[54] COATED METAL AND METHOD
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References Cited

UNITED STATES PATENTS

2,777,785 1/1957 Schuster et al. 148/6.2
2,901,385 8/1959 Curtin 148/6.16

3,189,488 6/1965 Schiffman 148/6.2
3,318,716 5/1967 Schuster et al. 148/6.2 X
3,671,331 6/1972 Malkin et al. 148/6.16 X
3,679,493 7/1972 Beiswanger et al. 148/6.16

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[57] **ABSTRACT**

A coating on a metal substrate of CrO₃ and pulverulent metal in aqueous medium and containing particular organic liquid provides a corrosion and alkali resistant coating to the metal. The pulverulent metal, of which metal flake is of special interest, the liquids and the CrO₃, typically all supplied by chromic acid, are mixed and applied to the metal substrate. The resulting coated substrates have electroconductivity, e.g., for application of electrocoating primer, after the application and baking of the coating composition on a substrate.

21 Claims, No Drawings

COATED METAL AND METHOD

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. pending application Ser. No. 173,243, filed Aug. 19, 1971 and now abandoned.

BACKGROUND OF THE INVENTION

Chromic acid and pulverulent metal in a liquid medium have heretofore been applied to metal substrates followed by baking to attain a corrosion-resistant coating, such as disclosed in U.S. Pat. No. 3,687,738. Such compositions are typically dispersions of pulverulent metal powder or metal flake in water or t-butanol and resulting coatings offer corrosion resistance and electroconductivity to coated substrates.

Working with such systems depending primarily upon t-butanol can present a fire hazard whereas working in such systems that are essentially aqueous media, and especially where the pulverulent metal is supplied in flake form, can provide problems in achieving a resulting coated substrate wherein the coating displays excellent uniformity and adhesion. It is difficult to upgrade such characteristics without deleterious effect on other coating characteristics plus coating bath stability.

Compositions of typically aluminum flake, a polymeric glycol plus a wetting agent have been taught in U.S. Pat. No. 3,318,716 as useful anti-foaming compositions in paste or liquid form. They may be used to supply very minor amounts of pigmentation to coating compositions but do not ostensibly lend particular advantages to resulting coatings except as attributed to the metal flake component.

The compositions containing aluminum flake provide a barrier coating or film on the underlying substrate. This barrier coating provides an essentially inert metallic flake that resists attack, such as from mild alkali, and thus protects the underlying substrate metal, through the mechanism of its generally inert nature. On the other hand, compositions containing zinc flake, and which compositions are of particular interest herein, provide a coating that under attack sacrifices the coating in place of, and thereby protects the underlying metal. Such action typically provides protection through galvanic action.

It has also been found useful to prepare reaction products of chromium compound, e.g. chromic acid, plus high boiling organic solvents in coating compositions. For example, in U.S. Pat. No. 2,355,889 the reaction product of chromic acid and ethylene glycol monoethyl ether is shown to have utility when incorporated into a paint. More recently, in U.S. Pat. No. 3,679,493 reaction products of typically glycol-ethers and chromic acid have been shown to be useful in their own right and when simply used as such reaction product in water, for obtaining corrosion resistant coatings on metallic surfaces. For such simple coating compositions, the low molecular weight ethers of glycols are employed for the reaction product.

It has also been known in the art of metal treating solutions where a hexavalent-chromium compound, e.g., chromic acid, is supplied in such composition as a reaction product, that compatible co-solvents may be serviceable. For example, in U.S. Pat. No. 3,189,488 where such a chromium compound and formaldehyde are co-reacted, the resulting coating composition liquid

medium may be water plus up to 20 weight percent of a co-solvent for improving spreadability and flow characteristics. Such co-solvents are represented by various alcohols and ethers of glycol, for example the mono and diethyl ethers of ethylene glycol.

Moreover, in U.S. Pat. No. 3,671,331 it has been disclosed that compositions containing a hexavalent-chromium-providing substance along with a pulverulent metal may further contain up to ten volume percent of a surface active agent. Such agent may be an alkyl ether of an alkylene glycol or a polyalkylene glycol.

SUMMARY OF THE INVENTION

A coating composition for metals has now been found that offers excellent coating uniformity on the coated substrate. Resulting coatings exhibit augmented adhesion and desirable color and non-staining characteristics. The coating uniformity extends to non-tearing, a particular problem of prior aqueous medium compositions that is exhibited by variations in coating uniformity resulting when parts removed from a coating bath drained unevenly leaving excessive coating composition build-up where the drainage was greatest.

Such coating characteristics have been obtained without sacrifice to coating bath stability, including retention of pulverulent metal flake inertness in the bath as well as excellent dispersion in the coating bath. In addition to providing coatings of excellent protective value, and including augmented resistance to mild alkali, such coatings exhibit electroconductivity, e.g., for subsequent weldability or application of electrocoat paint.

These characteristics are obtained through the use of specific high boiling organic compounds. Since these compounds, to demonstrate significant performance characteristics for resultant coatings, must be present in substantial amount, i.e. at least substantially above 15 volume percent of the liquid medium, they will have some impact on the flowability of the resultant coating composition. However, their presence in the coating composition at such proportions has been found to go beyond a mere modification of the fluid characteristics of the coating; and furthermore, to provide the resultant composition with more than merely a supplemental dispersing agent along with the other compositional ingredients. Thus, for example, the high boiling hydrocarbons have been found to provide for a significant increase in corrosion protection of resulting coatings, as well as for augmented coating adhesion, and this even when achieving boosted coating weights. Moreover, such properties of the coating are herein achieved without especial recourse to the formation of reaction products such as have been taught in U.S. Pat. No. 3,679,493 which has been discussed hereinabove.

Broadly, the present invention is directed to an aqueous coating composition for application to, and curing on, a metal substrate, thereby preparing an adherent, water insoluble, alkali and corrosion resistant as well as substantially resinfree coating on said substrate, which composition before curing comprises an intimate mixture in aqueous liquid medium of: (a) a hexavalent-chromium-providing substance, supplied by about 80 to 100 weight percent chromic acid and providing below about 100 grams per liter of chromium, expressed as CrO_3 ; (b) below about 500 grams per liter of liquid medium of pulverulent metal selected from

the group consisting of zinc, aluminum, mixtures thereof and alloys of same, said composition having a weight ratio of chromium, expressed as CrO_3 , to pulverulent metal of between about 1:1 and 1:15; (c) below about 50 volume percent but substantially above 15 volume percent, based on the volume of the total liquid of the aqueous composition, of water soluble organic liquid substance maintains liquidity above 100°C . and is selected from the group consisting of tri-, and tetraethylene glycol, di-, and tripropylene glycol, and the water soluble low molecular weight ethers of all such foregoing glycols, diacetone alcohol, the water soluble low molecular weight ethers of diethylene glycol, and mixtures of the foregoing; and (d) above about 0.0005 volume percent, basis total volume of such coating composition, of dispersing agent.

In addition, the present invention relates to a coated metal substrate, and the preparation of such a substrate, exhibiting the above described adherent, alkali and corrosion resistant coating. It is further directed to the preparation of weldable substrates and to welded articles, and additionally to precursor constituents for preparing aqueous coating compositions.

The metal substrates contemplated by the present invention are exemplified by the metal substrates to which a chromic acid plus pulverulent metal in a liquid coating may or can be applied for enhancing corrosion resistance of such substrate metals. For example, such metal substrates may be aluminum and its alloys, zinc and its alloys, copper and cupriferous, e.g., brass and bronze. Additionally, exemplary metal substrates include cadmium, titanium, nickel, and its alloys, tin, lead, chromium, magnesium and alloys thereof, and for weldability, preferably a ferrous metal substrate such as iron, stainless steel, or steel such as cold rolled steel or hot rolled and pickled steel. All of these for convenience are usually referred to herein simply as the "substrate."

For convenience, the hexavalent-chromium-containing aqueous coating composition is often referred to herein as "treating compositions" and the "residue" on a metal surface is such resulting surface condition obtained after application of such composition to, and heating resulting applied composition on, a metal substrate. Also for convenience, the high boiling organic compound is often termed herein as the "high boiling hydrocarbon" or just the "hydrocarbon."

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The corrosion-resistant, hexavalent-chromium-containing aqueous composition contains chromic acid as the hexavalent-chromium-providing substance or its equivalent in aqueous medium, for example, chromium trioxide or chromic acid anhydride. But a minor amount, e.g., 20 percent or less, of such chromium can be 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., include trivalent chromium compounds. Although the aqueous composition might contain only a small amount, e.g., 5 grams per liter of hexavalent chromium, expressed as CrO_3 , and may contain as much as about 100 grams per liter of composition of

hexavalent chromium, expressed as CrO_3 , it will typically contain between about 20–60 grams.

For supplying the liquid medium, without considering the contribution by the hydrocarbon, water virtually always supplies the whole amount. Other liquids may possibly be used, but preferably only a very minor amount of the aqueous medium, basis the high boiling organic compound free medium, is such other liquid material. Such other liquids that might be contemplated include alcohols, most notably t-butanol, and halogenated hydrocarbon liquid, some of which have been discussed in U.S. Pat. Nos. 2,762,732 and 3,437,531.

A substantial amount of liquid in the aqueous liquid medium, i.e., up to 50 volume percent based on the total volume of liquid in the aqueous medium, can be supplied by the high boiling hydrocarbon. Such organic liquid compound also must supply substantially above 15 volume percent, on a similar basis, of such total liquid and advantageously for enhanced coating characteristics, supplies above about 20 volume percent. Lesser amounts of such total liquid will not contribute sufficient hydrocarbon to assure consistently augmented properties of the coating, although such amounts might achieve enhanced dispersion and compositional flow characteristics. It is most important that this high boiling organic compound be liquid at 100°C ., and by such herein it is meant to be liquid at 100°C . at atmospheric pressure.

Since for economy and efficiency water supplies such a large amount of the aqueous composition liquid medium, and since the high boiling hydrocarbon is a critical ingredient in the formation of the resulting coating, it is necessary for such hydrocarbon to be liquid at the water boiling point. The hydrocarbon should also be easily soluble in water to at least contribute to twenty volume percent of the liquid medium at ambient temperature. It is meant herein to include such hydrocarbons as may be termed "miscible" in water at such proportion under such temperature condition. Hence, those hydrocarbons as are more specifically detailed hereinbelow are serviceable as being soluble in water so long as they mix or blend uniformly with water and preferably at the 20–50 volume percent range. Yet, such hydrocarbons must not be highly toxic to avoid uneconomical expense in handling and use.

Such hydrocarbons as are serviceable in the present invention are also those that are retained during baking on the metal substrate in sufficient amount and duration to permit participation of the hydrocarbon in the formation of a coating. This participation is best exemplified by such characteristics as reduction of chromium in the coating from hexavalent to the trivalent state, most desirable leading into a layered, substantially uniform coating of the metallic flake as well as characteristics of the resultant coating, for example as exhibited from mild alkali resistance testing. The organic compounds contain carbon, oxygen and hydrogen and have at least one oxygen-containing constituent that may be hydroxyl, or oxo, or a low molecular weight ether group, i.e., a $\text{C}_1\text{--C}_4$ ether group. Since water solubility is sought, polymeric hydrocarbons are not particularly suitable and advantageously serviceable hydrocarbons contain less than about 15 carbon atoms. Particular hydrocarbons which can or have been used include tri-, and tetraethylene glycol, di- and tripropylene glycol, the monomethyl, dimethyl, and

ethyl ethers of these glycols, as well as diacetone alcohol, the low molecular weight ethers of diethylene glycol, and mixtures of the foregoing. It will be appreciated that because of their limited water solubility, it is not meant to include herein either the hexyl or dibutyl ethers of diethylene glycol.

The pulverulent metal flake, e.g., zinc flake or aluminum flake, or mixtures of such flakes, but preferably zinc flake for galvanic protection and coatability, is most typically such a pulverulent metal flake having a thickness on the order of 0.1–0.3 micron and most typically a size in the longest dimension of not substantially above about 50 microns. Aluminum flake, also sometimes termed leafing aluminum pigment has been discussed, for example, in U.S. Pat. No. 2,312,088. Flake may be blended with pulverulent metal powder, but typically in only minor amounts of the powder, and such powder should have particle size so that all particles pass 100 mesh and a major amount pass 325 mesh ("mesh" is used herein as U.S. Standard Sieve Series). The powders are generally spherical as opposed to the leafing characteristic of the flake.

The coating composition, should be made up with an amount of pulverulent metal sufficient to supply not substantially above about 500 grams of metal per liter of coating composition liquid medium. The presence of greater than about 500 grams per liter of pulverulent metal flake is undesirable, for example, can add expense without a significant increase in protection for the coated substrate. Advantageously, for economy and desirable coating characteristic, the composition contains at a minimum about 50 grams of metal per liter and preferably contains between about 150–400 grams of metal per liter.

With the preferred zinc flake it has been found to be particularly serviceable to preblend this flake with the hydrocarbon. Optionally, a very minor amount of dispersing agent is also added in this pre-blend. Such a pre-blend, or admix, is desirably stable and may therefore have advantages in mixing prior to storage or shipment. It can thereafter be readily admixed with other ingredients, e.g., water and chromic acid, for the formation of the coating composition.

In the admix, when the dispersing agent is present it will form less than about 3 weight percent, and typically from about 0.2 to about 0.9 weight percent, of such blend basis of the total weight of the blend. Further, because the pre-blend has been found to be suitable with the preferred zinc flake, such flake preferably contributes from about 80 to 100 weight percent of the pulverulent metal present therein. The admix, which may also be termed a coating composition precursor constituent, is prepared to contain a weight ratio of the hydrocarbon to the pulverulent metal flake of between about 1:2.5 – 1:0.3. Within this ratio, and preferably within a weight ratio of hydrocarbon to pulverulent metal flake of between about 1:2 to 1:0.8, the admix will exhibit desirable stability while providing ready mixing with further compositional constituents to yield the aqueous coating composition.

Also, for such coating compositions, the chromium, expressed as CrO_3 , should not exceed more than about 100 grams per liter of composition medium. Greater than about 100 grams per liter of chromium is uneconomical and can deleteriously detract from the characteristics of the coated metal surface, for example, the most desirable corrosion resistance for the coated

metal substrate. Further such composition should have a weight ratio of chromium, expressed as CrO_3 , to metal flake of between about 1:1 to 1:15.

A ratio of beyond about 1:15 may not provide sufficient chromium in the coating to achieve augmented bonding of the pulverulent metal to the metal substrate. A ratio of about 1:1 may be achieved, but should preferably be at metal concentrations of less than about 100 grams per liter. As the metal content approaches about 500 grams per liter and thus the chromium content can approach about 100 grams per liter the upper weight ratio of chromium, expressed as CrO_3 , to pulverulent metal approaches 1:5. These coating compositions are virtually always made as very concentrated coating compositions at a ratio of between about 1:4 and 1:9 and have particular utility in the coating of small parts as opposed to application to large substrate areas such as metal coils.

As touched upon hereinbefore, the coating ingredients may be combined into separate packages, e.g., a two package system with one containing the hexavalent-chromium-providing substance in an aqueous medium, and the other package being a water-free dispersion in high boiling hydrocarbon of pulverulent metal; each package may additionally contain some surface active agent, or it may all be in the package with the metal. Such separate packages are then mixed before application to the metal substrate.

Such coating compositions 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, or combinations of techniques as, for example, spray and brush techniques. Typically the composition is applied by simply dipping the article into the composition. The metal surface can be a preheated metal surface to assist in the curing of the composition, or the coating composition may be applied from a heated bath, for example, one heated up to 200°F.

The coating composition should contain some, and generally contains up to, for example, about 0.05 volume percent, basis total composition liquid, and typically not above about 1–2 volume percent, of a dispersing agent. Such agent may be present in as little as 0.0005 volume percent, also on a total liquid basis. It is generally contemplated to employ a dispersing agent that is a nonionic surfactant which may be an ethoxylated alkylphenol such as a nonyl or octyl phenol. It is also contemplated to employ the nonionic ethoxylated aliphatic alcohols, representatives of which include the oleyl, lauryl, and stearyl alcohols. Other suitable nonionic surfactants that are also readily commercially available and are contemplated for use in the present invention include, for example, carboxylic esters that encompass the glycerol esters and the anhydrosorbitol esters, as well as the polyoxyethylene esters of fatty, rosin, and tall oil acids. It is also further contemplated to use carboxylic amide nonionic surfactants for dispersing the pulverulent metal and these are meant herein to include the polyoxyethylene fatty acid amides. The preferred agents for effecting pulverulent metal dispersibility are polyethoxy adducts, exemplified by the alkylphenoxypolyethoxyalkanols, and derivatives thereof, some of which are described in U.S. Pat. No. 3,281,475. Such agents are nonionic and have between about 7 and 50 oxyethylene units in the molecule. Advantageously, for best dispersibility the agent

is present in the coating composition in an amount between about 0.001–0.02 volume percent, on a total liquid basis.

The resulting coating weights on the metal substrate may vary to a considerable degree but, exclusive of the metal flake the residue will most typically always be present in an amount supplying above about 5 milligrams per square foot of chromium, expressed as chromium and not CrO_3 . Furthermore, residues containing below about 15 milligrams per square foot of chromium, expressed as chromium and not CrO_3 , should be topcoated to impart significant enhancement in corrosion resistance of the coated substrate. Also if the coated metal substrate is to be subsequently formed, the residue should contain not substantially above about 150 milligrams per square foot of chromium as the coating may be subjected to cracking or crazing during forming operation, although for typically finished products when subsequent forming is not contemplated, and extended corrosion resistance without topcoating may be desirable, such residue may contain up to about 500 milligrams per square foot of chromium.

A subsequent paint topcoating is also a consideration for the amount of pulverulent metal that should be present on the surface of the substrate in the coating residue. Such residues containing about 10–200 milligrams per square foot of pulverulent metal are virtually always topcoated. However, subsequently topcoated residues can contain substantially more pulverulent metal, e.g., 600–700 milligrams per square foot of such metal, and the substrate may contain up to about 5,000 milligrams per square foot of pulverulent metal, whereas an excess of that amount is usually uneconomical.

It can be appreciated that the present invention is directed to coatings wherein there is an excess of pulverulent metal to chromium, even at the lesser concentrations of the metal. Generally, the coating should have a weight ratio of chromium, expressed as chromium and not CrO_3 , to pulverulent metal of less than about 0.5:1, and such ratio is most usually for the less heavy coating weights, since as the coating weights approach, for example, 5,000 milligrams per square foot of pulverulent metal, the weight ratio of chromium to pulverulent metal will be less than about 0.2:1. It has also been found that for coating small parts, e.g., parts adapted for individual dipping in a coating bath, which can be final products that will not be normally subjected to subsequent forming, and where coating weights may approach 5,000 milligrams per square foot of pulverulent metal, the weight ratio of chromium to pulverulent metal in the coating may be as low as about 0.02:1.

Other compounds may be present in the hexavalent-chromium-containing liquid compositions but, even in combination, are present in very minor amounts so as not to deleteriously affect the coating integrity, e.g., with respect to electroconductivity and galvanic protection. Thus, such compositions should be substantially resin-free and can be substantially pigment free, i.e., contain little, if any, pigment or resin such as 10 grams per liter total of both or less and should preferably be resin free. It may however be desirable to include, within such total of 10 grams per liter, substances that can thicken the coating composition. And although these substances, e.g., water soluble cellulose

ethers such as hydroxyethylcellulose, may be considered as resinous substances, they will be used for their thickening ability. Thus, and especially when present in typical amounts of 2–5 gram per liter, such agents do not impart a resin film to the coating composition residue. Other such agents include xanthan gum hydrophilic colloids, as well as additional gums, e.g., guar gum and karaya gum. Also, since the adherence for the particulate metal to the metal substrate is achieved by the chromium-providing-substance ostensibly through the interaction of such substance with the high boiling hydrocarbon during baking, such coating compositions need not contain resin, and such coatings that will be subsequently topcoated are virtually always pigment-free, exclusive of the pulverulent metal.

These other compounds further include inorganic salts and acids as well as organic substances, often typically employed in the metal coating art for imparting some corrosion resistance or enhancement in corrosion resistance for metal surfaces. Such materials include zinc chloride, magnesium chloride, various chromates, e.g., strontium chromate, molybdates, glutamic acid, succinic acid, zinc nitrate, and succinimide and these are all preferably avoided, but if present, are most usually employed in the liquid composition in a total maximum amount of less than 5 grams per liter.

For the metal substrates containing applied liquid composition and pulverulent metal, the preferred temperature for the subsequent heating, which is also often referred to as curing and which may be preceded by drying such as air drying, is within the range from about 400°F. but more typically from about 450°F. at a pressure of 760 mm. Hg up to not essentially above about 1,000°F. Such an elevated substrate temperature may be attained by preheating the metal prior to application of the liquid composition. However, such curing temperatures do not often exceed a temperature within the range of about 450°–700°F. At the elevated curing temperatures the heating can be carried out in as rapidly as about one second or less but is often conducted for several minutes at a reduced temperature.

Before starting the treatment of the present invention it is, in most cases, advisable to remove foreign matter from the metal surface by thoroughly cleaning and degreasing. Degreasing may be accomplished with known agents, for instance, with agents containing sodium metasilicate, caustic soda, carbon tetrachloride, trichloroethylene, and the like. Commercial alkaline cleaning compositions which combine washing and mild abrasive treatments can be employed for cleaning, e.g., an aqueous trisodium phosphate-sodium hydroxide cleaning solution. In addition to cleaning, the substrate may undergo cleaning plus etching.

After heating, the resulting coated substrate of the present invention can be further topcoated with any suitable paint, i.e., a paint, primer, including electrocoating primers, and weldable primers such as the zinc-rich primers that can be applied before, typically, electrical resistance welding, and paints such as enamel, varnish, or lacquer. Since the coated metal surfaces of the present invention can exhibit a desirable upgrading in topcoat adhesion when compared, for example, to the uncoated substrate metal, paints are often applied over such coated substrates. 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 watersoluble 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.

The weldability of coated substrates is of particular interest in regard to electrical resistance welding that can be exemplified by electrical resistance spot welding wherein opposing electrodes are closed against weldable substrates maintained for welding within the gap between the electrodes. For this spot welding the opposing electrodes are closed onto the substrate to be welded under pressure, for example of a 500-600 pound load, and for a weld heat that is measured in amperes. Also of particular interest is the application of the coating composition to weldable metal studs that are typically solid, cylindrical metallic articles having a length of a few inches or less and are used in a welding gun for electrically resistance welding to a metal substrate. The coatings of the present invention on the surface of these steels, in addition to providing the other coating characteristics, offer reduced sputtering during welding that can be a problem at the weld when studs are used that have a galvanized protective surface coating.

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

PREPARATION OF TEST PARTS

Test parts are typically prepared for subsequent treatment by immersing in water which has incorporated therein 2-5 ounces of cleaning solution per gallon of water. The cleaning solution is typically 75% by weight of potassium hydroxide and 25 weight percent tripotassium phosphate. The bath is maintained at a temperature of about 150°-180°F. After the cleaning treatment the panels are rinsed with warm water and may be dried.

APPLICATION OF COATING TO TEST PARTS AND COATING WEIGHT

Clean parts are typically coated by placing in a wire basket and dipping the basket into coating composition, removing the basket and draining excess composition therefrom with a mild shaking action and then immediately baking or air drying at room temperature until the coating is dry to the touch and then baking, the parts being usually placed on a sheet for baking. Baking proceeds under infrared lamps or in a hot air convection oven at a substrate temperature of about 450°F. unless otherwise specified, for a time up to 1 minute, also unless otherwise specified.

Coating weights for parts, generally expressed as a weight per unit of surface area, are determined by selecting a random sampling of parts of a known surface area and weighing the sample before coating. After the sample has been coated, it is reweighed and the coating weight per selected unit of surface area, most always presented as milligrams per square foot (mgms./sq.ft.), is arrived at by straightforward calculation.

CORROSION RESISTANCE TEST (ASTM B-117-64) AND RATING

Corrosion resistance of coated parts is measured by means of the standard salt spray (fog) test for paints and varnishes ASTM B-117-64. In this test, the parts 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 parts are then compared one with the other by visual inspection.

In the following examples the efficacy of the corrosion resistance obtained on coated parts is, in part, quantitatively evaluated on a numerical scale from 0 to 10. The parts are visually inspected and compared with one another and the system is used for convenience in the reviewing of results. In the rating system the following numbers are used to cover the following results:

10. retention of film integrity, no red rust;
8. initial coating degradation, pinpoints of red rust;
6. less than 3% red rust basis total surface area of the part;
4. 3 to 10% red rust, i.e., a significant amount of rust;
2. 10 to 25 percent surface area red rust;
0. greater than 25 percent red rust.

EXAMPLE 1

Sufficient zinc flake having particle thickness of about 0.1-0.2 micron and a longest dimension of discrete particles of about 15 microns is dispersed in diethylene glycol monoethyl ether (DGME) together with 3 milliliters (mls.) of wetter which is a nonionic, modified polyethoxy adduct having a viscosity in centipoises at 25°C. of 180 and a density at 25°C. of 8.7 pounds per gallon, to provide in a final mixed dispersion 300 grams per liter (g./l.) of the D.G.M.E. Separately there is added to deionized water sufficient chromic acid to provide 60 g./l. of CrO_3 in the final mixture.

The chromic acid solution is slowly added to the metal flake dispersion to form the final mixture. During the addition, a slight evolution of heat is observed and some surface foam is formed which is removed by skimming. An additional blend is prepared in the same manner but the blend contains 250 ml./l. of tripropylene glycol monomethyl ether (TGME) in place of the DGME and only 2 mls. of wetter.

Each bath is used to coat five grade 8 bolts which are 11/16 inches long by about 1/4 inch in diameter at the threaded end and have 1/8 inch of threading on the shaft topped by a 3/8 inch smooth shaft section that terminates in the bolt head. Also, each bath is used to coat five No. 10-A clips, sometimes referred to as "speed clips," that are formed by doubling over an about 0.5 inch by 1.75 inch strip of thin sheet metal to provide a clip type configuration when viewed on edge, followed by punching a hole through the doubled configuration and leaving opposing, outwardly extending flanges around one outer clip section of the hole. These parts are coated as described above and the coating cured for 6-12 minutes at 475°F. On analysis, as described above, the bolts are calculated to average 1,135 mgms./sq.ft. of coating from the DGME bath and 1,370 mgms./sq.ft. from the TGME bath.

The parts are subjected to the above described corrosion resistance salt spray test and results of such testing are shown in the table below. In the table below the test

results are reported on the scale hereinabove described.

TABLE 1

Type	Bath		Salt Spray Results			
	Flake g./l.	CrO ₃ g./l.	Bolts		Clips	
			66 hrs.	168 hrs.	66 hrs.	168 hrs.
DGME	300	60	10	9	9	2
TGME	300	60	10	10	10	10

The above results demonstrate the excellent corrosion resistance that can be obtained on small parts where the coating composition employs either the diethylene glycol monoethyl ether or the tripropylene glycol monomethyl ether. As is evident from these results, the clips present a challenging problem in coating, but baths of the present invention can nevertheless achieve excellent results, as shown by the TGME bath, and for a greatly extended duration of testing.

EXAMPLE 2

Various coating compositions are prepared in the manner of Example 1 and using 300 grams per liter in each composition of the zinc flake described in Example 1. Each composition also contains 5 milliliters of the Example 1 wetter and contains a concentration of chromic acid as shown in Table 2 below. Also as shown in the table below, the compositions contain various amounts of organic compound. The first four compositions containing diethylene glycol monomethyl ether (MEE) and compositions 5-8 contain dipropylene glycol monomethyl ether (MME).

The baths identified in the table below as Nos. 3, 4, 7 and 8 are aged one day prior to use. Bath No. 8 is very viscous prior to use but is readily mixed to a smooth consistency. Bath No. 7 is smooth and viscous without noticeable viscosity change during the one day ageing. Bath No. 3 has a lower viscosity than 4 and both stir up very readily.

Each bath is used to coat both Grade 8 bolts and No. 10-A clips, as have been described in Example 1 and the coated parts are cured as described in Example 1 for curing times up to 14 minutes at a temperature of 475°F. With reference again to baths 3, 4, 7 and 8, the adhesion for the cured coating on the parts is rated as good except for the adhesion on the parts coated in Bath No. 8 where it does not exhibit the good coating adhesion of the other baths. Such adhesion is determined simply by holding the part firmly in the hand and scratching with a thumb nail and comparing many parts under such scratch test. The coating appearance for all such parts from the baths is metallic.

Coating weights per bolt for coatings obtained from each bath are determined, in the manner described hereinbefore, based upon a five bolt sample from each bath and the results are reported in Table 2 below. Also shown in the table below are the results of salt spray testing for both the bolts and the clips.

TABLE 2

No.	Compound Type	Bath		coating Weight on Bolts mgms./ft. ²	Salt Spray Results 168 Hours	
		Compound Conc.	CrO ₃ conc.		Bolts	Clips
		Mls./l.	g/l.			
1	MEE	250	60	850	9	10
2	MEE	250	90	935	10	10
3	MEE	125	60	785	10	6
4	MEE	375	60	2,180	10	6
5	MME	250	60	1,030	10	10
6	MME	250	90	1,100	10	10
7	MME	125	60	970	10	10
8	MME	375	60	1,975	10	10

MEE = Monoethyl ether of diethylene glycol

MME = Monomethyl ether of dipropylene glycol

The above results show excellent, consistent corrosion resistance, at a very extended test duration of 168 hours, for small parts having a considerable range in the weight of coating on the parts. The corrosion resistance under the salt spray testing has been rated in accordance with the manner hereinbefore discussed, and 13 out of the 16 parts rated scored the highest possible rating.

In further testing, i.e., beyond just the salt spray testing represented in Examples 1 and 2, it became apparent that for the 10-12 volume percent level of addition for the organic liquid substance, that although such results might, as above, be occasionally obtained under idealized laboratory conditions, they could neither be desirably reproduced nor consistently achieved. As already inferred, such results could not be obtained for a breadth of coating characteristics beyond the salt spray test, for example, such results as noted above in Table 2 for the lowest concentration of the glycols could neither with consistency nor assurance be translated over to desirable coating adhesion, or corrosion resistance in water soak, or corrosion resistance under an electrocoat paint. Such findings are most dramatically represented by the results as detailed hereinbelow.

EXAMPLE 3

Various coating compositions are prepared in the manner of Example 1 and using 300 grams per liter (g/l) in each composition of zinc flake. Each composition is also prepared to contain 40 g/l of chromic acid. Further, with one exception, each composition is prepared with 3 milliliters per liter (m./l) of the wetter described in Example 1. The one compositional exception, as shown in Table 3 below, is the last formulation reported in the table. In this last formulation, test results are obtained from a composition wherein the dispersing agent is used in an amount supplying 21 volume percent of the coating bath. This coating blend is prepared to determine the suitability of the dispersing agent as a complete replacement for the high boiling organic liquid substance that would otherwise be present. As above noted, all of the other compositions that are represented in the table, include the 3 ml./l of dispersing agent, including the composition first reported in the table. This formulation first reported then contains no further organic liquid substance and is used for comparative purposes.

The other coating blends listed in the table contain, as shown in the table, either 10 volume percent of tet-

raethylene glycol (TEG) or 10, 11 or 21 volume percent, of dipropylene glycol (DPG). Each coating composition is then employed for the coating of $\frac{1}{4}$ inch $\times$ $\frac{3}{4}$ inch hex head screws or for the coating of $\frac{1}{4}$ $\times$ $\frac{3}{4}$ SAE grade 2 hex bolts. The coating is conducted in a manner and the coated parts are cured as described in Example 1. Coating weights for the parts, as are shown in the table below, are determined in the manner as described hereinabove.

In the table below corrosion resistance test results are shown for the parts in the water soak test. In this test, 3-5 coated parts, selected at random, are submersed in 50 milliliters of deionized water contained in a glass beaker. The beaker is then covered. The test quickly provides corrosion resistance data in a testing procedure that is readily conducted.

Test results are reported, as determined for various submersion times, all as shown in the table below; such a showing underscores the achievement of significant results in a short elapsed time. In the test, parts are rated in accordance with the system as described hereinabove for salt spray testing and the results as reported in the table are an average for the parts subjected to the test.

TABLE 3

Compound Type	Compound Conc. Vol. %	Coating Weight mgms./ft. ²	Water Soak, Hours			
			16	65	72	144
None	-0-	1824	—	10	—	4
TEG	10	1734	8+	—	5	—
DPG	10	1472	7	—	5	—
DPG	11	1185	8	—	—	—
DPG	21	1920	10	10	—	9
WETTER	21	2608	—	8	—	5

TEG= Tetraethylene glycol
DPG= Dipropylene glycol

As highlighted in the above reported results, the absence of a high boiling organic liquid substance, although providing a significant coating weight, does not result in a composition that will yield a coating having desirable extended corrosion resistance. Moreover, as shown by the results last reported in the table, the simple addition of high boiling organic liquid substance, i.e. dispersing agent, which also can lead to significant coating weights, will also yield a very undesirable corrosion resistant coating. As is also further evidenced in the table, the 10-11 volume percent of high boiling organic liquid substance is insufficient to achieve coatings that will assure excellent corrosion resistance.

EXAMPLE 4

The coating compositions of Example 3, with the exception of the formulation containing 11 volume percent DPG, are used in the manner of Example 3 to coat screws or bolts all in the manner of Example 3. Coated parts, selected at random, are then subjected to a coating adhesion test. This test, which may be conveniently termed a "wipe adhesion" test, is manually conducted with the bolt or screw and a paper towel.

While the threaded portion of the screw or bolt is firmly held in one hand, a paper towel is held on a flat surface with the other hand. A flat portion of the head of the coated part is then manually pressed on to the towel and the part drawn across the towel in a short firm stroke as the towel is held in place. Following this

procedure, the paper towel is then removed and visually inspected for the size and area of the grayish-silver streak that will be left on the towel.

From this visual observation, and by comparing many such streaks one with the other, the wipe adhesion for parts is rated in accordance with a system using the following guidelines:

- 10 no coating removal;
- 8 initial coating removal, incipient deposit on paper towel;
- 6 light removal;
- 4 medium coating removal, i.e. darker, large deposit on paper towel than for (6);
- 2 heavy removal;
- 0 heavy removal approaching complete removal of coating.

In accordance with the above guidelines, the results for the parts are shown below in Table 4.

TABLE 4

Compound Type	Compound Conc. Vol. %	Coating Weight mgms./ft. ²	Wipe Adhesion
None	-0-	1824	5
TEG	10	1734	4
DPG	10	1472	4
DPG	21	1920	9+
WETTER	21	2608	2

TEG= Tetraethylene glycol
DPG= Dipropylene glycol

As detailed in the above reported results, wipe adhesion is more than a function of coating weight. It is further interesting to note that the replacement of the high boiling organic liquid substance simply with the dispersing agent provides for a coating of very poor adhesion. Moreover, simply eliminating the high boiling organic liquid substance, provides for better coating adhesion than for adding such substance in insufficient amount, e.g. 10 volume percent. However, better than doubling this amount of high boiling organic liquid substance provides for excellent coating adhesion.

EXAMPLE 5

Many of the coating compositions of Example 3, with the exception of the formulation containing 11 volume percent DPG, are again employed in the manner of Example 3 to coat hex head screws. An additional formulation, prepared and used in the manner as described for the compositions of Example 3, is used; in this fresh formulation, 21 volume percent TEG is employed. As in the above Table 3, in Table 5 below the high boiling organic compound, as well as its concentration, is shown for each formulation in further combination with the coating weight obtained from the formulation.

Some of the coated screws, selected at random, are subjected to the above described salt spray test. In the test, parts are rated in accordance with the system described hereinabove for salt spray testing. The results are reported in Part B in Table 5 below. In Part A of Table 5, results are listed for the salt spray test, and in accordance with the rating systems described hereinabove for such test, but it is conducted with coated panels.

These panels tested in Part A are 4 $\times$ 8 inches cold rolled, low carbon steel panels. These panels are typically prepared for coating in the manner described hereinabove for preparing parts for coating. They are

then simply coated by immersing the panels in the coated formulation, removing the panel from the formulation and permitting it to drain, followed by baking as described hereinabove for curing coated test parts.

In Part C of Table 5, results are shown for salt spray testing rated in the manner described hereinabove for such test, but prior to the test the screws have had applied thereto a coating of electrocoat paint. Thus, this testing provides an indication of the adaptability of the coating for receiving subsequent topcoatings. The electrocoat paint is a commercial water-based, black-pigmented polyester-based paint. It is anodically deposited with an impressed voltage of 100–150 volts for a duration of 30–60 seconds. Upon removal from the electrocoat paint bath, the coating is rinsed and then baked and the resulting coated articles are dry to the touch and have the visual appearance of articles ready for commercial use, prior to their being subjected to the salt spray test.

TABLE 5

Part A: Panels			
Compound Type	Compound Conc. Vol. %	Coating Weight mgms./ft. ²	Salt Spray 72 Hours
DPG	10%	728	1
DPG	21%	720	8
Part B: Hex-Head Screws			
Compound Type	Compound Conc. Vol. %	Coating Weight mgms./ft. ²	Salt Spray 72 Hours
DPG 10%	1472	1	
TEG	10%	1734	1
DPG	21%	1920	9
Part C			
Under Electrocoat; Hex-Head Screws			
Compound Type	Compound Conc. Vol. %	Coating Weight mgms./ft. ²	Salt Spray One Week
None	0-	1824	4
DPG	10%	1472	2
TEG	10%	1734	3
TEG	21%	2336	6
DPG	21%	1920	7
WETTER	21%	2608	3

The above tabulated results most particularly underscore the significant enhancement of corrosion resistance that can be obtained when the high boiling organic liquid is used above the 20 volume percent level as opposed to around the 10 volume percent level. Further, it is especially noteworthy that a mere use of the dispersing agent, and at a substantial concentration in a coating composition, will not yield a coating that is a desirable topcoat base. Also, for receiving a topcoating and forming a corrosion resistant composite, the above results in Part C underscore that it would be more desirable to omit the high boiling organic liquid substance rather than employ it at a mere 10 volume percent concentration. For achieving excellent corrosion resistance in the coating composite, one must employ the high boiling organic liquid substance at a substantial level, e.g., the 21 volume percent level.

We claim:

1. An aqueous coating composition for application to, and curing on, a metal substrate, thereby preparing an adherent water insoluble, alkali and corrosion resistant as well as substantially resinfree coating on said

substrate, which composition before curing comprises an intimate mixture in aqueous liquid medium of:

- A. a hexavalent-chromium-providing substance, supplied by about 80 to 100 weight percent chromic acid and providing above 5 but below about 100 grams per liter of chromium, expressed as CrO_3 ;
- B. above 50 but below about 500 grams per liter of liquid medium of pulverulent metal selected from the group consisting of zinc, aluminum, mixtures thereof and alloys of same, said composition having a weight ratio of chromium, expressed as CrO_3 , to pulverulent metal of between about 1:1 and 1:15;
- C. below about 50 volume percent but substantially above 15 volume percent, based on the volume of the total liquid of the aqueous liquid medium, of water soluble organic liquid substance that maintains liquidity above 100°C . and is selected from the group consisting of tri-, and tetraethylene glycol, di-, and tripropylene glycol, and the water soluble low molecular weight ethers of all such foregoing glycols, diacetone alcohol, the water soluble low molecular weight ethers of diethylene glycol, and mixtures of the foregoing; and
- D. above about 0.0005 volume percent, basis total volume of said coating composition, of dispersing agent.

2. The coating composition of claim 1 wherein said organic liquid substance is selected from the group consisting of dipropylene glycol, tripropylene glycol monomethyl ether, tetraethylene glycol, diethylene glycol monoethyl ether, dipropylene glycol monomethyl ether, and mixtures of the foregoing.

3. The coating composition of claim 1 wherein said chromium-providing-substance supplies not substantially above about 60 grams per liter of chromium, expressed as CrO_3 , and said composition has a weight ratio of chromium, expressed as CrO_3 , to pulverulent metal of between about 1:4 and 1:9.

4. The coating composition of claim 1 wherein said pulverulent metal is zinc flake and said flake is present in an amount above about 150 grams per liter of said coating composition.

5. The coating composition of claim 1 wherein said organic liquid substance is present in an amount above about 20 volume percent.

6. A pulverulent metal containing precursor constituent adapted for blending into chromium-containing aqueous blend for preparing a substantially resin-free, liquid coating composition for metal substrates, said coating composition having a ratio of chromium, expressed as CrO_3 , to pulverulent metal of between about 1:1 and 1:15, wherein said precursor constituent consists of pulverulent metal the preponderance of which is zinc flake, water soluble organic liquid substance that maintains liquidity at 100°C . and is selected from the group consisting of tri-, and tetraethylene glycol, di-, and tripropylene glycol, and the water soluble low molecular weight ethers of all such foregoing glycols, diacetone alcohol, the water soluble low molecular weight ethers of diethylene glycol, and mixtures of the foregoing, and 0–3 weight percent basis the total weight of said precursor constituent, of dispersing agent, and wherein said precursor constituent has a weight ratio of said organic liquid substance to said pulverulent metal of between about 1:2.5 – 1:0.3.

7. The coating composition precursor constituent of claim 6 wherein said pulverulent metal is 80-100 percent zinc flake by weight.

8. The coating composition precursor constituent of claim 6 wherein said organic liquid substance is selected from the group consisting of dipropylene glycol, tripropylene glycol monomethyl ether, tetraethylene glycol, diethylene glycol monoethyl ether, dipropylene glycol monomethyl ether, and mixtures of the foregoing.

9. The coating composition precursor constituent of claim 6 wherein said dispersing agent contributes between about 0.2-0.9 weight percent of same and said constituent has a weight ratio of organic liquid substance to pulverulent metal of between about 1:2 and 1:0.8.

10. A coated metal substrate having on the surface thereof an adherent alkali and corrosion resistant water-insoluble and substantially resin free coating, which coating comprises above 10 but not substantially above about 5,000 milligrams per square foot of coated substrate of pulverulent metal selected from the group consisting of zinc, aluminum, mixtures thereof, and alloys of same in intimate mixture with the residue from a substantially resin-free hexavalent-chromium-containing aqueous coating composition containing a hexavalent-chromium-providing substance, below about 50 volume percent but substantially above 15 volume percent, basis total composition liquid, of water soluble organic liquid substance that maintains liquidity above 100°C and is selected from the group consisting of tri-, and tetraethylene glycol, di-, and tripropylene glycol, and the water soluble low molecular weight ethers of all such foregoing glycols, diacetone alcohol, the water soluble low molecular weight ethers of diethylene glycol, and mixtures of the foregoing, and said coating composition provides said residue with not above about 500 milligrams per square foot of coated substrate of chromium, wherein said coating contains a weight ratio of chromium, as chromium, to pulverulent metal of not substantially above about 0.5:1, and said residue is obtained by applying to said metal surface said hexavalent-chromium-containing composition and heating said substrate at a temperature, and for a period of time, sufficient to vaporize volatile constituents from said coating composition and deposit on said surface said residue.

11. The coated metal substrate of claim 10 wherein said residue is the residue remaining after heating applied coating at a temperature above about 400°F. and for a time of at least about 1 second.

12. The method of preparing a coated metal substrate having on the surface thereof an adherent, alkali and corrosion resistant, water insoluble and substantially resin-free coating, which method comprises:

1. applying to said surface a hexavalent-chromium-containing aqueous coating composition of hexavalent-chromium-providing substance, supplied by about 80 to 100 weight percent chromic acid, said composition containing above about 0.0005 volume percent, basis total composition liquid, of dispersing agent and below about 50 volume percent but substantially above 15 volume percent, same basis, of water-soluble organic liquid substance that maintains liquidity above 100°C and is selected from the group consisting of tri-, and tetraethylene glycol, di-, and tripropylene glycol, and

the water soluble low molecular weight ethers of all such foregoing glycols, diacetone alcohol, the water soluble low molecular weight ethers of diethylene glycol, and mixtures of the foregoing, said composition being applied in an amount sufficient to provide not above about 500 milligrams per square foot of coated substrate of chromium, said composition also containing pulverulent metal selected from the group consisting of zinc, aluminum, mixtures thereof, and alloys of same in sufficient amount to provide not substantially above about 5,000 milligrams per square foot of coated substrate of said pulverulent metal and to provide said coating with a weight ratio of chromium, as chromium to pulverulent metal of not substantially above about 0.5:1, and

2. heating said substrate at a temperature, and for a period of time, sufficient to vaporize volatile constituents from said aqueous coating composition and deposit on said surface said coating.

13. The method of claim 12 wherein said substrate is heated at a substrate temperature above about 400°F and for a time of at least about one second.

14. The method of claim 13 wherein said aqueous coating composition is applied to said surface in an amount sufficient to provide from about 10 to about 200 milligrams per square foot of said pulverulent metal, said aqueous coating composition further providing from about 5 to about 15 milligrams per square foot of chromium, and said coated metal substrate is subsequently topcoated.

15. The method of preparing a weldable substrate for electrical resistance welding and having desirable corrosion and alkali resistance, which method comprises:

1. establishing on the surface of said substrate, on at least a portion thereof where welding will take place, above 10 but not substantially above about 5,000 milligrams per square foot of coated substrate of pulverulent metal selected from the group consisting of zinc, aluminum, mixtures thereof, and alloys of same in intimate mixture with the residue from a substantially resin-free hexavalent-chromium-containing aqueous coating composition containing a hexavalent-chromium-providing substance, between below about 50 volume percent, but substantially above 15 volume percent, basis total composition liquid, of water-soluble organic liquid substance that maintains liquidity above 100°C and is selected from the group consisting of tri-, and tetraethylene glycol, di-, and tripropylene glycol, and the water soluble low molecular weight ethers of all such foregoing glycols, diacetone alcohol, the water soluble low molecular weight ethers of diethylene glycol, and mixtures of the foregoing, and above about 0.0005 volume percent, same basis, of dispersing agent, and said coating composition providing said residue with not above about 500 milligrams per square foot of coated substrate of chromium, wherein said coating contains a weight ratio of chromium, as chromium to pulverulent metal of between about 1:1 and 1:15,
2. heating said substrate at a temperature, and for a period of time, sufficient to vaporize volatile constituents from said coating composition and deposit on said surface a composition residue and pulverulent metal, thereby preparing said substrate for

welding with a coating providing corrosion resistance and weldable electroconductivity.

16. The method of claim 15 wherein said substrate is heated at a temperature in excess of about 400°F. and for a time of at least about one second.

17. A weldable metal substrate prepared for electrical resistance welding according to the method of claim 15.

18. The weldable metal substrate of claim 17 wherein said substrate prepared for electrical resistance welding is the substrate of a metallic stud.

19. The method of electrical resistance welding metallic articles which comprises:

1. establishing on the surface of said substrate, on at least a portion thereof where welding will take place, above 10 but not substantially above about 5,000 milligrams per square foot of coated substrate of pulverulent metal selected from the group consisting of zinc, aluminum, mixtures thereof, and alloys of same in intimate mixture with the residue from a substantially resin-free hexavalent-chromium-containing aqueous coating composition containing a hexavalent-chromium-providing substance, between below about 50 volume percent, but substantially above 15 volume percent, basis total composition liquid, of water soluble organic liquid substance in said aqueous liquid medium, and above about 0.0005 volume percent, same basis, of dispersing agent, with the organic liquid substance maintaining liquidity above 100°C. and being selected from the group consisting of tri-, and tetraethylene glycol, di-, and tripropylene glycol,

and the water soluble low molecular weight ethers of all such foregoing glycols, diacetone alcohol, the water soluble low molecular weight ethers of diethylene glycol, and mixtures of the foregoing and said coating composition providing said residue with not above about 500 milligrams per square foot of coated substrate of chromium, wherein said coating contains a weight ratio of chromium, as chromium, to pulverulent metal of not substantially above about 0.5:1,;

2. heating said substrate at a temperature and for a period of time sufficient to vaporize volatile substituents from said coating composition and deposit on said surface a substantially water insoluble and resin-free coating of said residue and pulverulent metal, said coating providing corrosion resistance and weldable electroconductivity thereon;
3. contacting at least a portion of said one article with another article of metal to be welded;
4. passing an electrical resistance welding current through said articles of metal and said coating thereon at the zone selected for welding; and
5. fusing said articles together in said zone of said welding.

20. The method of claim 19 wherein said coating is deposited on the substrate of a weldable metal stud and thereafter said stud is electrically resistance welded to another article of metal.

21. A welded metal article prepared according to the method of claim 20.

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