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CORROSION RESISTANT METAL

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This invention relates to the treatment of zinc and cadmium including castings thereof and particularly galvanized metal, but may also be used in the treatment of iron and steel as well as brass and copper and copper alloys including bronzes.

The primary object of the invention is to provide the metal surface with a corrosion resistant coating having a permanent and attractive black decorative effect throughout its area.

Another object of the invention is to produce an insoluble, integral, corrosion resistant and visible coated metal surface by means of an aqueous dip containing a water soluble chromium compound, an organic acid or salt thereof and a color forming ingredient in the nature of a soluble ferric salt which is capable of chemical modification to impart a decorative black color to the resultant coating. In some cases for the purposes of forming a highly smooth or polished coating, the dip also includes compounds which will liberate anions of mineral acids.

An equally important object of the invention is to provide a color imparting ingredient which does not affect the corrosion resistance of the protective chromium coating, nor substantially change or objectionably lengthen the procedure of forming the chromium coating. That is to say, the color forming member (1) is relatively chemically inert as regards the other constituents of the dip and the resultant coating, but (2) itself is modified by simple selective chemical treatment after the coating is formed to impart a definite and permanent black color thereto.

The dip of this invention reacts with the metal surface to be coated, for example, zinc, and in the case of the galvanized metal, for instance, forms the coating on the surface of the relatively thin surface layer of spelter as a molecular film, i. e., combines with the zinc spelter layer to produce the visible corrosion resistant coating.

Broadly stated, I include in an aqueous dip containing a soluble chromium compound and formic acid or a formate, a suitable amount of a soluble ferric salt as, for instance, ferric chloride and ferric nitrate. The reaction between this dip and the metal surface to be coated produces a resistant coating in which the chromium compound is apparently formed as a precipitated gel upon the surface of the metal to be protected. This gel evidently absorbs or holds the ferric compound which apparently is now wholly or partly converted to the hydroxide and is also present in the coating as a gel. Thereafter, by subjecting the gel coating to treatment with a suitable amount of a natural or synthetic ("Syntans") tannin or a tannin derivative, for example, gallic acid or tannic acid, the latter selectively reacts with the ferric compound and there is imparted to the entire coating a permanent and definite black color while at the same time, the color modified coating loses none of its desirable corrosion resistant properties.

In order that the invention may be more clearly understood, I will describe several satisfactory examples of dips:

Example I

In this example, substantially 100 grams of chromic acid per liter and substantially 60 cc. of formic acid per liter are employed, and substantially 20 grams ferric chloride are included per liter of this mixture. An immersion of about 15 seconds to about a minute and a half or about 2 minutes may be used, and the temperature may vary from about room temperature to about boiling. Heating appears to accelerate the deposit and, hence, reduces the time period of immersion required.

The coated metal, for example, zinc, has a greenish color due to the presence of contained ferric chloride in the water of the precipitated gel coating and apparently also to the co-precipitation of ferric hydroxide.

After the coating has been formed, it is washed in water and then immersed in a water solution of gallic or tannic acid, preferably a saturated solution and at room temperature. A selective chemical reaction takes place between the ferric compound and the acid, and it is believed the ferric compound is converted to a ferric tannate usually described as ferric gallotannate. At the completion of this selective reaction, the whole coating turns a deep black color. The coated metal is again rinsed in hot or cold water and dried at ordinary temperature or by accelerated drying at elevated temperature or by means of a blower. A corrosion resistant surface is produced which has an attractive, permanent and decorative black color.

Example II

In this example, other water soluble ferric salts are employed instead of ferric chloride, notably ferric nitrate.

Example III

In this example about 60 cc. per liter of formic acid and about 30 grams per liter of chromic acid are contained in the dip. The temperatures and

time periods are substantially the same as in Example I.

Example IV

In this example, soluble chromates such as potassium or sodium chromate or di-chromates, such as sodium or potassium di-chromates, are employed and substituted for the chromic acid of Examples I, II or III. I find that satisfactory coatings are obtained if the chromates and di-chromates are used in substantially twice the amount of the chromic acid in Examples I, II or III, the proportions, as well as time of immersion and temperature being about the same as in the two previous examples.

Example V

Here a soluble formate such as sodium formate or ammonium formate is substituted for the formic acid in Examples I, II, III or IV. Where a formate is used, it is desirable to include a mineral acid, such as nitric acid, hydrochloric acid or sulfuric acid to liberate formic acid, as well as impart a smooth polished surface to the coating.

Example VI

In each of the coatings described in Examples I to V a mineral acid, namely, hydrochloric, sulfuric or nitric, or a salt of the mineral acid, such as cobalt nitrate, zinc nitrate, zinc chloride, sodium chloride, copper sulphate or ferric sulphate, are added in amount sufficient to render the coating produced by the reaction of the chromium compound and the formic compound smooth and polished.

It will be observed from the foregoing that either the chromium compound or the formic compound may be used in greater or less amount depending upon the coating desired. In all cases a visible surface coating is produced which, as explained above, has substantially improved corrosion resistant properties.

In preparing suitable dips, the chromic acid may be present in amounts from about 15 grams per liter to about 150 grams per liter, and the formic acid may be used in amounts from about 40 cc. per liter to about 100 cc. per liter while the soluble ferric salt is present in amounts of about 5 to 50 grams per liter of the mixture. The mineral acid will be used in amount of about 5 to 10 cc. per liter for smoothing and brightening purposes and larger amounts are employed where a formate is employed to liberate the formic acid, e. g., up to about 50 cc. per liter. As explained above, where chromates or di-chromates are used, the amount is substantially twice the chromic acid. Where salts of mineral acids are used, from 1 to 50 grams per liter have been found satisfactory. Also, as explained above, where soluble formates are employed instead of formic acid, they are used in substantially the same amounts as formic acid.

Example VII

In this example, ferrous salts are employed instead of the ferric salts in the previous examples and in substantially the same amounts. I find that the instability of ferrous salts and their tendency to oxidize, even from air exposure, results in a rapid oxidation to the ferric state when the ferrous salts such as ferrous chloride or ferrous nitrate are introduced, for example, to a solution containing sodium di-chromate. Other ferrous salts and chromium compounds may be employed as described herein. In some cases, it is desirable to allow the dip containing the ferrous salt to stand for from about 5 minutes to 24 hours before using the same. This is to assure complete oxidation of the ferrous salt addition to the ferric state. The working of the bath from this stage follows the procedure outlined in Example I.

As indicated in the examples, the temperature may vary from substantially room temperature to about boiling, and the time period of immersion from about 15 seconds to substantially a minute and a half or 2 minutes or until a visible coating having the desired properties is formed.

In the claims, I refer to a "chromium compound" and by that term intend to include not only chromic acid but the chromates and di-chromates as well, it being understood that other soluble chromates and di-chromates than mentioned herein are susceptible of use in accordance with the present invention. I have defined the formic acid and formates in the claims as organic compounds, it being understood that like the chromium compounds, soluble formates other than recited herein may be utilized. In referring to the mineral acids and salts of mineral acids, I have described these in the claims as "anions of a mineral acid," it being understood that numerous mineral acids as well as salts of mineral acids other than those given as examples may be utilized provided they are soluble, and also in the case of formates will act to liberate formic acid.

The claims are intended to cover the use of mixtures of the chromium compounds, mixtures of the formic compounds, mixtures of the mineral acids, mixtures of the salts of mineral acids as well as mixtures of such acids and salts.

Referring to Example V wherein a formate is substituted for formic acid and a mineral acid is employed for the purpose of liberating formic acid, sufficient mineral acid is employed to bring the pH of the solution to about pH 0.5 to about pH 2.5. The pH will necessarily vary in the preparation of dips in accordance with Example V depending upon the constituents employed and their proportions.

While I have specifically mentioned as water soluble ferric salts, ferric chloride and ferric nitrate, it is to be understood that practically any or equivalent ferric salt may be used, of which there are a large number commercially available. Also, other acids than gallic and tannic may be used, i. e., acids which are equivalents therewith and chemically react with the ferric compound in the coating to give the desired black decorative effect.

As will be observed, the invention may be carried out in a very simple manner and can be utilized for continuous treatment to reliably give a uniform product at low cost. While corrosion resistance is a most important consideration, the etched metal is moreover provided with an equally desirable characteristic, namely an attractive black decorative coating.

From the foregoing, it will be understood that the soluble ferric salt is chemically inert to the other ingredients of the dip and its presence does not interfere with the reaction of the dip with the metal to be coated and formation of a desirable corrosion resistant surface. Moreover, the presence of the ferric compound or compounds in the resistant coating does not affect the corrosion resistance of the same, i. e. the ferric compound is chemically inert to the coating and the reaction of the tannic or gallic acid is permitted to be selective with respect to the ferric compound to produce therewith the decorative black surface.

I claim:

1. A method of producing an adherent corrosion resistant coating on metals of the group consisting of zinc, iron, steel, copper, copper base alloys and cadmium, comprising subjecting the same to an aqueous acidic solution essentially consisting of a water soluble chromium compound selected from the group consisting of chromic acid and its salts and an organic compound which is easily oxidized by chromic acid and selected from the group consisting of formic acid and soluble formates and a water soluble iron salt until a visible coating is formed, the amount of the organic compound being sufficient to cause the chromium compound in conjunction with the organic compound to produce a visible corrosion resistant chromium containing coating on the base metal, and then while the coating is wet subjecting the coated metal to the action of an acid which will, by chemical reaction with the iron salt, impart a black color to the coating without impairing its corrosion resistance.

2. A method of producing an adherent corrosion resistant coating on metals of the group consisting of zinc, iron, steel, copper, copper base alloys, and cadmium, comprising subjecting the same to an aqueous acidic solution essentially consisting of chromic acid and an organic compound which is easily oxidized by chromic acid and selected from the group consisting of formic acid and soluble formates and a water soluble iron salt until a visible coating is formed, the amount of the organic compound being sufficient to cause the chromium compound in conjunction with the organic compound to produce a visible corrosion resistant chromium containing coating on the base metal, and then while the coating is wet subjecting the coated metal to the action of an acid which will, by chemical reaction with the iron salt, impart a black color to the coating without impairing its corrosion resistance.

3. A method of producing an adherent corrosion resistant coating on metals of the group consisting of zinc, iron, steel, copper, copper base alloys and cadmium comprising subjecting the same to an aqueous acidic solution essentially consisting of a water soluble chromium compound selected from the group consisting of chromic acid and salts thereof and an organic compound which is easily oxidized by chromic acid and selected from the group consisting of formic acid and soluble formates and anions of another mineral acid and a water soluble ferric salt, until a visible coating is formed, the amount of the organic compound being sufficient to cause the chromium compound in conjunction with the organic compound to produce a visible corrosion resistant chromium containing coating on the base metal, and then while the coating is wet subjecting the coated metal to the action of an acid which will, by chemical reaction with the iron salt, impart a black color to the coating without impairing its corrosion resistance.

4. A method for producing an adherent corrosion resistant coating on metals of the group consisting of zinc, iron, steel, copper, copper base alloys and cadmium comprising subjecting the same to the aqueous acidic solution essentially consisting of sodium dichromate, formic acid and zinc nitrate and a water soluble ferric salt, until a chromium containing visible coating is formed, the amount of the formic acid being sufficient to cause the chromium compound in conjunction with the formic acid and zinc nitrate to produce a visible corrosion resistant chromium containing coating on the base metal, and then while the coating is wet subjecting the coated metal to the action of an acid which will, by chemical reaction with the iron salt, impart a black color to the coating without impairing its corrosion resistance.

5. A method of producing an adherent corrosion resistant coating on metals of the group consisting of zinc, iron, steel, copper, copper base alloys and cadmium, comprising subjecting the same to an aqueous acidic solution essentially consisting of a water soluble chromium compound selected from the group consisting of chromic acid and its salts and an organic compound which is easily oxidized by chromic acid and selected from the group consisting of formic acid and soluble formates and a water soluble iron salt until a visible coating is formed, the amount of the organic compound being sufficient to cause the chromium compound in conjunction with the organic compound to produce a visible corrosion resistant chromium containing coating on the base metal, and then subjecting the coated metal to the action of an acid selected from the group consisting of gallic and tannic acids which will, by chemical reaction with the iron salt, impart a black color to the coating without impairing its corrosion resistance.

6. A method of producing an adherent corrosion resistant coating on metals of the group consisting of zinc, iron, steel, copper, copper base alloys and cadmium comprising subjecting the same to an aqueous acidic solution essentially consisting of a water soluble chromium compound selected from the group consisting of chromic acid and salts thereof and an organic compound which is easily oxidized by chromic acid and selected from the group consisting of formic acid and soluble formates and anions of another mineral acid and a water soluble ferric salt, until a visible coating is formed, the amount of the organic compound being sufficient to cause the chromium compound in conjunction with the organic compound to produce a visible corrosion resistant chromium containing coating on the base metal, and then subjecting the coated metal to the action of an acid selected from the group consisting of gallic and tannic acids which will, by chemical reaction with the iron salt, impart a black color to the coating without impairing its corrosion resistance.

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