Patented Jan. 29, 1946 2,393,663

UNITED STATES PATENT OFFICE

2,393,663

COATING FOR CADMIUM AND ZINC

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No Drawing. Application March 22, 1943, Serial No. 480,096

15 Claims. (Cl. 148—6)

This invention relates to the treatment of zinc and cadmium and particularly galvanized metal to produce thereon an insoluble adherent corrosion resistant coating which is visible and may be prepared in a variety of shades from a yellow iridescent surface through olive drab to black.

The use of chromium compounds for coating is well known and many compositions or dips are commercially available. The present invention is an improvement in such dips and possesses the characteristic of reliability, freedom from complicated procedure and may be carried out at commercially acceptable costs.

We have discovered that whereas chromium compounds alone do not produce a desirable coating, and whereas organic acids notably formic acid, alone do not produce a satisfactory surface, when such compounds are combined in a dip, a very satisfactory corrosion resistant finish is obtained according to this invention. Thus we use chromic acid, chromates, and dichromates with formic acid or formates, and dependent upon the relation of the ingredients in the dips, e. g., as described in the examples set forth below, obtain corrosion resistant coatings of various shades which are highly desirable. The temperatures and time periods of treatment may also be varied to speed up as well as modify the coatings. One particular coating has a distinctly olive-drab appearance and meets the demand for a color of this character in which the coating is corrosion-resistant under such conditions as those encountered by contact with salt water, and in tropical climates.

In order to smooth or polish as well as vary the color and enhance corrosion resistance of the coatings, we include in the dip compounds which will liberate anions of mineral acids. Thus, we may include in the dip mineral acids in amounts effective for the purpose of brightening the coating, or we may include salts of the mineral acids for the purpose.

The dip reacts with the zinc and in the case of galvanized metal 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. We attribute the effectiveness of the dip, at least in part, to the reduction in valence of the chromium which takes place in the presence of formic acid or a formate, and the action of the formic acid or formate in maintaining the oxidation reduction reaction between the base metal, e. g., zinc, and the chromic ion at the optimum for obtaining a favorable deposit. This opinion is based upon observation and is simply our explanation of what we consider occurs. Having experimented with chromate dips including chromium compounds and mineral acids as well as organic acids, we can safely say that through a wide range of proportions, temperatures and immersion periods, the present invention provides a reliable coating which has markedly improved corrosion resistance.

In order that the invention may be more clearly understood, we 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. 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.

Example II

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 III

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

Example IV

Here a soluble formate such as sodium formate or ammonium formate is substituted for the formic acid in Example I, II, or III. 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 V

In each of the coatings described in Examples I to IV a mineral acid, namely, hydrochloric, sul-

furic 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. The mineral acid or salt of mineral acid enhances corrosion resistance and acts as a color varying agent.

An article having a surface of zinc or cadmium or galvanized metal or containing these materials, when treated in accordance with Example V has a coating comprising a plurality of identifiable superposed films. That is, the coating comprises a water insoluble interfacial film composed essentially of an oxide of the base metal, which film is integrally united with the base metal surface and bonds thereto a second superposed visible film composed essentially of compounds containing trivalent and hexavalent chromium in which the water insoluble trivalent compounds are in greater amount than the hexavalent compounds.

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. 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. In other words, the chromium compounds are present in amounts equivalent to 15 to 150 grams per liter of chromic acid, and the organic compound is present in amount equivalent to 40 cc. to 100 cc. per liter of formic acid, while the mineral acid salts are used in amounts equivalent to 5 to 10 cc. per liter of the mineral acid, and larger amounts are used where a formate is employed as explained above.

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, we 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. It is to be 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, we 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 where formates are used will act to liberate formic acid.

In referring to "cadmium and zinc" in the claims, we intend to include by this expression galvanized metal whether prepared by plating or hot-dipped and in which cadmium or zinc or mixtures thereof are employed.

Likewise, 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.

Preferably, the coatings described herein are obtained by simply immersing the zinc or cadmium, or galvanized metal to be coated in the solution until the desired coating is formed. This will vary with changes in concentration, temperature, time of immersion and salts or acids used. The coated object is rinsed in hot or cold water to obtain an even finish or allowed to dry without rinsing at which time an attractive mottled appearing coating will be formed. Pretreatment other than cleansing is not necessary in coating zinc or cadmium or galvanized metal. No special rinse is necessary to increase the corrosion resistance.

Referring to Example IV 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 IV depending upon the constituents employed and their proportions.

As will be observed, the invention may be carried out in a very simple manner and one which we find can be utilized for continuous treatment to reliably give a uniform product at low cost. While corrosion resistance is the most important consideration, the etched metal is provided with attractive coatings of yellow, green, or black, and particularly coatings having a most desirable olive-drab shade.

The expression "essentially consisting of" is intended in the appended claims to mean the particular constituents recited in amounts effective to produce a visible corrosion resistant coating on zinc and cadmium when subjected to the solution, but does not exclude the use in the solution of other components where the latter do not substantially alter the basic character of the coating obtained by use of the essential components recited.

We claim:

1. A method of producing an adherent corrosion resistant coating on zinc 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 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.

2. A method of producing an adherent corrosion resistant coating on zinc and cadmium, com-

prising 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 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.

3. A method of producing an adherent corrosion resistant coating on zinc 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, 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.

4. A method in accordance with claim 3 wherein the metal is subjected to the dip for about fifteen seconds to about two minutes.

5. A method in accordance with claim 3 wherein the metal is subjected to the dip at a temperature from about room temperature to about 212° F.

6. An aqueous acidic solution for producing an adherent corrosion resistant coating on zinc and cadmium consisting essentially 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, said chromium compound and said organic compound being present in amounts effective to produce a chromium containing visible coating on zinc and cadmium subjected to the solution, and the organic compound being used in amount greater than the equivalent of about 40 cc. per liter of formic acid.

7. An aqueous acidic solution for producing an adherent corrosion resistant coating on zinc and cadmium consisting essentially of a water soluble chromium compound selected from the group consisting of chromic acid and salts thereof, 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, the amount of the organic compound being sufficient to cause the chromium compound in conjunction with the organic compound and said mineral acid ions to produce a visible corrosion resistant chromium containing coating on the base metal.

8. An aqueous acidic solution for producing an adherent corrosion resistant coating on zinc and cadmium consisting essentially of sodium dichromate, formic acid and zinc nitrate, 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.

9. A method of producing an adherent corrosion resistant coating on zinc and cadmium comprising subjecting the same to the aqueous acidic solution essentially consisting of sodium dichromate, formic acid and zinc nitrate, until a chromium containing visible coating in 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.

10. An article having a surface of zinc and cadmium provided with a coating in accordance with claim 3, said coating comprising a water insoluble interfacial film composed essentially of an oxide of the base metal, said film being integrally united with the base metal surface and bonding thereto a second visible film composed essentially of compounds containing trivalent and hexavalent chromium in which the water insoluble trivalent compounds are in greater amount than the hexavalent compounds.

11. An article having a surface of zinc and cadmium provided with a coating in accordance with claim 9, said coating comprising a water insoluble interfacial film composed essentially of an oxide of the base metal, said film being integrally united with the base metal surface and bonding thereto a second visible film composed essentially of compounds containing trivalent and hexavalent chromium in which the water insoluble trivalent compounds are in greater amount than the hexavalent compounds.

12. An aqueous acidic solution for producing an adherent corrosion resistant coating on zinc and cadmium consisting essentially of a water soluble chromate and an organic compound which is easily oxidized by chromic acid and selected from the group consisting of formic acid and soluble formates, 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.

13. An aqueous acidic solution for producing an adherent corrosion resistant coating on zinc and cadmium consisting essentially of a water soluble dichromate and an organic compound which is easily oxidized by chromic acid and selected from the group consisting of formic acid and soluble formates, 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.

14. An aqueous acidic solution according to claim 12 also containing anions of a mineral acid.

15. An aqueous acidic solution according to claim 12 also containing anions of a mineral acid.

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Certificate of Correction

Patent No. 2,393,663. January 29, 1946.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 64, claim 15, for the claim reference numeral "12" read *13*; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 3rd day of September, A. D. 1946.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.