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BRIGHT CORROSION RESISTANT COATING OF METALS

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The present invention relates to the treatment of metal surfaces containing zinc, cadmium, aluminum, copper and alloys including appreciable amounts thereof, and is useful both in connection with castings and coatings of these metals, notably galvanized iron.

The principal object of the invention is to impart a bright, colorless, water-repellant surface or film, having improved corrision resistance, to zinc, cadmium, aluminum and copper, and their alloys, by subjecting the metal surface to a single immersion treatment.

Another object of the invention is to provide a treating solution and method which will enable the above-mentioned results to be uniformly obtained on a commercial scale.

A further object of the invention is to provide a treating solution and method which will render the metal surface suitable for the reception of paint. That is, whereas the untreated metal surfaces will not afford adequate paint adhesion for commercial purposes, metal surfaces treated according to the present invention exhibit marked paint adherence.

The use of solutions containing chromic acid and sulphuric acid to impart corrosion resistance usually causes discoloration. I have found that a clear coating can be obtained by including acetic acid in such solutions and maintaining a relatively high acidity. In any case, where the acid number of the solution is relatively low and the acetic acid is not sufficiently active, any tendency toward discoloration is overcome by the addition of nitric acid.

The term "acid number of the solution" as used herein is based upon the results obtained by conventional acidimetry practice where it is usual for the determination of the amount of acid present in solutions to base calculations upon the amount of standardized solution of alkali required by titration to neutralize the acid.

In explanation, a solution of chromic acid (CrO_3) and sulphuric acid in the ratio of 16 grams of chromic acid per liter to 1 cubic centimeter per liter of sulphuric acid will produce discoloration. However, when acetic acid is included in such a solution and the acid number thereof is between about 150 and 250, discoloration is avoided. When for any reason, the acid number of the solution is below about 150, or the acetic acid is not sufficiently effective to preclude discoloration by reason of its inactivity with respect to the metal surface, this situation is readily avoided by the addition of nitric acid. The results described are particularly true in the case of zinc, alloys of zinc and galvanized coatings.

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Treatments of the character described have certain practical requirements, notably economy in the use of the chemicals making up the solution, and the speed and facility with which the desired results may be obtained. With the present invention, an appreciably lower ratio of chromic acid and sulphuric acid has been found satisfactory, namely 16:1, and of equal importance, a single dip in the solution produces the improved colorless film.

The invention is operative through a wide range of acidities of the solutions employed, as illustrated in the following examples:

Example I

Chromic acid gms./l.	160
Sulphuric acid cc./l.	10
Acetic acid cc./l.	80
Solution acid No.	200.0

Example II

Chromic acid grams/liter H_2O	160
Acetic acid cc./liter H_2O	99
Sulphuric acid cc./liter H_2O	10

Example III

Chromic acid gms./l.	80
Sulphuric acid cc./l.	5
Acetic acid cc./l.	55
Nitric acid cc./l.	10
Solution acid No.	112.7

Example IV

Chromic acid gms./l.	40
Sulphuric acid cc./l.	2.5
Acetic acid cc./l.	80
Nitric acid cc./l.	10
Solution acid No.	96.8

Example V

Chromic acid gms./l.	20
Sulphuric acid cc./l.	1.25
Acetic acid cc./l.	80
Nitric acid cc./l.	10
Solution acid No.	79.0

Example VI

Chromic acid gms./l.	10
Sulphuric acid cc./l.	0.625
Acetic acid cc./l.	80
Nitric acid cc./l.	10
Solution acid No.	70.5

In each of the above formulations, the amounts recited are, as indicated, based upon their use per liter of water.

In preparing the mixes of the foregoing examples, the chemicals are supplied in concentrated form, the concentration being to the practical limits of solubility. As will be appreciated, this affords a substantial saving in shipping since the amount of water will be much less than that indicated above for the actual working solutions.

For example, 12½ gallons of concentrate according to Example I is placed in a carboy and will consist of 66.8 pounds of chromic acid (CrO_3), 40 pounds acetic acid (99.6% acetic acid), sulphuric acid 1899.6 cc. and water to make 12½ gallons. Such concentrate, when used, will be diluted with three parts of water so as to produce a bath of 50 gallons.

In the case of Example III, the ingredients are placed in a carboy in the amount of 12½ gallons. This concentrate will consist of chromic acid 50 pounds, acetic acid 4.12 gallons (99.5 acetic acid), sulfuric acid 1453.8 cc., nitric acid 2635 cc. and sufficient water to make 12½ gallons. This concentrate is prepared for working operations by introducing 5 parts of water to make a bath containing 75 gallons.

The use of acetic acid is necessary in all of the mixtures to produce a bright, colorless, film by a single treatment or immersion. The amount of acetic acid recited is slightly in excess of that theoretically required in order to take care of vaporization occasioned by the heating of the solution during treatment.

Although ratios of chromic acid to sulphuric acid of from 1:12 to 1:30 may be used in this invention, from the practical standpoint, ratios below about 1:16 or above about 1:16 present objections from the standpoint of commercial operation in many cases.

It will be observed that Example I possesses an acidity sufficiently high for the acetic acid alone to produce a colorless, bright film. On the other hand, the acidity of solutions III to VI is relatively lower, and the acidity of these formulations is rendered effective by means of a strong inexpensive acid which, in solution with chromic acid, will not produce a colored film. Nitric acid possesses this characteristic in that even minute additions of sulphuric and hydrochloric acid to the compositions of the foregoing examples will result in discoloration. The nitric acid appears to stabilize the solution, or in other words, where the activity of the acetic acid alone is insufficient to prevent discoloration, as where the acid number of the solution is too low, the addition of the nitric acid accelerates and supplements the action of the acetic acid.

If chromic acid is not available, sodium bichromate can be substituted for part of the chromic acid, and excess nitric acid may be employed in such a case to maintain the desired acidity, if necessary.

For carrying out the treatment, the solution may be maintained at a temperature from 60° to 212° F. and the period of immersion may extend from 1 to 120 seconds, depending upon concentration, acid number and temperature of the solution. A preferable temperature range for the solution is between 85° and 95° F. and a preferable immersion period is between 5.0 and 20 seconds.

In the examples, the amount of chromic acid may be increased to as much as 320 grams provided the ratio of sulphuric acid to chromic acid is maintained at about 1:16. The amount of acetic acid included in the solution may vary from 25 to 200 cc. per liter and the amount of nitric acid from 1 to 50 cc. per liter. The examples above-recited are preferred, and have particular value for the treatment of zinc, zinc alloys and galvanized metal.

In some cases it is desirable to introduce a suitable wetting agent in the bath in order to overcome any tendency of the coating to develop a blue or yellow streak on flat work.

After the materials have been treated in the bath, a hot water rinse is preferably employed to remove any streaking.

In addition to imparting corrosion resistance, it is found that the coating exhibits to a most surprising extent the desirable property of imparting to the treated surface the characteristic of being water-repellant, e. g., on zinc.

So-called bright finishing dips are not necessary, but in some cases due to the character of the zinc, cadmium, aluminum or copper surface, an aqueous bright dip or rinse consisting of about one-half of one per cent nitric acid or a dilute solution of caustic soda is used after the treatment and accelerates the bringing out of a bright finish on the treated article.

While I have indicated that a hot rinse is preferred after treatment, satisfactory results are obtained by a rinse in cold water.

It is preferred to immerse the castings of zinc, aluminum, cadmium, or copper, or the articles coated with such metals in a bath, but the treatment may, in some cases, be carried out by other means, as, for example, by spraying the aqueous acidic solution upon the surfaces to be treated.

The zinc, cadmium, aluminum and copper surfaces to be treated are introduced into the aqueous bath until a preferred, bright surface is formed. It is desirable to agitate the bath during the treatment. Articles treated with the solution in the manner above set forth, as by immersion or spraying, and particularly zinc, exhibit an enhanced salt spray resistance.

A significant feature of the invention, as above-indicated, is the maintenance of a critical acidity. That is, when the acid number of the solution is above 150, the acetic acid alone is active to prevent discoloration. Where, however, the acid number of the solution is below 150, it is necessary to include nitric acid in order to avoid discoloration. It is found that solutions having an acid number from about 50 to 250 are preferable, the acetic acid being effective alone when the acid number is between 150 and 250, and the nitric acid being added when the acid number of the solution is below 150 to produce a solution having an acid number between 50 and 150.

In the appended claims, the expression "zinc, cadmium, aluminum or copper articles" is intended to cover castings and coatings of zinc, cadmium, aluminum or copper, or alloys thereof, as well as mixtures in which the aluminum, zinc, cadmium or copper are present in substantial amount.

This application is a continuation-in-part of my application Serial No. 648,823, filed February 19, 1946, now abandoned.

I claim:

1. An aqueous acidic solution for treating metals selected from the group consisting of zinc and cadmium and alloys thereof to impart a bright, colorless surface to the metal consisting essentially of chromic acid 10 grams per liter to 320 grams per liter, sulfuric acid and acetic acid, the chromic acid and sulfuric acid being present in the ratio of about 1 cc. per liter of sulfuric acid to about 16 grams per liter of chromic acid, the

acetic acid being present in amount of about 25 to about 200 cc. per liter.

2. An aqueous acidic solution according to claim 1 containing nitric acid in amount of about 1 to about 50 cc. per liter.

3. A process of treating metals of the group consisting of zinc and cadmium and alloys thereof which comprises subjecting the same to an aqueous acidic solution consisting essentially of chromic acid 10 grams per liter to 320 grams per liter, sulfuric acid and acetic acid, the chromic acid and sulfuric acid being present in the ratio of about 1 cc. per liter of sulfuric acid to about 16 grams per liter of chromic acid, the acetic acid being present in amount of about 25 to about 200 cc. per liter, the temperature of the solution being maintained between about 60° and 212° F. and the treatment being continued until a bright, colorless surface is imparted to the metal, removing the metal from the bath and rinsing the metal.

4. The process according to claim 3 wherein the solution contains nitric acid in amount of about 1 to about 50 cc. per liter.

5. A process of coating zinc which comprises immersing the zinc in a solution consisting of about 48 to 288 grams per liter chromic acid, about 5.1 to 34.2 grams per liter H_2SO_4, about 2 to 41 grams per liter HNO_3, about 26.3 to 82 grams per liter $HC_2H_3O_2$, and the balance water at 60° F. to 130° F., the treatment being continued until a bright colorless transparent protective coating is imparted to the zinc, and removing the zinc from the solution.

6. A process of coating zinc which comprises immersing the zinc in a solution consisting of about 10 to 320 grams per liter chromic acid, about 1.4 to 34.2 grams per liter H_2SO_4, about 1.4 to 70.0 grams per liter HNO_3, about 26.0 to 208.0 grams per liter $HC_2H_3O_2$, and the balance water at 60° F. to 212° F., the treatment being continued until a bright colorless transparent protective coating is imparted to the zinc, and removing the zinc from the solution.

7. An aqueous acidic solution for treating zinc to impart a bright colorless transparent protective coating thereto consisting of about 10 to 320 grams per liter chromic acid, about 1.4 to 34.2 grams per liter H_2SO_4, about 1.4 to 70.0 grams per liter HNO_3, about 26.0 to 208.0 grams per liter $HC_2H_3O_2$, and the balance water.

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