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DYED METALS

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This invention relates to dyed metal surfaces notably of non-ferrous metals such as zinc and galvanized metal and cadmium.

In the production of a colored metal surface it is necessary to obtain continuous coverage, faithfulness of color, with absence of objectionable fading, control of opacity and, of course, permanent retention and adherence of the dye. Also, it is frequently important that an attractive polished surface be provided. Moreover, in many cases, it is desirable that the metal surface be corrosion resistant as in the case of zinc. These requirements present well known problems created for instance, by the nature of the metal and character of the dye and are particularly difficult to satisfy when corrosion resistance is also a factor.

I have discovered when a metal surface is treated with an aqueous solution as described in the application of Thomas and Ostrander, Serial No. 480,096, filed March 22, 1943, that the corrosion resistant coated surface produced by such treatment appears to have surprising mordant properties which contribute markedly to the production of fast colored metal surfaces which satisfy the above mentioned requirements. This is particularly true of relatively thick coatings which produce solid, i. e., opaque dyed surfaces and also in the case of relatively thin coatings where translucent or transparent dyed surfaces are desirable. Furthermore, effective results are obtained by using a minimum of dye which is of decided economic advantage.

I have successfully dyed abrasion and corrosion resistant metal surfaces which have been produced in accordance with the Thomas and Ostrander process. The dyeing was accomplished while such corrosion resistant and mordant coatings were still wet and a polished or flat appearance was obtained in accordance with the said application. I am not sure that these unusual results are due to absorption, chemical action or penetration but, notwithstanding the character of the metal and the corrosion resistance treatment, products of high quality have been uniformly obtained provided the dye is applied to the coating produced by the aforesaid application before such coating has been dried.

In carrying out the invention, the preferable procedure is to form on the metal surface the corrosion resistant and mordant coating as described, and after rinsing the same with water, and while it is still wet, subjecting the wet coated metal to the dyeing treatment, as in an aqueous bath of the dye solution. The dyes which may be successfully employed to form such a bath are water soluble, i. e., are directly soluble in water or capable of forming colloidal aqueous solutions, or are water soluble or form colloidal solutions under such mildly acid or alkaline conditions as do not objectionably affect the corrosion resistant coating.

DYES

Dyes	Shade
Naphthylamine Black 10 Br. Conc. CF	Gray black.
Brilliant Black BRX	Blue black.
Chrome Fast Black LSW	Red black.
Calcochrome Black FA	Purple black.
Nigrosine WSB	Gray black.
Acid Black BX	Blue black.
Diamond Black PBBA extra	Brown black.
Black mix: 50 pt. Diamond Black PBBA, 50 pt. Alizarine Blue SAP	Jet black.
Black mix: 66⅔ pt. Acid Black BX, 33⅓ pt. Acid Brilliant Red BB	Do.
Acid Orange A	Orange brown.
Metanil Yellow	Yellow brown.
Purpurine 4B Conc	Bronzy brown.
Milling Green	Bright green.
Tartrazine	Yellow green.
Alizarine Cyanine Green GG extra	Green.
Acid Alizarine Flavine RA	Light green.
Azo Fuchsine 6B Conc	Maroon.
Direct Fast Red BBL	Medium red.
Diamond Red 8HA	Brown red.
Acid Brilliant Red BB	Dark red.
Alizarine Blue SAP	Dark blue.
Fastusol Turquoise Blue LGLA	Blue green.

The dye baths are adjusted to a suitable pH, for example about pH 3.0 to about pH 8.0. Usually an immersion time of about 1 to about 10 minutes is sufficient, which is quite rapid and hence economical. Bath temperatures from about 20° C. to about 90° C. are satisfactory; in fact successful results have been obtained by dyeing at normal or room temperature. Dye concentrations in the aqueous bath are quite low, e. g., from about 0.05 to about 0.50% have been successfully employed with resultant substantial economy. After dyeing the surfaces are suitably dried at normal or room temperature in the air, using a blower if desired, or by centrifuging or at temperature which is slightly elevated. Suitable adjustment of the dye bath may be carried out, e. g., by acid or basic additions as required to give the most satisfactory pH for accomplishing dyeing.

CORROSION RESISTANT COATINGS

The initial corrosion resistant coating is obtained by subjecting the metal in accordance with the aforesaid pending application to an aqueous acidic dip containing as it main constituents water, a water soluble chromium compound selected from the group consisting of chromic acid and salts thereof and an organic compound having the formula H.COO—R in which R is a substance selected from the group consisting of hydrogen, a metal, and an inorganic radical until a visible coating is formed.

The following examples are taken from the Thomas and Ostrander application and in every case a visible corrosion resistant and mordant coating is obtained:

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 di-chromates, 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 dichromates 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 Examples 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, 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 for the various metals, 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.

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.

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 from 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.

In the claims, I refer to a "chromium compound" and by that term intend to include not only chromic acid but the chromates and dichromates 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.

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.

DYED, CORROSION RESISTANT SURFACES

In the following examples, the coating and dyeing of a surface containing zinc and cadmium is given merely for purposes of illustration, and it is to be understood that the articles may have only a metal covering or be of the type which are made of the cast metal.

EXAMPLES

In each example, a corrosion resistant mordant coating of desired thickness is first produced on a sheet or article of non-ferrous metal according to any of the aforementioned coating examples. Upon removal from the coating dip tank, the wet sheet is rinsed with cold water and then while the coating is still wet, the sheet is introduced into one of the following aqueous dye baths and dyed under the conditions described:

Example A

Tartrazine CL extra on zinc
Concentration—0.1%
pH—5.0
Temp. 35° C.
Immersion time—7 minutes
Color produced—light green

Example B

Alizarin Blue SAP on zinc
Concentration—0.05%
Temp.—45° C.
pH—4.0
Immersion time—10 minutes
Color produced—dark blue

Example C

Direct Fast Red 8BL on cadmium
Concentration—0.1%
pH—4.9
Temp.—40° C.
Immersion time—2 minutes
Color produced—medium red

Example D

Acid Black BX on zinc
Concentration—0.1%
pH—4.3
Temp.—50° C.
Immersion time—two minutes
Color produced—black

Example E

Acid Orange A on zinc
Concentration—0.1%
pH—4.6
Temp.—40° C.
Immersion time—five minutes
Color produced—brown

Example F

Dye mixture on zinc
Concentration:
.067% Acid Brilliant Red BB
.133% Acid Black BX
pH—4.0
Temp.—30° C.
Immersion time—three minutes
Color produced—black

The sheet or article upon removal from the dye bath and dried as described above, was found to be corrosion and abrasion resistant and had an attractive appearance.

The examples just mentioned may be repeated with any of the dyes listed above and with the various non-ferrous metals described. The important considerations are that (1) the organic dye be water soluble as described above and (2) the corrosion resistant coating be not dried but rather still be in its wet state at the time of dye application as explained. Rinsing of the wet coating with water before dyeing is preferred in order to remove any substantial excess of the coating solution.

I have also successfully carried out the invention by adding the dye to the corrosion resistant imparting dip, thereby utilizing a single immersion treatment. The two bath procedure is preferred to the single bath.

Organic water soluble dyes and mixtures, other than those mentioned, may be used to obtain a variety of colors and shades, those described above being representative. The dye concentrations in the aqueous baths may be varied but in any event are relatively low and substantially of the order above set forth. Likewise, the time period of immersion in the dye bath may be increased or decreased slightly beyond the range referred to. The pH of the aqueous dye bath must be kept within limits such as will preclude substantial impairment of the corrosion resistance of the coating where this latter quality is required.

Where corrosion resistance is not a factor, it is only necessary to utilize a dip solution of the character described and an immersion treatment such as will produce a slight coating on the non-ferrous metal. When this light or thin coating is dyed while still wet, its mordant properties are effective to receive and retain the dye.

As pointed out, I am not sure of the physical or chemical effects which produce the remarkable results obtained by following this invention. Apparently some of the dyes react chemically with the wet corrosion resistant coating while in other cases adsorption accompanied by an electrostatic effect evidently takes place or there is simply penetration of the dye into the wet coating. In any event, I have found that the coating forms a substantially universal mordant for organic, water soluble dyes and the improved results are obtained by applying the dye to the wet or undried coating whether the latter be light or of the relatively heavier and more corrosion resistant type.

I 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, and while the coating is wet, subjecting the same to an aqueous solution of a water soluble organic dye and thereby imparting a desired color to the surface of the metal.

2. 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 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, and while the coating is wet, subjecting the same to an aqueous solution of a water soluble organic dye and thereby imparting a desired color to the surface of the 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, and while the coating is wet, subjecting the same to an aqueous solution of a water soluble organic dye and thereby imparting a desired color to the surface of the metal.

4. 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 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 while the coating is wet, subjecting the same to an aqueous solution of a water soluble organic dye and thereby imparting a desired color to the surface of the metal.

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