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ANODIC COATING OF ZINC BASE METALS

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This invention relates to the coating of zinc base metals by anodic action, and has for its object the provision of an improved method of producing useful anodic coatings on such metals, as well as the provision, as new articles of commerce, of zinc base metals so coated. By "zinc base metal" we mean metals and alloys composed principally of zinc.

The invention is particularly concerned with the production of anodic coatings on zinc and zinc base alloys for the purpose of protection, ornamentation, or of serving as a base for the application of paints, lacquers and the like so as to secure good adhesion of the latter. Ordinary commercial zinc (in particular, rolled or strip zinc), zinc base alloys such as die-casting alloys containing over 90% zinc (for example, the alloys of United States Patents Nos, 1,596,761, 1,663,215, 1,779,525, 1,852,434, 1,852,441 and 1,852,442), and wrought zinc base alloys (for example, the alloys of United States Patents Nos. 1,716,599, 1,832,653, 1,832,733 and 1,835,450) may be advantageously coated by the method of the invention. Numerous other zinc base alloys, particularly those containing small amounts of copper and/or aluminum, are likewise amenable to treatment in accordance with the invention.

In copending applications for Letters Patent of the United States, Serial Nos. 642,608, and 642,609 filed November 14, 1932, on behalf of two of us (Truesdale and Wilhelm) there is disclosed the production of useful anodic coatings on zinc from alkaline electrolytes. These coatings consist essentially of zinc oxide, are dark in color with relatively strong alkaline electrolytes and light gray to white in color with more dilute alkaline electrolytes. In the course of an exhaustive investigation of the anodic coating of zinc, we have discovered that useful coatings can be produced with certain substantially neutral electrolytes. Thus, we have found that useful anodic coatings can be produced on zinc with substantially neutral electrolytes containing an anion (other than hydroxyl ion) capable of producing by anodic action with zinc an insoluble coating on the zinc anode, or containing an anion (other than hydroxyl ion) capable of forming an insoluble compound with zinc. Such coatings vary in color depending upon the nature of the dominant anion, and while the coating may contain some zinc oxide, it is characterized by a substantial content of the dominant anion or a derivative thereof.

The method of the present invention, based on the foregoing discoveries, involves subjecting a zinc base metal, as anode, to electrolytic treatment in a substantially neutral electrolyte containing an anion (other than hydroxyl ion) capable of producing by anodic action with zinc an insoluble coating on the zinc metal. The hydrogen ion, or hydroxyl ion, concentration of the electrolyte may vary to a slight extent from exact neutrality, and under practical operating conditions such variations are inevitable. Thus, we have determined that the hydrogen ion, concentration of the electrolyte may vary from a pH value of about 6 to about 8, without departing from the principle of the invention.

In carrying out the invention, the articles of zinc or zinc base alloys to be coated are subjected to an electrolytic treatment as anode while immersed in a substantially neutral electrolyte containing an anion of the characteristic properties hereinbefore described. When so treated at appropriate voltages, current densities and temperatures, the zinc articles become coated with a firm adherent film which contains a substantial amount of the dominant anion or a derivative thereof. Thus, the coating may consist of insoluble compounds (usually insoluble compounds of zinc) formed by anodic reaction of zinc with anions other than hydroxyl ions present in the electrolyte, or of combinations of such or other insoluble compounds with zinc oxide. In general, the composition of the coating produced in any particular electrolyte will depend upon the relative amounts of hydroxyl ions and other anions (capable of forming an insoluble compound with zinc or by anodic action with a zinc anode) which are discharged at the zinc anode, and in turn, the relative concentrations and relative reactivities of hydroxyl and other anions will determine which of these will be predominantly discharged at the anode.

Since the anodic coating of the invention usually reproduces, in minute detail, the surface markings originally present on the zinc article, the appearance of the coating may be improved by buffing the zinc article before anodic treatment. This buffing procedure may advantageously be of the same character as used on zinc prior to electro-plating. Other preliminary treatment, such as sand-blasting or etching which, like buffing, removes a surface film especially likely to be present on cast zinc surfaces, may be employed to facilitate the subsequent anodic treatment. Such preliminary surface treatment of the zinc article, may, of course, be dispensed with if desired.

The zinc article should be appropriately cleaned prior to anodic treatment. This cleaning may be

advantageously accomplished in a trisodium phosphate solution containing about six ounces per gallon of water (45 grams per liter of water). This solution is used hot as an electro-cleaner, with the zinc article to be cleaned as the cathode, and with sufficient current to produce copious gassing. When used in this manner, grease (e. g. acquired during rolling or buffing) and loose dirt are completely removed after one-half to three minutes of cleaning. After cleaning, the zinc article is rinsed in hot and then in cold water to remove the residual cleaning solution, following which the zinc article is ready for anodic treatment.

The cathode used in the anodic treatment may be of nickel, iron or other metal insoluble in the electrolyte.

Substantially neutral electrolytes for the practice of the invention may be made up of various substances. Thus, salts composed of a weak acid and a weak base, which, although highly hydrolyzed, remain essentially neutral, may be used. The acid radical of such a salt should be capable of forming an insoluble salt with zinc. Ammonium hydroxide may be taken as an example of such a weak base, while carbonic acid (the zinc salt of which is insoluble) is an example of such a weak acid. Salts composed of a strong base and an acid sufficiently strong to give an essentially neutral solution may also be used, as, for example, potassium ferrocyanide. Substantially neutral solutions of certain oxidizing agents, and various other compounds, may likewise be used in practicing the invention, such, for example, as solutions of potassium permanganate, potassium dichromate; ammonium oxalate, ammonium molybdate, potassium ferrocyanide, potassium ferricyanide etc. Buffers may be added to these solutions to aid in maintaining suitable pH values during operation.

A satisfactory neutral electrolyte for the practice of the invention is an aqueous solution of ammonium oxalate containing 35 grams of $(NH_4)_2C_2O_4 \cdot H_2O$ per liter of water. Anodic treatment of zinc in this electrolyte at room temperature yields an adherent coating varying in color from white to light gray. An initial current density of 24 amperes per square foot falls off to about 9.6 amperes per square foot in ten minutes of anodic treatment. Initial current densities of from 14 to 72 amperes per square foot have been used, and the operating temperature and composition of the electrolyte may likewise be varied, but the stated conditions are satisfactory. Such anodic coatings may be dyed with alizarine or with nigrosine dyes. Analysis of an anodic coating produced under the specified conditions showed it to contain about 73% of zinc oxalate.

Anodic treatment of zinc and zinc base alloys in a solution containing 50 grams of potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) per liter of water, for three minutes at an initial current density of 24 amperes per square foot at room temperature, produces a thin, adherent, iridescent coating, ranging in color from pink to green. On account of polarization, the current density drops rapidly. Thus, in the example given, the current density may drop from the initial value of 24 amperes to less than 0.5 amperes per square foot in less than one minute. Because of this fact, the solution may be operated within a rather wide range of initial current densities, while the time of treatment may be more or less than three minutes. The operating temperature of the solution, and its composition may also be varied, but the conditions specified are preferred.

A hard, adherent anodic deposit ranging in color from brown to black is obtained by treating zinc or zinc base alloys in aqueous solutions of potassium permanganate. The concentration of potassium permanganate may vary from dilute solutions, say 10 to 20 grams per liter of water, up to a saturated solution. The preferred operating conditions are a temperature of room temperatures to 50° C., a current density of 5 to 24 amperes per square foot and a duration of treatment of from 5 to 20 minutes. The use of too high a current density causes the coating to check and crack, a tendency that is decreased by operating at the higher temperature of 50° C. These conditions may be varied without departing from the spirit of the invention. The anodic deposit can be dyed in aqueous solutions of nigrosine or the alizarine dyes. A chemical analysis of the coating (carefully removed by scraping so as not to remove any zinc from the specimen) showed the presence of about 23% of zinc and 19% of manganese, calculated as the metals. Upon heating the coating to a temperature between 700 and 800° C., the manganese compound then present was identified as Mn_3O_4 by its X-ray pattern.

Other alkali metals, such as sodium, may be substituted for potassium in the compounds hereinbefore mentioned as suitable for the practice of the invention. Similarly substantially neutral solutions of alkali metal oxalates may be used in place of ammonium oxalate.

The anodic coatings of the invention not only protect the zinc or zinc base alloy from corrosion but are also useful for decoration. These coatings may also be used as a base to increase the adherence of paint, enamel, lacquer, etc. When the coatings produced in accordance with the invention are light in color, these coatings may be given various light or dark colors by dyeing. The color of the darker coatings may also be improved in some cases by dyeing. The dyeing may take place during the electrolytic treatment by solution of the dye in the electrolyte, or dyeing may be carried out by immersion of the coated article in an appropriate solution of the dye.

We claim:

1. As a new article of commerce, a zinc base metal having a thin, dense and firmly adherent anodic coating containing an insoluble compound other than or in addition to zinc oxide.

2. As a new article of commerce, a zinc base metal having a thin, dense and firmly adherent anodic coating containing zinc oxide in combination with another insoluble compound.

3. As a new article of commerce, a zinc base metal having a thin, dense and firmly adherent anodic coating containing zinc or an insoluble compound thereof in combination with an insoluble compound derived from an anodic radical other than hydroxyl.

4. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a substantially neutral electrolyte containing an anion (other than hydroxyl) capable of producing by anodic action with zinc an insoluble, adherent coating on the zinc metal.

5. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a substantially neutral electrolyte containing an anion

(other than hydroxyl) capable of forming an insoluble compound with zinc.

6. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a solution of ammonium oxalate having a pH of about 6 to 8.

7. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in an electrolyte containing about 35 grams of ammonium oxalate per liter.

8. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a solution of potassium ferrocyanide having a pH of about 6 to 8.

9. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in an electrolyte containing about 50 grams of potassium ferrocyanide per liter.

10. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a solution of potassium permanganate having a pH of about 6 to 8.

11. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in an electrolyte containing potassium permanganate in amount of from about 10 grams per liter to saturation.

12. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in an electrolyte containing 10 grams or more of potassium permanganate per liter, at a temperature of room-temperature to 50° C. and a current density of 5 to 24 amperes per square foot of anode surface.

13. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a substantially neutral electrolyte containing one or more substances of the group comprising potassium ferrocyanide, potassium ferricyanide, potassium permanganate, potassium dichromate, ammonium oxalate, and ammonium molybdate.

14. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in an electrolyte having a pH of about 6 to 8 and containing one or more substances of the group comprising potassium ferrocyanide, potassium ferricyanide, potassium permanganate, potassium dichromate, ammonium oxalate, and ammonium molybdate, and thereby producing on said zinc base metal a thin, dense and firmly adherent anodic coating containing a derivative of the anion radical of one of said substances.

15. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a substantially neutral electrolyte containing an oxalate ion capable of producing by anodic action with zinc an adherent coating on the zinc metal.

16. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a substantially neutral electrolyte containing an alkali metal permanganate.

17. The method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a substantially neutral electrolyte containing an alkali metal ferrocyanide.

18. A method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a substantially neutral electrolyte formed from a salt composed of a weak acid and a weak base, the acid radical of said salt forming by anodic action an insoluble salt with the zinc adhering as a coating on the zinc base metal.

19. A method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a substantially neutral electrolyte formed from a salt composed of a strong base and an acid sufficiently strong to give an essentially neutral solution, the acid radical of said salt forming by anodic action an insoluble salt with the zinc adhering as a coating on the zinc base metal.

20. A method of producing a coating on a zinc base metal which comprises subjecting the metal as anode to electrolytic treatment in a substantially neutral electrolyte containing an oxidizing agent in solution, said oxidizing agent in solution being adapted to produce by anodic action with the zinc an insoluble adherent coating on the zinc base metal.

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