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ANODIC TREATMENT OF ZINC AND ZINC-BASE ALLOYS

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11 Claims. (Cl. 204—56)

This invention relates to a process for producing protective coatings on articles formed of or coated with zinc and zinc-base alloys.

Coating baths are frequently used for the surface treatment of metals to prevent corrosion. The coating may be formed by dipping, or by anodic treatment of the metal, in a suitable bath. Such coating baths are usually aqueous solutions of alkali metal salts, in particular, alkali metal chromates. These coating baths have been found to be helpful in improving the corrosion resistance of certain metals, including zinc, but have not been entirely satisfactory, particularly for producing a strong, hard film or coating on zinc and zinc-base alloys that is resistant to both corrosion and abrasion.

I have found that a smooth, strong, hard, abrasion-resistant and corrosion resistant coating for zinc and zinc-base alloys can be formed by anodic treatment in a chromate bath containing phosphate and fluoride radicals provided that the only salts present in the bath are ammonium salts. Similar solutions have been proposed for the treatment of magnesium but I do not know of any similar solution for the treatment of zinc, nor do I know of any solution that has been proposed in the prior art that will produce a satisfactory coating on zinc.

The present process has the important advantages that it is inexpensive and is relatively simple to operate. The hard, non-corroding film is smooth, tightly adhering and is resistant to abrasion and corrosion. However, these are conditions which must be observed in the preparation of the electrolyte and in the operation of the process.

I have found that the electrolyte for the anodic treatment of zinc and zinc-base alloys should contain from 0.15 to 0.75 mole per litre of chromate, $CrO_4^{=}$; from 0.40 to 1.50 moles per litre of phosphate, $PO_4^{\equiv}$; and from 0.4 to 3.0 moles per litre of fluoride, F^{-}; and have a pH value within the range of from about pH 6 to about pH 8.

The chromate, phosphate and fluoride contents can be supplied to the bath by the use of the corresponding chromic, phosphoric and hydrofluoric acids or by the use of the ammonium salts of these acids, or by a mixture of the acids and their ammonium salts. The pH value of the electrolyte can be adjusted to within the desired range by the addition of ammonia if it is too low or by the addition of one or more of the aforesaid acids if it is too high.

Either alternating or direct current can be employed in the electrolysis. Alternating current is preferred as it is usually more convenient and direct current requires a somewhat higher voltage. It is found that when using alternating current, a current density should be employed of from about 15 to about 200 amperes per square foot of surface area of the metal to be coated. When using direct current, a current density of from 15 to 50 amperes per square foot should be employed. With alternating current, the current density is preferably about 200 amperes per square foot of electrode area initially, and is dropped to about 50 amperes per square foot after coating formation has begun. With direct current, the current density is maintained at about 50 amperes per square foot of anode area throughout the operation, including the initial stage.

When alternating current is employed, both the electrodes can be formed of or coated with zinc or zinc-base alloy. For example, these electrodes can be objects formed of zinc or zinc-base alloy, such as die castings, or they can be objects coated with zinc by electroplating or hot dipping methods.

When direct current is employed, only the anode is formed of or coated with zinc or zinc-base alloy and the cathode is formed of conductive material which is inert to the solution to prevent contamination of the coating bath by corrosion products. Suitable cathode materials are carbon and nickel.

It is found that under the above conditions, provided the only salts present in the solution are ammonium salts and the solution is free or substantially free from metal ions, the anodic process proceeds rapidly and efficiently to form a hard, tightly adhering, non-corroding film on the zinc or zinc-base alloy surfaces.

In the operation of the process, the chromate and fluoride radicals are preferably provided in the form of ammonium salts, such as ammonium chromate,

$$(NH_4)_2CrO_4$$

in the amount of from about 0.5 to about 0.7 mole per litre; ammonium fluoride, NH_4F, in the amount of from about 0.5 to about 1.0 mole per litre; and the phosphate radical as phosphoric acid, H_3PO_4, in the amount of from about 0.5 to about 1.40 moles per litre.

The pH value of the solution can be easily adjusted to within the from pH 6 to pH 8, preferably about pH 7, such as by the addiiton of ammonia or ammonium hydroxide if the solution is below pH 6, or by the addition of chromic, phosphoric, or hydrofluoric acid if the pH value is above pH8. The solution should be free or as free as possible of metal ions as the presence of metal cations in the solution results in an unsatisfactory coating. The electrolysis can be conducted at a temperature within the range of from about 15° to about 100° C. but it is preferred to maintain the temperature of the electrolyte within the range of from about 60° to 95° C. during the electrolysis.

Operating under the above described conditions, a very satisfactory smooth, hard, abrasion resistant, tightly adhering, non-corroding film is formed on zinc or zinc-base alloy surfaces within a very short period of time, of the order of about 10 minutes.

The following examples illustrate the results which can be obtained in the operation of the process of this invention.

Example 1

The surfaces of panels of rolled zinc were thoroughly cleaned. The panels were suspended as electrodes in an aqueous solution which contained 0.5 mole per litre of chromate radical, $CrO_4^{=}$, supplied as ammonium chromate, $(NH_4)_2CrO_4$; 0.6 mole per litre of phosphate radical, $PO_4^{\equiv}$, supplied as phosphoric acid, H_3PO_4; and 0.5 mole per litre of fluoride radical, F^{-}, supplied as ammonium fluoride, NH_4F. The pH value of the solution was adjusted to pH 7 by the addition of ammonium hydroxide.

The electrodes were connected to a 60 cycle alternating current supply of electrical energy having a range of from 0 to 240 volts. Current was supplied to the cell in amount sufficient to provide a current density of about 200 amperes per square foot of electrode surface. The electrolyte was agitated and maintained at a temperature of from 75° to 80° C. during the electrolysis. Within from two to three minutes of the initiation of the electrolysis, the voltage began to rise due to the resistance of the film or coating being formed on the electrodes. The current density was then reduced to 50

amperes per square foot of electrode surface. The voltage continued to rise steadily over a period of about 10 minutes to about 200 volts and then levelled off. The electrolysis was terminated at this voltage levelling value and the coated zinc panels were removed from the bath, and were washed and dried.

The initial voltage is low, of the order of from 2 to 3 volts, determined by the conductivity of the electrolyte. The terminal voltage reached during the electrolysis may be as high as 250 volts with alternating current or 280 volts with direct current depending on the concentration of salts in the bath, but under preferred conditions, is usually about 200 volts. The electrolysis can be continued after the terminal or levelling voltage is reached but unless unusually thick coatings are desired, there is no advantage to be gained in continuing it.

Example 2

Die castings made from zinc-base alloy comprised of 96% zinc and 4% aluminum were inserted in a coating bath in an electrolytic cell and connected as electrodes to a 60 cycle alternating current power supply with a voltage range of from 0 to 240 volts. The process described in Example 1 was repeated with the differences that the electrolyte contained 0.6 mole per litre of chromate radical; 1.0 mole per litre of phosphate radical; and 0.5 mole per litre of fluoride radical; and the electrolyte was maintained at a temperature of 90° C. during the electrolysis. The electrolysis was terminated when the voltage levelled off at about 200 volts. This occurred after about 10 minutes of operation.

The film or coating produced on zinc or zinc-base alloy surfaces of this invention is smooth, closely adherent and hard and is resistant to abrasion and corrosion. In an accelerated corrosion test, treated and untreated test pieces of rolled zinc were exposed to fog which contained 5% sodium chloride, in a closed chamber maintained at 95° F. The untreated zinc corroded badly in 24 hours as evidenced by the formation of a heavy coating of corrosion product known as white rust. The zinc which had been treated by the anodic process of this invention showed no visible evidence of corrosion after 1000 hours in the fog chamber.

The surfaces of articles treated by the process of this invention are a light gray-green colour with a smooth, matte-like finish. The treated articles require no further treatment unless a different colour or a glossy finish is desired, in which case they can be painted, lacquered or varnished.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. An anodic process for treating a metal selected from the group consisting of zinc and zinc-base alloys which comprises subjecting to electrolysis an aqueous solution which consists essentially of chromate radical in amount of from about 0.15 to about 0.75 mole per litre, phosphate radical in amount of from about 0.40 to about 1.5 moles per litre, and fluoride radical in amount of from about 0.40 to about 3.00 moles per litre, said radicals being provided by compounds selected from the group consisting of chromic acid, phosphoric acid, hydrofluoric acid, and the ammonium salts thereof, and which has a pH value of from about pH 6 to about pH 8 about and which is substantially free from metal ions, using in said electrolysis at least one electrode having exposed surfaces formed of a metal selected from the group consisting of zinc and zinc-base alloys and continuing said electrolysis with increasing voltage until the voltage rises to a levelling value of at least about 200 volts

2. The process according to claim 1 in which alternating current is employed in the electrolysis, and the electrolysis is continued with increasing voltage until the voltage rises to a levelling value within the range of from about 200 to about 250 volts.

3. The process according to claim 2 in which each electrode has exposed surfaces formed of a metal selected from the group consisting of zinc and zinc-base alloys and the electrolysis is conducted with an alternating current at a density within the range of from about 15 to about 200 amperes per square foot of electrode surface.

4. The process according to claim 1 in which direct current is employed in the electrolysis, the cathode is insoluble in the electrolyte, the anode has an exposed surface formed of a metal selected from the group consisting of zinc and zinc-base alloys, and the electrolysis is continued with increasing voltage at a current density within the range of from about 15 to about 50 amperes per square foot of anode area until the voltage rises to a levelling value within the range of from about 200 to about 280 volts.

5. The process according to claim 1 in which the temperature of the aqueous solution is maintained within the range of from about 15° to about 100° C. during the electrolysis.

6. The process according to claim 1 in which the pH value of the aqueous solution is adjusted to within the range of from about pH 6 to about pH 8 by addition to the solution of a member selected from the group consisting of ammonia, ammonium hydroxide, chromic acid, phosphoric acid and hydrofluoric acid.

7. An article of manufacture having surfaces formed of a metal selected from the group consisting of zinc and zinc-base alloys and coated with a hard, adherent, corrosion resistant film produced by the process according to claim 1.

8. An anodic process for treating a metal selected from the group consisting of zinc and zinc-base alloys which comprises the steps of suspending electrodes in an aqueous electrolyte which consists essentially of from about 0.15 to about 0.75 mole of ammonium chromate per litre, from about 0.40 to about 1.50 moles of ammonium phosphate per litre and from about 0.40 to about 3.00 moles of ammonium fluoride per litre, said electrodes having exposed surfaces formed of a member selected from the group consisting of zinc and zinc-base alloys, subjecting said electrolyte to the action of alternating current with increasing voltage until the voltage rises to a levelling value between 200 and 250 volts, maintaining the pH of said electrolyte at a value of from about pH 6 to about pH 8, maintaining the temperature of said electrolyte between about 15° and about 100° C., and varying the current density from about 200 amperes per square foot of electrode area when current is passed through said electrolyte initially to between about 15 and 50 amperes per square foot as the voltage rises to its levelling value.

9. The process according to claim 8 in which the electrolyte contains initially from 0.50 to 0.70 mole of ammonium chromate per litre; from 0.50 to 1.40 moles of phosphoric acid per litre; and from 0.50 to 1.40 moles of ammonium fluoride per litre, and the pH of the electrolyte is adjusted to 7 by the addition of ammonium hydroxide.

10. An article of manufacture having surfaces formed of a metal selected from the group consisting of zinc and zinc-base alloys and coated with a hard, adherent, corrosion resistant film produced by the process according to claim 8.

11. The process according to claim 1 in which the electrolysis is conducted with a direct current having a density within the range of from about 15 to about 50 amperes per square foot of anode area.

References Cited in the file of this patent

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,011,958 December 5, 1961

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 38, for "these" read -- there --; column 2, line 30, after "the" insert -- range of --; line 31, for "addiiton" read -- addition --.

Signed and sealed this 1st day of May 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents