

[54] **COMPOSITION AND METHOD FOR FORMING A PROTECTIVE COATING ON A ZINC METAL SURFACE**

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[56]

References Cited

UNITED STATES PATENTS

3,444,007	5/1969	Maurer et al.....	148/6.16
3,677,827	7/1972	Weaver et al.....	148/6.14

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[57]

ABSTRACT

This invention provides a composition and method for forming a protective coating on a zinc metal surface. The composition of the invention comprises an aqueous solution of an inorganic water soluble compound, a metal ion and a salt of an alkanolamine.

13 Claims, No Drawings

COMPOSITION AND METHOD FOR FORMING A PROTECTIVE COATING ON A ZINC METAL SURFACE

Protective coatings are formed on a zinc metal surface by the use of an aqueous solution of an inorganic water soluble compound, a metal ion and a salt of an alkanolamine.

BACKGROUND OF THE INVENTION

In the prior art, alkaline coating compositions have been used for coating zinc and zinc alloys. Compositions for this purpose are disclosed in U.S. Pat. No. 3,444,007. They consist of an aqueous alkaline solution of a metal ion selected from the group consisting of silver, magnesium, cadmium, aluminum, tin, titanium, antimony, molybdenum, chromium, cerium, tungsten, manganese, cobalt, ferrous and ferric with a complexing agent to hold the ion in solution. The present invention provides an improvement over the prior art in that none of the complexing agents according to U.S. Pat. No. 3,444,007 are required to secure an adherent, corrosion resistant film on a zinc metal surface. Other improvements are: 1) simpler formulations, 2) ease of waste treatment, 3) less costly than employing chelating agents, e.g., sodium gluconate, EDTA, 4) can be formulated as a dry mixture. From the aforementioned patent it can be seen that without the use of one of the disclosed complexers it was not possible to place a corrosion resistant film on a zinc surface. Note Table I, panel series No. 2. Contrary to the teachings of this patent, applicants have found that the use of water soluble alkanolamine salt with an additional inorganic alkaline material will produce a tough adherent corrosion resistant coating on a zinc metal surface. This is surprising since U.S. Pat. No. 3,444,007 discloses only the free base form of triethanolamine as being useful for developing an alkaline pH in solutions that have one of a recited class of complexers.

As used herein and in the appended claims zinc metal surface is used to include zinc metal objects, zinc coated objects and alloys which contain zinc as a principal component.

DESCRIPTION OF THE INVENTION

The present invention provides a composition for coating zinc metal surfaces. The composition may be applied to a substrate by spraying, immersing, dip-coating or painting the object which is to be coated. The coating may be used as a corrosion barrier or as a base coat that may be used to improve the adhesion of paints.

The composition of the invention comprises:

- a. an inorganic water soluble alkaline compound;
- b. at least one metal ion selected from the group consisting of cadmium, manganese, aluminum, tin, titanium, molybdenum, chromium, tungsten, cobalt, ferrous, ferric and nickel; and
- c. a water soluble salt of an alkanolamine in an amount sufficient to maintain said metal ions in solution.

The solvent to be used is water which may include a sufficient amount of a surface active agent to reduce the surface tension and facilitate the contacting of the zinc metal surface with the coating solution. The particular surface active agent is not critical and anyone may be employed if it is compatible with the particular

metal ions employed at the particular pH level of a given solution.

In general the pH of the solution should be above 7.5. Usually it will be preferred to use solutions having a pH of from 10.0 – 12.5. Those skilled in the art will be able to select the optimum pH level to be used in a particular system. It is preferred to use the alkali metal hydroxides, such as sodium, lithium or potassium hydroxide to maintain the desired alkalinity although inorganic alkaline compounds may be employed such as sodium silicate, potassium silicate, lithium borate, sodium carbonate, potassium carbonate, lithium carbonate or mixtures thereof with or without the alkali metal hydroxides.

Examples of particular metal salts which may be used as a source of ions include nickel nitrate, aluminum chloride, sodium molybdate, manganese nitrate, chromium nitrate, cadmium chloride and cobalt nitrate. Other useable salts of the desired metal ion may be selected by those skilled in the art. For example, Lange's Handbook of Chemistry, Fifth Ed., Handbook Publishers, Inc. (1944) at pages 154–263, which is incorporated herein by reference, discloses numerous water soluble salts of the useable metal ions that may be employed in the practice of the present invention.

The water soluble salts of suitable alkanolamines include triethanolamine hydrochloride; monoethanolamine hydrochloride, diethanolamine hydrochloride, triisopropanolamine hydrochloride, aminoethylethanolamine hydrochloride, triethanolamine phosphate, monoethanolamine phosphate, diethanolamine phosphate, triisopropanolamine phosphate and aminoethylethanolamine phosphate.

The compositions of the invention may be prepared as concentrates and diluted to the optimum concentration prior to use. When diluted for use, it is preferred to use a sufficient amount of an inorganic alkaline compound to yield a pH in the range of 7.5 – 13, from about 0.002 to about 0.25% by weight of metal ion and more preferably from about 0.01 to about 0.1% by weight of the particular metal ion. It is preferred to employ two or more different ions in a given composition. The water soluble alkanolamine salt is employed at a level which will be sufficient to maintain the metal ions in solution. This will vary with the concentration of the metal ions but it has been found that from about 0.05 to about 10% by weight, preferably from about 0.1 to about 5.0% by weight may be employed. There does not appear to be any advantage in employing an excess of the alkanolamine salt apart from that amount needed for the actual complexing reaction. Because of the inherent acidity of some of the water soluble salts of the alkanolamine compounds, it may be necessary to increase the concentration of the water soluble inorganic alkaline compound in order to satisfy the above stated pH requirements.

Combinations of cobalt-iron, chromium-cobalt, cobalt-molybdenum, aluminum-molybdenum, and the like may be used to obtain advantageous results. The application of the composition may be at ambient conditions such as room temperature or at any temperature up to the boiling point of the particular composition. Preferred conditions enabling the formation of the coating involve the use of the treating solution at a temperature of from 25°C to about 88°C for a time of from about 2 seconds to about 60 seconds. Satisfactory coatings are obtained in about 10 to 15 seconds and at a temperature of about 38°C to 71°C. Very acceptable

coatings may also be obtained in shorter times with solutions of higher alkali and metal ion strength, i.e., higher concentrations and/or higher temperatures. In general, slightly longer times are required for immersion applications but the composition of this invention is equally adaptable to spray or roll coating applications with the appropriate modifications in concentration, time and temperature.

The appearance of the complex-oxide coating formed on the surface of the zinc ranges in color from a very slight iridescence to a dark blue-gray depending on the time employed in effecting the coating and the nature of the zinc alloy surface. Variations in the color of the complex-oxide coating in no way affect its corrosion resistant properties.

Maximum corrosion resistance and paint adhesion are realized with this treating process when a dilute acidic rinse is used following the initial formation of the protective coating on the zinc surface. The dilute acidic rinse may employ a dilute mineral acid rinse such as 0.01 to 0.5% by weight of phosphoric or chromic acid.

When the coating compositions are to be prepared at a location which is remote from the location where the coating operation is actually carried out, it is desirable to supply the composition in dry form to save shipping expense. Dry formulations according to the invention may comprise from 1 to 500 parts by weight of an inorganic water soluble compound; from 0.5-200 parts by weight of a water soluble salt of an alkanolamine; and from 0.001 to 50 parts by weight of a salt of a metal ion selected from the group consisting of cadmium, manganese, aluminum, tin, titanium, molybdenum, chromium, tungsten, cobalt, ferrous and ferric iron, and nickel.

A preferred dry mixture comprises 30.0 grams of sodium hydroxide, 3.9 grams of triethanolamine hydrochloride, 0.25 grams of ferric nitrate nonahydrate and 0.29 grams of cobalt nitrate hexahydrate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following Examples illustrate the invention. They are set forth as a further description but are not to be construed as limiting the invention thereto.

EXAMPLE I

30.0 grams of sodium hydroxide, 3.9 grams of triethanolamine hydrochloride, 0.25 grams of ferric nitrate nonahydrate and 0.29 grams of cobalt nitrate hexahydrate were dissolved in sufficient water to result in a total volume of one liter, and had a final composition of 2.94% as sodium hydroxide, 0.39% as triethanolamine hydrochloride, 0.0034% as ferric ion, and 0.0059% as cobalt ion. The resulting solution had a pH of 12.2.

Clean test panels of both electrogalvanize and hot-dip zinc were immersed in the above aqueous alkaline solution at 120°F. for a total contact time of about 5 seconds, the panels were then withdrawn and rinsed in clean cold water for about 10 seconds and then immersed in a dilute chromic acid rinse containing about 0.1% hexavalent chromium and 0.1% phosphoric acid and with a pH of 2.5. Temperature of the chromic acid rinse was 120°F. and total contact time with the acidic solution was about 5 seconds. The panels were then dried in a hot air stream and visually inspected. It was found that a uniform light blue-gray coating was formed on the panels which resisted mild abrasion without exposing the original zinc surface. The treated

panels were then painted in a conventional painting system and allowed to dry after which they were subjected to a standard ASTM 5% salt spray and 100% humidity testing procedures. The results of the tests are reported in Table I.

Results of these tests shown in Table I indicated that a very high degree of corrosion resistance, both in salt spray and humidity conditions, was afforded the zinc panels. Furthermore, additional tests were performed to determine the degree of paint adhesion for these panels as processed above, and it was also found that a comparable degree of paint adhesion was afforded to the test panels after processing in the aqueous alkaline treating solution.

EXAMPLE II

An aqueous alkaline solution was prepared in accordance with Example I to contain 0.10% sodium hydroxide, 0.1% diethanolamine hydrochloride, a nonionic wetting agent consisting of a propylene glycol/propylene oxide condensate, 0.0049% nickel ion added as nickel nitrate hexahydrate, and 0.0058% molybdenum ion added as sodium molybdate dihydrate. The resulting solution had a pH of 11.0.

Clean electrogalvanize and hot-dip zinc test panels were processed as in Example I and painted using a conventional painting system. The finished test panels were subjected to standard salt spray, humidity, deformation and paint adhesion test methods. Results given in Table I showed that a very high degree of corrosion resistance and paint adhesion was afforded by the coating produced by the solution of this invention.

EXAMPLE III

An aqueous solution was prepared in accordance with Example I to contain 2.94% sodium hydroxide, 0.39% monoethanolamine hydrochloride, 0.0025% trivalent chromium ion added as chromium nitrate nonahydrate, 0.0059% cobalt ion added as cobalt nitrate hexahydrate. The resulting solution had a pH of 12.2.

Pieces of Zamak No. 3 alloy were processed as in Example I and painted using a conventional painting system. The finished articles were subjected to standard salt spray humidity, deformation and paint adhesion test methods. Results shown in Table I indicate a very high degree of corrosion resistance and paint adhesion was afforded by the coating produced by the solution of this invention.

EXAMPLE IV

As aqueous solution prepared in accordance with Example I to contain 0.40% sodium hydroxide, 0.39% triethanolamine phosphate, 0.003% cobalt ion added as cobalt nitrate hexahydrate, and 0.003% molybdenum ion added as sodium molybdate dihydrate. The resulting solution had a pH of 11.5.

Clean electrogalvanize and hot-dip test panels were processed as in Example I and painted using a conventional painting system. The finished test panels were subjected to standard salt spray, humidity, deformation and paint adhesion test methods. Results shown in Table I indicate a very high degree of corrosion resistance and paint adhesion was afforded by the coating produced by the solution of this invention.

EXAMPLE V

An aqueous solution prepared in accordance with Example I to contain 2.94% sodium hydroxide, 0.39% aminoethylethanolamine hydrochloride, 0.027% aluminum ion added as aluminum chloride hexahydrate, and 0.029% molybdenum ion added as sodium molybdate dihydrate. The resulting solution had a pH of 12.2.

Clean electrogalvanize and hot-dip zinc test panels were processed as in Example I and painted using a conventional painting system. The finished test panels were subjected to standard salt spray, humidity, deformation and paint adhesion test methods. The results are reported in Table I.

TABLE I

Panel Series	Salt Spray 500 Hours*	Humidity**	Adhesion***
Example I	0-2	F 9-10	10
Example II	1-3	VF 8-9	9
Example III	1-2	VF 9	10-9
Example IV	0-1	F 9-10	8-9
Example V	1-3	VF 9	9

*The panels are rated on a numerical basis from 0 to 10, with 0 representing no creepage of the corrosion from the cross scribe; where corrosion occurs, the degree of corrosion is rated in terms of sixteenths of an inch of creepage from the scribed line.

**The degree of blistering in the humidity test was rated in accordance with the standard method of ASTM D714-56, in which the size and frequency of blisters is evaluated on a numerical scale from 10 to 0, in which 10 represents no blistering and the size of the blisters increases as the numbers decrease. The frequency of the blisters is evaluated by letters in which D represents dense, MD medium dense; M represents medium, FM represents few medium, F represents few and VF represents very few.

***The knife adhesion test comprises manually drawing a knife blade across the surface of the coating and comparing the resistance of dislodgement of the coating. The difficulty of dislodgement is rated in numerical values, from 10 to 0, with 10 representing excellent, 8 good, 6 fair, 4 poor, 2 very poor, and 0 representing complete loss of adhesion.

Obviously, other modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that changes may be made in the particular embodiments of the invention described which are within the full intended scope of the invention as defined by the appended claims.

What is claimed is:

1. A method for forming a protective coating on a zinc metal surface which comprises contacting said surface with an aqueous solution which consists essentially of an inorganic water soluble alkaline compound, at least one metal ion selected from the group consisting of cadmium, manganese, aluminum, tin, titanium, molybdenum, chromium, tungsten, cobalt, ferrous and ferric iron and, nickel and triethanolamine hydrochloride in an amount sufficient to hold said metal ions in solution.

2. The method of claim 1 wherein said inorganic water soluble alkaline compound is an alkali metal hydroxide.

3. The method of claim 1 wherein said aqueous solution contains both cobalt and ferric iron ions.

4. The method of claim 1 wherein said aqueous solution is applied at a temperature between room temperature and the boiling temperature of said aqueous solution.

5. The method of claim 1 wherein said aqueous solution has a pH above 7.5.

6. An aqueous composition for the formation of a protective coating on the surface of a zinc metal surface which consists essentially of:

- an inorganic water soluble alkaline compound;
- at least one metal ion selected from the group consisting of cadmium, manganese, aluminum, tin, titanium, molybdenum, chromium, tungsten, cobalt, ferrous, ferric and nickel; and

c. triethanolamine hydrochloride in an amount sufficient to maintain said metal ions in solution.

7. The composition of claim 6 wherein said inorganic water soluble alkaline compound is an alkali metal hydroxide.

8. The composition of claim 6 wherein said aqueous solution contains both cobalt and ferric iron ions.

9. An aqueous composition for the formation of a protective coating on the surface of a zinc metal surface which consists essentially of water, an alkali metal hydroxide, ferric ions, cobalt ions and triethanolamine hydrochloride.

10. A dry mixture, for the formation of a protective coating on the surface of a zinc metal by dissolving in water, which consists essentially of sodium hydroxide, at least one soluble metal salt selected from the group consisting of cadmium, manganese, aluminum, tin, titanium, molybdenum, chromium, tungsten, cobalt, ferrous, and ferric iron, and nickel; and triethanolamine hydrochloride.

11. The mixture of claim 10 in which, the water soluble metal salts are cobalt and ferric iron, and the water soluble salt of an alkanolamine is triethanolamine hydrochloride.

12. A dry mixture for the formation of a protective coating on the surface of zinc metal by dissolving in a liter of water the composition consisting of 30.0 grams of sodium hydroxide, 3.9 grams of triethanolamine hydrochloride, 0.25 grams of ferric nitrate nonahydrate, and 0.29 grams of cobalt nitrate hexahydrate.

13. A method for forming a protective coating on a zinc metal surface which comprises contacting said surface with an aqueous solution which consists essentially of an inorganic water soluble alkaline compound, at least one metal ion selected from the group consisting of cadmium, manganese, aluminum, tin, titanium, molybdenum, chromium, tungsten, cobalt, ferrous and ferric iron and nickel, and triethanolamine hydrochloride in an amount sufficient to hold said metal ions in solution.

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