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3,756,864

CYANURIC ACID AS A SCALE REDUCING AGENT IN COATING OF ZINC SURFACES

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15 Claims

ABSTRACT OF THE DISCLOSURE

An alkaline composition suitable for forming a coating on zinc and zinc alloy surfaces wherein the improvement comprises employing a scale reducing amount of cyanuric acid in the composition.

This invention relates to the art of forming protective coatings on the surfaces of zinc and zinc alloys from aqueous alkaline solutions.

Heretofore, it has been well known and widely commercially practiced to prepare the surface of zinc and zinc alloys for the reception of paint or other siccative coatings by using aqueous acidic solutions, particularly phosphate solutions. A number of commercially satisfactory phosphate coating processes and systems are known and for a certain type of product manufacture are entirely satisfactory. In other types of zinc or zinc alloy products, however, such as those which require deformation of the painted metal surfaces subsequent to painting, certain defects have been encountered, including loss of paint adhesion, decreased corrosion resistance to both humidity and salt spray or its equivalent.

Previously, it has been discovered that corrosion resistant coatings can be formed on the surfaces of zinc or zinc alloys from certain aqueous alkaline solutions and that these coatings provide bases for paint which are unexpectedly superior in adhesion to any of the heretofore known coatings produced from conventional aqueous acidic solutions including the best known phosphates.

The problem that has occurred with these alkaline solutions is that a zinc oxide scale has formed in the nozzles of the spray apparatus as well as in the tanks in which the alkaline solutions are kept during coating of the metal surfaces.

In accordance with this invention, it has been found that adherent corrosion resistance coatings are formed on the surface of zinc and zinc alloys by contacting the surfaces for a short time with an aqueous zinc oxide alkaline solution and a scale reducing amount of cyanuric acid.

In U.S. Pat. No. 3,444,007 is described a zinc oxide coating solution for coating zinc and zinc alloy surfaces. The contents of that patent are hereby incorporated by reference.

In a preferred form of the present invention, the aqueous alkaline solution contains at least two metal ions other than, and/or in addition to alkali metal ions and a sufficient quantity of complexing agent to maintain these ions in solution. It has been found that useful coatings are produced from the aqueous solutions of this invention when those solutions contain a wide range of variation of alkali strength, metallic ion concentration, complexing agent concentration, temperature and time of processing as well as type of application of the coating solution to the surface, each of which component and variations in operating conditions will be discussed in greater detail hereinafter.

The alkalinity of the solution may be developed by using any of the commonly available alkaline compounds and alkaline salts, such as triethanolamine and the alkali metal hydroxides, carbonates, phosphates, borates, silicates, polyphosphates, and pyrophosphates, or mixtures

thereof as needed to give the desired pH. It has been found that the preferred operating conditions for the use of the solution of this invention include the use of a solution which has a pH numerically greater than about 11, and that better results are obtained from solutions having a pH in the range of 12.6 and 13.3. However, some improvement is obtained from aqueous alkaline solutions having less alkali strength and lower pH values but the operation conditions for such solutions including time to produce the desired coating and temperature necessary to form the same are less advantageous commercially than those which are satisfactorily employed when using solutions of the greater alkali strength. Using any of the above described solutions, adherent coatings have been produced which vary in color from colorless to light yellow, to tan-yellow, to brown and finally to blue-black, depending upon the particular application conditions and solution constituency which is being used. The above described coatings are obtained from solutions which contain extremely small quantities of metal ions other than the alkali metal ions and, in general, the color of the coating increases in intensity toward brown as the time of treatment is increased and as the concentration of metallic ion therein is increased, as the temperature of treatment is increased and as the alkali strength is increased.

It has been found that the solution should contain at least one metal ion other than an alkali metal ion, which is normally introduced with the alkaline salts, in order to produce a rate of coating formation and/or quality of coating which enables such coatings to function as superior bases for paint or other siccative coating. It has also been found that such other metal ion is incapable of functioning to increase the coating rate or coating formation mechanism unless it is sufficiently complexed by a complexing agent to dissolve that metal ion in the coating solution. Based on the experimental evidence on hand, it is believed that any metal ion, other than an alkali metal ion which is complexed and in solution functions to improve the formation of the desired coatings since metals falling within each of the groups of the periodic system including the rare earth metals have been found to be satisfactory for this purpose. Satisfactory results have been obtained from the use of solutions containing the sodium ion and at least one other ion from the group comprising silver, magnesium, cadmium, aluminum, tin, titanium, antimony, molybdenum, chromium, cerium, tungsten, manganese, cobalt, ferrous and ferric iron and nickel. As above indicated, extremely minor quantities of such metal ion provide improvement. Good results have been obtained from solutions containing as low as about 0.002% iron in addition to the sodium ion introduced into the solution as sodium hydroxide to form a solution having a pH above 12. Good results have also been obtained from high concentrations of the metal ion or ions and although there appears to be no particular advantage gained from large quantities of the metal ions such excess quantities do not appear to be detrimental and any quantity of metal ion up to the limit of solubility thereof can be used satisfactorily. Somewhat better results have been obtained from the use of solutions which contain at least two metal ions other than the alkali metal ion, e.g., iron and cobalt, iron and silver, cobalt and cerium, etc.

The complexing chelating or sequestering agent functions to complex the metal ion other than the alkali metal ion and maintain the same dissolved in the coating solution. For this purpose a wide variety of complexing, chelating, and sequestering agents have been found to be satisfactory. It is suitable to use the inorganic complexing agents such as cyanides, condensed phosphates, ammonia and the like; the organic chelating agents include the dicarboxylic acids such as malonic acid, fumaric

acid, etc.; the amino acids, such as glycine; the hydroxycarboxylic acids such as citric, gluconic, lactic, etc.; the hydroxyaldehydes such as acetyl acetone; the polyhydroxyaliphatic compounds such as sorbitol, 1,2-ethanediol; the phenolic carboxylic acids such as salicylic acid, phthalic acid; the amine carboxylic acids such as ethylene diamine tetraacetic acid; the polyamino acids such as diethanolaminomethane phosphate; the salts of lower molecular weight lignosulfonic acids such as derived from wood pulping processes such as sodium lignosulfonate. The proportion of complexing agent which should be present is an amount at least sufficient to completely complex the metal ion other than alkali metal ion, which is present. It will be apparent that as the concentration of metallic ion other than alkali metal ion increases the concentration of the complexing agent will also increase and since increasing quantities of certain of the complexing agent which are acidic in nature tends to reduce the effective alkali strength of the solution, it is preferred to employ the complexing agent in the form of neutral salts, particularly the alkali metal salts. Moreover, no advantage has been observed from the presence of concentrations of complexing agent in excess of that required to maintain the metal ion dissolved in the coating solution. Particularly good results have been obtained from the use of sodium hexahydroxyheptanoate, sodium gluconate and the sodium salt of ethylenediaminetetraacetic acid.

The solutions of this invention may optionally include a compatible surface active agent and the presence of such a surface active agent is particularly advantageous when the surface to be coated is soiled with grease, oil, or the like. For this purpose, the only requirement for the surface active agent is that it be compatible with the other ingredients of the solution, both under normal storage conditions and under the elevated temperature application conditions, that is, the surface active agent should not cause precipitation or agglomeration of the metal ions which are present, cause gelling or itself precipitate or gel in the solutions. It has been found that there are non-ionic, anionic and cationic wetting agents which are compatible in the solutions of this invention and when included up to about 5% of the solution, w./v., can be used.

In general, the process of this invention comprises the step of contacting the zinc or zinc alloy surface to be coated by spraying, dipping, brushing, or the like, at a temperature between ordinary room temperature and the boiling point of the solution and for a time period sufficient to produce the desired total coating. The preferred method of application in the formation of coatings adapted for use as a base for paint is spraying. Preferred conditions for continuous production which enables the formation of the desired coating in the least time involves the use of the solution at a temperature between about 90° F. and 200° F. for a time between about 2 seconds and about 60 seconds. Commercially satisfactory coatings have been obtained in about 10 to 15 seconds at about 100° F.-160° F. and may be obtained in even shorter periods of time with solutions containing relatively high concentrations of alkali and other metal ion and/or at the higher temperatures. Slightly longer contact periods are required for immersion application, but a satisfactory quality of coating is obtained from immersion contact times between about 30-90 seconds with solutions having a temperature of about 130° F.-180° F.

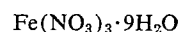
The complete process of this invention also includes the use of a subsequent dilute aqueous chromic acid rinse on the preliminarily formed coating of this invention. A suitable solution for this purpose is one which contains about 0.01% to 0.5% CrO₃, w./v. or percent by weight per unit volume. When the chromic acid solution is relatively concentrated, it is preferred to remove the excess by squeezing the excess off with rolls. A preferred dilute rinse solution for the purpose of this invention is one which is disclosed and described in detail in copending application Ser. No. 230,729, filed Oct. 15, 1962, now U.S. Pat.

No. 3,279,958, and assigned to the assignee of this application, namely, one which includes a hexavalent chromium and chromium complex ion which contains at least about 0.001% w./v. of the trivalent chromium ion and has a pH within the range of about 3.8 to 6.0, preferably about 4.5. After rinsing the coating may be water rinsed or dried without rinsing as desired and after drying the coating is in condition for the reception of paint or other siccative coating.

The process of this invention has been found to be useful in forming coatings on the surfaces of pure zinc, electroplated zinc, hot-dipped zinc surfaces including hot-dipped zinc containing small quantities of alloying ingredients such as aluminum, etc., and zinc alloys per se or electrodeposited zinc alloy surfaces. Where the surface to be coated includes iron or steel in addition to zinc or zinc alloy, such as a partially galvanized steel or iron base or a composite article which includes assembled steel or iron portions and zinc or zinc alloy portions, it has been found that such solutions of this invention are uniquely useful. For such surfaces the solutions of this invention are first applied by the procedures and temperature application conditions above specified to first clean the steel or iron portion of the article and clean and form a coating on the zinc or zinc alloy portion of the article, and this step is advantageously combined with a subsequent conventional phosphate coating step. It has been found that the coating formed on the zinc or zinc alloy portion of such surface is not removed by an aqueous acidic zinc phosphate or aqueous acidic alkali metal phosphate coating solution of any conventional constitution, and the cleaned steel or iron portion of the surface receives an adherent protective phosphate coating having at least equal corrosion resistance and utility as a base for paint as conventionally cleaned iron or steel surfaces. For the purposes of such modified process use it is satisfactory to employ aqueous acidic zinc phosphate solutions or aqueous acidic alkali metal phosphate solutions having any of the present-day conventional constitution, which are now well known to those skilled in the art.

The composition of the present invention may be prepared by mixing the alkali metal hydroxide with the zinc oxide in water which is heated to about 180° F. To this mixture is added the sequestering agent plus the ions other than the alkali metal. This concentrate is then diluted with water which contains the scale reducing agent.

A preferred scale reducing bath composition was prepared by mixing 897 grams of sodium hydroxide with 212 grams of zinc oxide in 1255 grams of water. This material was heated for a short period of time to about 180° F. This mixture then had added thereto 180 grams of Seqlene Fe 1300 (sodium hexahydroxyheptanoate), 74 grams of 40% Co(NO₃)₂·6H₂O and 52 grams of



Eighty-seven (87) grams of the above concentrate were added to 900 milliliters of water which had present therein 0.1% of cyanuric acid.

The following examples will illustrate in greater detail the specific variant conditions and typical coating solutions of this invention. But it is to be understood that they are presented for the purposes of illustration only and do not represent the definite limits of the invention which have been here and before set forth.

EXAMPLE I

Hot dipped galvanized metal surfaces were alkaline cleaned and then treated with the above scale reducing bath composition. No scale formation was noted. An equivalent bath composition was used as a control except that in place of the cyanuric acid, 5% by weight of trisodiumphosphate, a commercial product was used. There was no decrease in the formation of the blue zinc oxide scale on the spraying apparatus and the holding tanks.

The above example is an accelerated test to determine the scale decreasing capability of the additive. In the normal processing of zinc surfaces, no zinc is introduced other than as the metal surface to be treated. In other words, the zinc in the bath is the result of the coating process.

EXAMPLE II

A preferred aqueous alkaline solution was prepared to contain 0.40% sodium hexahydroxyheptanoate, 0.40% cobalt added as cobalt nitrate $6\text{H}_2\text{O}$, and 0.041% iron added as ferric nitrate $9\text{H}_2\text{O}$. This bath contained 0.2% by weight cyanuric acid. The bath had a free alkalinity of 13.3 points (0.1 N sulfuric acid titrated with phenolphthalein as indicator). Electro-galvanized strip was sprayed with the above solution at 120°F . to produce a contact time of about 10 seconds.

After this procedure was followed for two weeks, the processing tanks were emptied. No indication of scale formation could be detected in the tank using cyanuric acid while scale formation was evident on the squeegee rolls, pipes and walls of the tanks not employing cyanuric acid.

While cyanuric acid may be used in an amount ranging from 0.05% by weight to about 1% by weight, a preferred amount is from 0.1 to 0.3% by weight.

It is understood that the following claims are intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

What is claimed is:

1. An aqueous composition suitable for forming a coating on zinc and zinc alloy surfaces, comprising:

- (a) cyanuric acid in a concentration between about 0.1 and 0.3% by weight of the composition, and
- (b) an alkaline material in an amount sufficient to effect a pH of the composition of at least about 11.

2. The composition of claim 1 wherein said alkaline material is selected from the group consisting of triethanolamine and the alkali metal hydroxides, carbonates, phosphates, borates, silicates, polyphosphates, and pyrophosphates, or mixtures thereof.

3. The composition of claim 1 wherein the amount of alkaline material is sufficient to effect a composition pH of between 12.6 and 13.3.

4. An aqueous composition suitable for forming a coating on zinc and zinc alloy surfaces, comprising:

- (a) at least one metal ion other than an alkali metal selected from the group consisting of silver, magnesium, cadmium, aluminum, tin, titanium, antimony, molybdenum, chromium, cerium, tungsten, manganese, cobalt, ferrous and ferric iron and nickel;
- (b) a complexing agent present in said solution in an amount sufficient to hold said other metal ions in said solution;
- (c) an alkaline material in an amount sufficient to effect a pH of the composition of at least about 11; and
- (d) cyanuric acid in an amount sufficient to reduce the rate of scale formation.

5. The composition of claim 4 wherein said alkaline material is selected from the group consisting of triethanolamine and the alkali metal hydroxides, carbonates, phosphates, borates, silicates, polyphosphates, and pyrophosphates, or mixtures thereof.

6. The composition of claim 4 wherein the amount of alkaline material is sufficient to effect a composition pH of between 12.6 and 13.3.

7. The composition of claim 4 wherein said cyanuric acid concentration is between about 0.05 and 1% by weight.

8. The composition of claim 7 wherein said cyanuric acid concentration is between about 0.1 and 0.3% by weight.

9. A method of coating zinc and zinc alloy surfaces comprising contacting said surface with an aqueous composition comprising:

- (a) cyanuric acid in a concentration between about 0.1 and 0.3% by weight of the composition, and
- (b) an alkaline material in an amount sufficient to effect a pH of the composition of at least about 11.

10. The method of claim 9 wherein said contact is effected by spraying the aqueous composition on the surface at a temperature of between 90 and 200°F . for a period of from about 2 to 60 seconds.

11. The method of claim 9 wherein said contact is effected by immersing said surface in said aqueous composition maintained at a temperature of about 130 – 180°F . for a period of from about 30–90 seconds.

12. The method of claim 9 wherein said alkaline material is selected from the group consisting of triethanolamine and the alkali metal hydroxides, carbonates, phosphates, borates, silicates, polyphosphates, and pyrophosphates, or mixtures thereof.

13. A method of coating zinc and zinc alloy surfaces comprising contacting said surface with an aqueous composition comprising:

- (a) at least one metal ion other than an alkali metal selected from the group consisting of silver, magnesium, cadmium, aluminum, tin, titanium, antimony, molybdenum, chromium, cerium, tungsten, manganese, cobalt, ferrous and ferric iron and nickel;
- (b) a complexing agent present in said solution in an amount sufficient to hold said other metal ions in said solution;
- (c) an alkaline material in an amount sufficient to effect a pH of the composition of at least about 11; and
- (d) cyanuric acid in an amount sufficient to reduce the rate of scale formation.

14. The method of claim 13 wherein said alkaline material is selected from the group consisting of triethanolamine and the alkali metal hydroxides, carbonates, phosphates, borates, silicates, polyphosphates, and pyrophosphates, or mixtures thereof.

15. The method of claim 13 wherein said cyanuric acid concentration is between about 0.05 and 1% by weight.

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