ABSTRACT

A zinc surface on a metal artifact may be colorized and rendered corrosion resistant by applying to the surface a solution of a trivalent chromium compound, plus at least one added metal salt selected from the group consisting of ferrous salts, nickel salts and cobalt salts capable of coloring the surface, along with the chromium compound in the presence of a phosphate at a pH of about 0.5 to 5, to provide a colored surface. Then, a top coat is provided to the colored surface, to achieve high corrosion resistance.
COLORED TRIVALENT CHROMATE COATING FOR ZINC

BACKGROUND OF THE INVENTION

[0001] This invention relates to hexavalent-free chromate coatings used to protect zinc and alloys thereof from corrosion, for example zinc coated steel articles such as screws, clips, and other steel devices used in the automotive industry and other industries.

[0002] In the prior art, U.S. Pat. Nos. 5,368,655, 6,719,842, and 6,287,704 teach the use of trivalent chromate coatings on zinc which are silvery-bluish or pale and iridescent in color.

[0003] There is a need in industry for zinc plated articles which are of other colors besides clear or silver. Particularly, black is an important, desired color, for example for use in the automotive field. Another color that finds significant use is olive drab (olive green), used typically in military applications. A third desirable color is yellow. However, to achieve these colors, either a dye has been required for addition to the coating or, as taught in Bishop et al. U.S. Pat. No. 5,415,702, high nickel or high iron/zinc alloys need to be used with a trivalent chromium salt to achieve a black coating.

[0004] By this invention, the above, desirable colors can be achieved on zinc coatings which comprise pure zinc, or zinc with low quantities of alloying material, without the need for added dye.

[0005] The resulting coatings, in preferred formulations, can pass 120 hours of saltwater corrosion testing, as required by the automotive industry, when preferred formulations are used, while providing black, olive drab or yellow color, as desired.

DESCRIPTION OF THE INVENTION

[0006] By this invention, a method is provided for treating and protecting a zinc surface of a metal artifact, which method comprises:

[0007] applying to the surface a coloring solution of a trivalent chromium compound, plus at least one added metal salt selected from the group consisting of ferrous salts, nickel salts and cobalt salts capable of coloring the surface, along with a trivalent chromium compound, in the presence of a phosphate at a pH of about 0.5 to 5, to provide a colored surface. Following this, a top coat is added to the colored surface. The top coat is preferably selected from the group consisting of (1) an aqueous sealing solution of a lithium silicate, and a sodium or potassium silicate; (2) a sodium or potassium silicate dispersed in a methacrylate coating polymer in a solvent; (3) an organosilicate-silicate coating; (4) a sodium or potassium silicate dispersed in a polyethylene wax; (5) anodic or cathodic e-coats; and (6) organic paints.

[0008] The zinc surface may comprise substantially pure zinc, containing preferably no more than about three weight percent of alloying impurities.

[0009] By this invention, when the added metal salt is a ferrous salt such as ferrous sulfate, ferrous chloride, ferrous acetate, or ferrous nitrate, and preferably pure zinc is used, a rich, black color may be formed on the pure zinc surface, which then may be coated by the top coat, to provide both the black color and strong corrosion resistance. The incidental presence of ferric ion may be tolerated, but is not preferred.

[0010] Similarly, when nickel or cobalt salts such as nickel or cobalt sulfate, or substantially any other anion including the ions listed above are used as the added metal salt in the solution applied to a substantially pure zinc coating, an olive drab color can result, which then may be coated by a top coat as specified above.

[0011] The above-described coloring solution may contain essentially any soluble trivalent chromium compound such as chromium nitrate, chromium sulfate, or a hexavalent chromium salt which has been reduced by hypophosphite or sulfites. The amount of trivalent chromium present can be preferably at least 0.25 g/L up to saturation, with a range of 1 g/L to 100 g/L being preferred.

[0012] As desired, chelating agents, acids, promoters, and corrosion protection agents may be added to the coloring solution. One particular corrosion protection agent may be a silicate corrosion protection agent added to the coloring solution itself, apart from or in addition to the subsequent top coat.

[0013] To obtain the black coating, the amount of ferrous ion present in the coloring solution may generally be from 0.5 to 100 g/L, with a generally preferred range of about 1-25 g/L and a generally preferred pH of 0.5 to 2.0. For obtaining of the olive drab color, one may add about 0.5 to 50 g/L of the nickel ion, the cobalt ion, or a combination of the two to the coloring solution. If it is desired to provide a yellow color to the zinc coating, the solution formula with the added ferrous salt may be used, along with acetic acid, but at a pH of 2.1 to about 4.5. This solution provides a coating with a yellow, iridescent color, mimicking the look of a hexavalent yellow chromate, while no hexavalent chromate is actually present.

[0014] For the phosphorous compound present, any appropriate source of phosphate ion appears to be suitable, for example, phosphoric acid, ammonium phosphate, trisodium phosphate. Other forms of phosphorous-containing acids or salts, such as phosphorous acid, monosodium phosphate, etc., or phosphorous oxides may also be used. One may obtain the desired pH with acetic acid.

[0015] For chelating agents, desirable materials include carboxylic acids, oxalic acid, citric acid, EDTA, gluconates, acetates, and the like.

[0016] The corrosion enhancing agent that is added to the solution may comprise an acid stabilized colloidal silicate. For example, one such additive is produced by Straus Chemical Corporation of Elk Grove Village, Ill. under the trade name of Anti-Cor 2000. This material, which is based upon Ludox® colloidal silica of W R Grace and Company, may be adjusted to a pH of 2-4 with an acid such as sulfuric acid, and, optionally, 2-50 g/L of the acidified Ludox® solution (having about 30-50 wt. percent of SiO₂) may be added to the coloring solution of this invention.

[0017] Similarly, strontium chloride may be added to the solution as an enhancer of the corrosion resistance.
Also, sometimes, the color which is created on the zinc coating can actually fade away if the zinc surface remains in contact with the coloring solution for an excessive length of time, typically times that are substantially greater than one minute, although the time will of course vary with the particular ingredients and their concentrations. Also, the zinc surface itself can be attacked, if it remains in contact with the coloring solution for an excessive length of time typically exceeding one minute. This effect can be suppressed by the addition of a carbonate salt to the solution, particularly from 0.25 to 50 grams per liter of a carbonate salt. For example, sodium carbonate, calcium carbonate, and nickel carbonate are candidates for addition to the solution to suppress subsequent removal of the color, for example, a black color from the zinc surface when the solution is in contact with the zinc surface for an excessive length of time.

Among the top coats that can be used, we found that one preferred top coating for the zinc with a colorized surface comprises an aqueous sealing solution of lithium poly silicate, potassium silicate, and molybdate.

Another effective top coat comprises sodium or potassium silicate with an acrylate or methacrylate formulation added (Cyanamer, from Cytec Corporation). This coating may be air dried.

A third effective top coat is polyethylene copolymer wax, such as Lugalan® DC, sold by the BASF Corporation, mixed in a solvent dispersion with potassium or sodium silicate. After coating, the zinc surfaces may be heated to 250°C for about 20 minutes.

Other effective top coats include anodic or cathodic e-coats, such as those provided by the technology of PPG Industries. This electrocoating process causes precipitation of paint particles onto the zinc surface. For example, an organic paint such as an epoxy melamine based paint may be used (Straus Chemical black 100) in an e-coat process. Alternatively, such a paint may be applied by dip spin application or spray or roller coating, and cured at 375°C F. for 3-30 minutes.

The term “solution” as used herein does not necessarily mean a true solution. Rather, liquid dispersions may also be included.

Preferred embodiments of the above do not exhibit significant, while corrosion after 120 hours of neutral salt spray as performed under the ASTM B-117 standard. Certain other, conventional coatings fail such a corrosion standard, as illustrated below.

The coloring solution formulations of this invention are preferably free of silicone materials, which are known to interfere with subsequent application of paint and other coatings to a surface. Accordingly, the initial, colored zinc surface generally should not have silicone present.

The above disclosure, and the examples below are offered for illustrative purposes only, and are not intended to limit the scope of the invention of this application, which is as defined in the claims below.

EXAMPLE 1

A. An aqueous passivating solution was made up with the following ingredients: 2 g/L of chromium nitrate; 5 g/L of oxalic acid; 4 g/L of citric acid; 10 g/L of phosphoric acid; and 2 g/L of ferrous sulfate, the balance being water.

The pH was adjusted with sodium hydroxide, phosphoric acid, or sulfuric acid to 1.5, the solution being kept at ambient temperature of about 22°C. A quantity of steel fasteners, electroplated with substantially pure zinc, were immersed in this solution for 60 seconds. They were then rinsed in clean tap water and dried. The fasteners exhibited a uniform, black color.

When the fasteners were subjected to a salt spray cabinet according to ASTM B-117, a copious amount of white corrosion formed in less than 24 hours.

B. Similar results are obtained when the phosphoric acid is replaced with ammonium phosphate.

EXAMPLE 2

For Comparison

A quantity of the steel fasteners treated in the blackening solution of Example 1A were immersed in a formulation containing 50 g/L potassium silicate solution, known as Kasil No. 1 (from the PQ Corporation) and allowed to dry at room temperature. Upon testing in accordance with ASTM B-117, copious amounts of white corrosion product formed in less than 48 hours.

EXAMPLE 3

A. A quantity of the fasteners treated as in Example 1A was provided with a top coat by dipping into an aqueous sealing solution of: lithium poly silicate in a concentration to provide 3.33 weight percent of SiO₂, to the total solution (Kasil No. 6 from PQ Industries), potassium silicate in a concentration to provide another 3.33 weight percent of SiO₂ to the total solution (Ludox LPS from W.R. Grace and Company); and 0.25 g/L of molybdate, the dipping time being one minute. The solution was prepared with 100 parts by weight each of the lithium poly silicate and potassium silicate solutions, each having 20 wt. percent SiO₂, plus 300 parts by weight of water, the resulting top coat solution having a total of essentially 6.57 wt. percent SiO₂. The fasteners were then dried, without rinsing, in a typical spin dryer as used in the production of zinc plated fasteners for two minutes, with no heat applied. Upon salt spray testing in accordance with ASTM B-117, the parts withheld 120 hours without formation of any significant white corrosion.

B. Steel fasteners treated as in Example 1A to achieve the uniform, black color were then dipped in a polyethylene wax known as Lugalan® DC ethylene copolymer aqueous emulsion, having a concentration of about 21% of ethylene copolymer. Lugalan® DC is a product of BASF Aktiengesellschaft, a German company. After heating at 250°C F. for 20 minutes, the coated fasteners were treated to the salt spray test of ASTM B-117, passing the test after 120 hours of treatment without forming any significant white corrosion.

C. Fasteners which have been coated with the black coating of Example 1A were then coated with a solution of organosilane and silicates known as Sealer 300W, sold by Units Coating, a German company, and described in Kunz Patent No. 6,478,886.
[0035] When the treated fasteners were tested with neutral salt spray for 120 hours as in previous examples, they endured 120 hours of such treatment without formation of significant white corrosion.

[0036] D. Other steel fasteners coated black in accordance with Example 1A were then coated after drying with a epoxy melamine paint (Straus Chemical Black 100) in conventional manner, and cured at 375° F. for 3-30 minutes.

[0037] After such cure, these fasteners also passed the ASTM B-117 salt spray test of 120 hours of such spray, without formation of significant, white corrosion.

[0038] E. A mixture of sodium silicate plus an anionic acrylamide/acrylic acid copolymer (Cyanamer A370 of Cytec Corp.), were mixed to provide a dispersion containing 50 g/L of silicate N from from PQ Industries, and 0.025 g/L of the cyanamer copolymer. Steel fasteners treated with the black coating in accordance with Example were coated with this new mixture and allowed to air dry, to provide black, corrosion resistant steel fasteners that pass 120 hours of neutral salt spray per ASTM B-117.

EXAMPLE 4

[0039] A solution similar to of Example 1A was prepared except that the ferrous sulfate copolymer was excluded, and replaced with 6 g/L of nickel chloride. A quantity of steel fasteners electroplated with substantially pure zinc were immersed in the solution for one minute, to obtain an olive-green colored fastener. These parts were respectively top coated as described in Example 3A, B, C, D and E. In each case, the resulting top coated fasteners passed a 120 hour salt spray test of the type previously described without significant signs of white corrosion.

EXAMPLE 5

[0040] To the solution of Example 1A, 2 g/L of strontium chloride was added, along with sufficient sucinic acid to prevent precipitation. The zinc plated fasteners of the previous examples were treated in the solution, forming a black coating, which, after rinsing and drying, passed 24 hours of salt spray in accordance with ASTM B-117 with no significant sign of white corrosion (without a top coat).

EXAMPLE 6

[0041] To the solution of Example 5, 50 g/L was added of acid stabilized colloidal silicate (Anti-Cor 2000 by Straus Chemical Company). Zinc plated steel fasteners as described in previous examples were dipped into this solution to form black coatings. Upon removal and drying, without a top coating, these fasteners passed 48 hours of salt spray under ASTM B-117 without significant signs of white corrosion.

EXAMPLE 7

[0042] To the solution of Example 1A, 25 g/L of glacial acetic acid were added, and the pH was adjusted to 1.4. Zinc plated steel fasteners were immersed in this solution and promptly exhibited a lustrous, black appearance. Upon top coating respectively as in Example 3 Sections A-F, the respective fasteners, after drying or curing, were tested with salt spray in accordance with ASTM B-117 for 120 hours, and no significant sign of white corrosion was present.

EXAMPLE 8

[0043] The solution of Example 7 had its pH raised to 2.17 with sodium hydroxide. Zinc plated parts were immersed in this solution, but rather than turning black, they acquired a yellow, iridescent color, mimicking the look of a hexavalent, yellow chromate coating. When top coated in accordance with any of the sections of Example 3 A-E, after drying or cure, the respective yellow fasteners were treated with the salt spray test of ASTM B-117 and endured 120 hours without significant sign of white corrosion.

EXAMPLE 9

[0044] A. The process of Example 1A was repeated, with the zinc-coated fasteners being immersed in the acidic solution for significantly more than one minute. The black color faded.

[0045] B. A solution similar to the acidic solution of Example 1A also contained from 0.5 to 10 grams/liter of sodium carbonate. Zinc fasteners were immersed in this solution for more than a minute. They acquire the desired black color, and retained the color despite the longer dipping time.

That which is claimed is:
1. A method for treating and protecting a zinc surface of a metal artifact, which comprises:
   - applying to the surface a solution of a trivalent chromium compound, plus at least one added metal salt selected from the group consisting of ferrous, nickel and cobalt salts capable of coloring the surface, along with a chromium compound, in the presence of a phosphate at a pH of about 0.5 to 5, to provide a colored surface; and
   - providing a top coat to said colored surface.
2. The method of claim 1 in which said top coat is selected from the group consisting of (1) an aqueous sealing solution of a lithium silicate, and a sodium or potassium silicate; (2) a sodium or potassium silicate dispersed in a coating polymer in a solvent; (3) an organosilane-silicate coating; (4) a sodium or potassium silicate dispersed in a polyethylene wax; (5) anodic or cathodic e-coats; and (6) organic paints.
3. The method of claim 1 in which said at least one added metal salt comprises a ferrous salt, to provide a black color.
4. The method of claim 1 in which said at least one added metal salt comprises at least one of a nickel salt and a cobalt salt to provide an olive drab color.
5. The method of claim 1 in which the nickel solution also comprises a chelating agent.
6. The method of claim 1 in which said solution contains acetic acid, the added salt is a ferrous salt, and the pH of the solution is from 2.1 to about 4.5, whereby the zinc surface acquires a yellow color.
7. The method of claim 1 which further includes a carbonate salt to suppress fading of the colored surface after it has formed.
8. The method of claim 1 in which from 0.5 to 10 grams per liter of said carbonate salt are present.
9. The method of claim 7 in which said carbonate salt is selected from the group consisting of sodium carbonate, calcium carbonate, and nickel carbonate.
10. A zinc surface of a metal artifact treated in accordance with the method of claim 1.
11. A method for treating and protecting a zinc surface of a metal artifact, which comprises:
applying to the surface a solution of a trivalent chromium compound, plus at least one added metal salt selected from the group consisting of ferrous salts, nickel salts and cobalt salts capable of coloring the surface along with the chromium compound, in the presence of a phosphorus-containing acid promoter, to provide a colored surface, and
applying to the colored surface an aqueous sealing solution of a lithium silicate plus a sodium or potassium silicate; and
allowing said surface to dry.
12. The method of claim 11 in which said at least one more metal salt comprises a ferrous salt to provide a black color.
13. The method of claim 11 in which said at least one more metal salt comprises at least one of a nickel salt and a cobalt salt to provide an olive drab color.
14. The method of claim 11 in which the trivalent chromium solution also comprises a chelating agent.
15. The method of claim 11 in which oxalic acid is present.
16. The method of claim 15 in which citric acid is present.
17. The method of claim 11 in which citric acid is present.
18. The method of claim 11 in which said solution contains acetic acid, the added salt is a ferrous salt, and the pH of the solution is from 2.1 to about 4.5, whereby the zinc surface acquires a yellow color.
19. The method of claim 11 in which oxalic acid is present.
20. The method of claim 19 in which citric acid is present.
21. The method of claim 11 in which citric acid is present.
22. The method of claim 11 which further includes a carbonate salt to suppress fading of the colored surface after it has formed.
23. The method of claim 22 in which from 0.5 to 10 grams per liter of said carbonate salt is present.
24. The method of claim 22 in which said carbonate salt is selected from the group consisting of sodium carbonate, calcium carbonate, and nickel carbonate.
25. A zinc surface of a metal artifact treated in accordance with the method of claim 11.
26. The method for treating and protecting a zinc surface of a metal artifact, which comprises:
applying to the surface a solution of a trivalent chromium compound plus at least one metal salt selected from the group consisting of ferrous salts, nickel salts, and cobalt salts capable of coloring the surface, along with the chromium compound in the presence of phosphate, and further in the presence of strontium chloride plus a chelating, solubilizing agent for the strontium chloride, at a pH of 0.5 to 5, to provide a colored, corrosion resistant surface.
27. The method of claim 26 in which said solution further comprises a colloidal silicate.
28. A solution which comprises a trivalent chromium compound plus at least one added metal salt selected from the group consisting of ferrous salts, nickel salts and cobalt salts, in the presence of a phosphate, at a pH of about 0.5 to 5, said solution being capable of providing color to a zinc surface.
29. The solution of claim 28 in which said at least one added metal salt comprises a ferrous salt.
30. The method of claim 28 in which said at least one added metal salt comprises at least one of a nickel salt and a cobalt salt.
31. The solution of claim 28 which also comprises a chelating agent.
32. The solution of claim 28 which also comprises a silicate corrosion protection agent.
33. The solution of claim 28 which further contains acetic acid, the added salt is a ferrous salt, and the pH of the solution is from 2.1 to about 4.5, whereby the zinc surface acquires a yellow color.
34. The solution of claim 28 which further includes a carbonate salt.
35. The method of claim 1 in which said solution contains from 1 g/L to 100 g/L of trivalent chromium.
36. The method of claim 1 in which said solution contains from 0.5 g/L to 100 g/L of ferrous ion.
37. The method of claim 1 in which said solution contains from 0.5 g/L to 50 g/L of at least one of nickel and cobalt ions.
38. The method of claim 12 in which said trivalent chromium solution also comprises a chelating agent and a carbonate salt.
39. The method of claim 1 in which said solution contains from 1 g/L to 100 g/L of trivalent chromium, from 0.5 g/L to 100 g/L of ferrous ion.

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