Abstract: The present invention provides a passivation formulation and a process for forming trivalent chromium-based passivation film on zinc and zinc alloys. The passivation film incorporates nano-ceramic particles resulting in higher corrosion resistance as compared to a trivalent chromium passivation film without nano-sized ceramic particles. The corrosion resistance of the coating is further enhanced by a topcoat or a sealant.
Corrosion Resistance Passivation Formulation and Process of Preparation thereof

Field of the invention

The present invention relates to a chemical composition and process of preparation thereof. More particularly, the present invention relates to a corrosion resistance passivation formulation for conferring high corrosion resistance to metals and their alloys.

Background of the invention

Conventionally, to improve the corrosion resistance, the surfaces of the components made from zinc, zinc alloy, aluminium, cadmium, cadmium alloy and the like are treated with chromium containing formulations. A variety of corrosion resistance passivation formulations are available in the public domain with varying degree of success. Specifically, US Patent No. 73 14671 describes chromium (VI)-free conversion layer and method for producing it. Another US Patent No. 6375726 describes corrosion resistance coatings for aluminium and aluminium alloys. Similarly, US Patent 438902 discloses trivalent chromium passivate composition and process.

Typically, corrosion resisting formulations contain chromium in its hexavalent form. However, environmental concerns and subsequent legislative action in the form of directives such as European Union's vehicle end of life directive led to efforts to find suitable alternatives for hexavalent chromium. As a result of these efforts, hexavalent chromium formulations have now been largely replaced by trivalent chromium-based formulations. However, though this technology has matured over the last few years, it is always desired by the end users to improve the performance of passivation films in terms of higher corrosion resistance as measured by the neutral salt spray life. Specifically, for zinc electrodeposits, applying a further coat of organic, inorganic or hybrid polymer formulation is a widely prevalent practice.
Such polymer formulations are referred as Sealers, Fixers or Topcoats in the industrial practice. However, such topcoats are not applied for passivation films on aluminium, magnesium and their alloys.

Another US Published Application No. 2010/0203327 describes corrosion resistant trivalent chromium conversion coating and formulation where silica particles are incorporated in the formulation. However, in their case the use of silica reduces the corrosion resistance from 300 hours to 240 hours.

**Deficiencies of the Prior Art**

- Trivalent chromium-based passivation or conversion coating formulations when used without a further topcoat do not consistently show high corrosion resistance as measured by neutral salt spray test.
- The use of a topcoat on trivalent chromium passivation gives better corrosion resistance. However, the coating thickness may be as high as 2 microns which may not be suitable for low tolerance components. This is particularly true in the case where the topcoat is based on purely organic materials such as epoxy, acrylic, and polyurethane among others.
- Moreover such sealants have not been developed for passivation films on aluminium, magnesium or their alloys.

**Objects of the invention**

Object of the present invention is to provide a chromium based passivation film formulation for improved corrosion resistance.

Another object of the present invention is to provide chromium based passivation film that incorporates ceramic particles in the passivation film.

Yet another object of the present invention is to provide a process of application of passivation film on zinc and zinc alloys.
Further object of the present invention is to provide a process of manufacturing chromium based passivation film/formulation for corrosion resistance.

**Brief description of figures**

Figure 1 describes a process of applying passivation formulation of the present invention on zinc and zinc alloys in accordance with the present invention.

**Summary of the invention**

Accordingly, the present invention provides a corrosion resistant passivation formulation for zinc and zinc alloys, the passivation formulation comprising:

- trivalent chromium ions in a range of 0.01 to 0.22 moles;
- organic acid in the range of 0 to 0.022 moles;
- transition metal ion in a range of 0 to 0.02 moles;
- boric acid in the range of 0 to 0.02 moles;
- fluoride ions in a range of 0 to 0.1 moles;
- ceramic nano-particles in a range of 0.08 to 0.4 moles; and
- water to dilute the passivation formulation to 1000 ml.

In another aspect, the present invention provides a process of application of passivation film on zinc and zinc alloy, the process comprising:

- plating zinc or zinc alloy;
- rinsing the plated zinc/zinc alloy with water;
- treating the rinsed zinc/zinc alloy with nitric acid for 10-60 seconds;
- rinsing the treated zinc/zinc alloy with water;
- applying a passivation formulation at pH 2.2 to 3.0 to the rinsed zinc/zinc alloy at temperatures ranging from 25° to 40° C for about 30-90 seconds;
- rinsing the passivated zinc/zinc alloy with water;
- treating the rinsed zinc/zinc alloy with a top coat/sealer for about 30-90 seconds;
drying the coated zinc/zinc alloy; and
baking the dried zinc/zinc alloy at 80 ° -120 ° C for 15-20 minutes to obtain a corrosion resistant zinc/zinc alloy.

Detailed description of the invention

The foregoing objects of the invention are accomplished and the problems and shortcomings associated with the prior art techniques and approaches are overcome by the present invention as described below in the preferred embodiment.

The present invention provides a passivation formulation and a process for forming trivalent chromium-based passivation film on zinc and zinc alloys. The passivation film incorporates nano-ceramic particles resulting in higher corrosion resistance as compared to a trivalent chromium passivation film without nano-sized ceramic particles. The corrosion resistance of the coating is further enhanced by a topcoat or a sealant.

The trivalent chromate passivation formulation (hereinafter "the formulation") in accordance with the present invention is an aqueous formulation which comprises trivalent chromium ions in a range of 0.01 to 0.22 moles. Preferably, the trivalent chromium ions are used above 0.05 moles. Further the formulation includes organic acid in the range of 0 to 0.022 moles; preferably, the organic acid is used above 0.005 moles. Furthermore, the formulation includes transition metal ion in a range of 0 to 0.02 moles. Preferably, the transition metal used above 0.01 moles.

The formulation includes boric acid in a range of 0 to 0.02 moles. Preferably, the boric acid is used above 0.01 moles. Further, the formulation includes fluoride ions in a range of 0 to 0.1 moles. Preferably, the fluoride ions are used above 0.02 moles. Furthermore, the formulation includes ceramic nano-particles in a range of 0.08 to 0.4 moles. Preferably, the ceramic nano-particles are used above 0.08 to 0.4 moles.

Water is used to dilute the passivation formulation to 1000 ml.
The trivalent chromium ions are selected from chromium salts such as chromium chloride \( \text{CrCl}_3 \), chromium nitrate \( \text{Cr(NO}_3)_3 \), and chromium sulphate \( \text{Cr}_2(\text{SO}_4)_3 \). Specifically, higher concentration of chromium in the formulation results in a thicker film and thus increases corrosion resistance of the film.

Further, the organic acids are selected from a group consisting of Ethanedioic acid, Butanedioic Acid, 2-3-dihydroxy butanedioic acid, Propanedioic acid, 3-carboxy-3-hydroxy penatanedioic acid and the like. Specifically, the organic acids are used to complex the chromium ion. More specifically, higher chromium ion concentration in the formulation requires a higher organic acid concentration as well.

Furthermore, the transition metal salts are used in the form of chlorides, sulphates, or nitrates of Manganese (Mn), Nickel (Ni), Cobalt (Co), Vanadium (V) and Iron (Fe). The transition metals salts are known to play a role in accelerating the chromate film formation. A higher transition metal salt concentration results in a faster chromate film formation and thereby reducing the time required for passivation. Moreover, fluoride is any one fluoride selected from sodium fluoride, potassium fluoride, ammonium fluoride, ammonium bifluoride, fluorosalicylic acid, fluorozirconic acid and the like. The fluorides play a role in improving the finish of the passivated film. A higher fluoride concentration gives a brighter and polished finish.

Also, nano-particles of ceramic materials are selected from nanoparticles of silicon dioxide \( \text{SiO}_2 \), aluminium oxide \( \text{Al}_2\text{O}_3 \), Zirconium oxide \( \text{ZrO}_2 \), titanium dioxide \( \text{TiO}_2 \), either alone or in combination or in the form of mixed oxide. Specifically, the ceramic particles have particle size in the range of 5 nm to 30 nm preferably smaller than 15 nm, and surface area above 50 g cm\(^{-3}\) and preferably above 200 g cm\(^{-3}\), which are stable and do not coagulate or gel in acidic as well as alkaline pH conditions on their own or during operation in the presence of other elements in the passivation formulation.
Referring now to figure 1, there is shown a flowchart for a process (100) of preparation of passivation of zinc/zinc alloy using the passivation formulation described above. The process (100) includes plating a zinc/zinc alloy. The plated zinc/zinc alloy is then rinsed with water. Thereafter, the rinsed zinc/zinc alloy is treated with nitric acid for 10-20 seconds. Specifically, the concentration of the nitric acid is in the range of 0.2 to 1% and preferably 0.5%. The treated zinc/zinc alloy is again rinsed with water. The passivation formulation at pH 2.2 to 3.0 is applied to the rinsed zinc/zinc alloy at temperatures ranging from 25°C to 40°C for about 30-90 seconds. The passivated zinc/zinc alloy is then rinsed with water and treated with a top coat/sealer for about 30-90 seconds and dried thereafter. The dried zinc/zinc alloy is baked at 80°C -120°C for 15-20 minutes to obtain a corrosion resistant zinc/zinc alloy surface.

The passivation formulation of the present invention act on the zinc coatings between pH 2.2 to 3.0 when contacted for 30 to 90 seconds at low temperatures ranging from 25°C to 40°C to form a chromate conversion coating that incorporates the ceramic particles and thereby offers a superior corrosion resistance. At higher temperatures of 60°C to 80°C, it is preferred to keep the pH at the higher end of the range mentioned above and the contact time can be reduced to as low as 5 to 10 seconds for an effective passivation film formation to take place. Specifically, the process conditions are suitable for treating hot dip galvanized surfaces. The corrosion resistance of the passivation film thus formed provides corrosion resistance of the order of 300 Hrs in salt spray compared to 240Hrs of salt spray provided by prior art method. Further, the corrosion resistance is further improved by using a topcoat or a sealant based on either organosilane or epoxy or acrylic polymers.

Further, the salt spray life obtained on components that are plated from a chloride bath in a barrel consistently exceed 168 hours (5% white rust). The components that are vat plated from alkaline bath offer a corrosion resistance of more than 216 hours for 5% white rust consistently. Furthermore, application of a top coat followed by oven baking results in a salt spray life in excess of 264 hours for the components.
that are plated with the chloride bath. The corresponding figure for vat plated articles from an alkaline bath is 416 hours.

Specifically, for passivation on aluminium and aluminium alloys, the ceramic nanoparticles are added to commercially available aluminium passivation formulations from the market. A salt spray life of 600 hours was obtained as against 300 hours without addition of ceramic nanoparticles. Similar results were envisaged for magnesium and its alloys.

Example 1

A passivation bath containing 0.04 M Cr3+ ions, 0.05 M ethanedioic acid, 0.06 M F- ions and 0.05 M SiO2 nanoparticles (average particle size 10 nm) was prepared. Steel test panels were subjected to an alkaline, non-cyanide electroplating vat process to deposit a zinc plating (average thickness of 8 microns) thereon after which they are thoroughly water rinsed followed by activation in 0.5 % nitric acid for 15 s. The panels were further rinsed with water and then dipped in the passivation bath prepared as above. The temperature was maintained at 35° C and pH of 2.6. The panels were then rinsed in water and dried and oven baked at 100° C for 15 minutes. The panels were then subjected to a salt spray test as per ASTM B117. White rust was first observed after 120 hours. On steel panels passivated in a bath without SiO2 nanoparticles white rust was first observed after 72 hours.

Similarly, steel fastener bolts (size M10 x 35) were subjected to an acid electroplating barrel process to deposit a zinc plating (thickness on the head was 8 microns) thereon, after which they are thoroughly water rinsed followed by activation in 0.5 % nitric acid for 15 s. The panels were further rinsed with water and then dipped in the passivation bath prepared as above. The temperature was maintained at 35° C and pH of 2.6. The panels were then rinsed in water and dried and oven baked at 100° C for 15 minutes. The panels were then subjected to a salt spray test as per ASTM B117. White rust was first observed after 96 hours. On steel panels passivated in a bath without SiO2 nanoparticles white rust was first observed after 48 hours.
Example 2

A passivation bath containing 0.09 M Cr\textsuperscript{3+} ions, 0.05 M propanedioic acid, 0.01 M cobalt nitrate and 0.1 M SiO\textsubscript{2} nanoparticles (average particle size 12 nm), was prepared. Steel test panels were subjected to an alkaline, non-cyanide electroplating vat process to deposit a zinc plating (average thickness of 8 microns) thereon after which they are thoroughly water rinsed followed by activation in 0.5 % nitric acid for 15 s. The panels were further rinsed with water and then dipped in the passivation bath prepared as above. The temperature was maintained at 30° C and pH of 2.7. The panels were then rinsed in water and dried and oven baked at 100° C for 15 minutes. The panels were then subjected to a salt spray test as per ASTM B117. White rust was first observed after 216 hours. On steel panels passivated in a bath without SiO\textsubscript{2} nanoparticles white rust was first observed after 120 hours.

Similarly steel fastener bolts (size M10 x 35) were subjected to an acid electroplating barrel process to deposit a zinc plating (thickness on the head was 8 microns) thereon after which they are thoroughly water rinsed followed by activation in 0.5 % nitric acid for 15 s. The panels were further rinsed with water and then dipped in the passivation bath prepared as above. The temperature was maintained at 35° C and pH of 2.7. The fasteners were then rinsed in water and dried and oven baked at 1000 C for 15 minutes. The panels were then subjected to a salt spray test as per ASTM B117. White rust was first observed after 168 hours. On steel panels passivated in a bath without SiO\textsubscript{2} nanoparticles white rust was first observed after 96 hours.

Example 3

A passivation bath was prepared by mixing 0.01 M SiO\textsubscript{2} nanoparticles (average particle size of 10 nm) with AL-28 passivation from Shree Rasayani. An aluminium panel was degreased with Kelco cleaner (Shree Rasayani) followed by a thorough rinsing, then activated by dripping in 50 % nitric acid for 1 minute followed by a further water rinsing. The aluminium panel was dipped in the passivation bath for 4 minutes maintained at 40° C and a pH of 4. The panels were then rinsed in
water and dried and oven baked at 1000 C for 15 minutes. The panels were then subjected to a salt spray test as per ASTM B117. White rust was not observed even after 600 hours. On panels passivated in a bath without SiO2 nanoparticles white rust was first observed after 288 hours.

Advantages of the present invention

1. The passivation formulation of the present invention is stable over the wide operating range of pH, temperature and Chromium (III) concentration as well as dissolved metals like zinc and aluminum.

2. The total thickness of the coating (including ceramic particle incorporated chromate passivation and a topcoat) is less than 1 micron. Thus, the coating is also suitable for low tolerance components.

3. This technology can be applied to not only electroplated zinc and zinc alloys but also to any zinc or zinc alloy surfaces such as hot dip galvanised surfaces as well as aluminium, magnesium and their alloys.

4. The nano ceramics when introduced in water based formulation of trivalent chromium ions, does not gel or coagulate while in operation. Thus, the physical stability of the system is adequate for satisfactory operation of the bath.

The foregoing descriptions of specific embodiments of the present invention have been presented for purposes of illustration and description. They are not intended to be exhaustive or to limit the present invention to the precise forms disclosed, and obviously many modifications and variations are possible in light of the above teaching. The embodiments were chosen and described in order to best explain the principles of the present invention and its practical application, to thereby enable others skilled in the art to best utilize the present invention and various embodiments with various modifications as are suited to the particular use contemplated. It is understood that various omission and substitutions of equivalents are contemplated as circumstance may suggest or render expedient, but such are intended to cover the application or implementation without departing from the spirit or scope of the present invention.
We claim

1. A passivation formulation for providing corrosion resistant metal/alloy, the passivation formulation comprising:
   - trivalent chromium ions in a range of 0.01 to 0.22 moles;
   - organic acid in the range of 0 to 0.022 moles;
   - transition metal ion in a range of 0 to 0.02 moles;
   - boric acid in the range of 0 to 0.02 moles;
   - fluoride ions in a range of 0 to 0.1 moles;
   - ceramic nano-particles in a range of 0.08 to 0.4 moles; and
   - aqueous vehicle to produce 1000 ml of the passivation formulation.

2. The passivation formulation of claim 1, wherein the trivalent chromium ions are selected from chromium chloride \((\text{CrCl}_3)\), chromium nitrate \((\text{Cr(NO}_3)_3\) and chromium sulphate \(\text{Cr}_2(\text{SO}_4)_3\).

3. The passivation formulation of claim 1, wherein the organic acids are selected from a group consisting of Ethanedioic acid, Butanedioic Acid, 2-3-dihydroxy butanedioic acid, Propanedioic acid and 3-carboxy-3-hydroxy penatanedioic acid.

4. The passivation formulation of claim 1, wherein the transition metal ion is selected in a form of chlorides, sulphates, nitrates of Manganese (Mn), Nickel (Ni), Cobalt (Co), Vanadium (V) and Iron (Fe).

5. The passivation formulation of claim 1, wherein the fluoride is selected from sodium fluoride, potassium fluoride, ammonium fluoride, ammonium bifluoride, fluorosaliclyc acid, and fluorozirconic acid.

6. The passivation formulation of claim 1, wherein the nano-particles of ceramic materials are selected from nanoparticles of silicon dioxide \((\text{SiO}_2)\), aluminium oxide \((\text{Al}_2\text{O}_3)\), Zirconium oxide \((\text{ZrO}_2)\), titanium dioxide \((\text{TiO}_2)\), and combination thereof.
7. The passivation formulation of claim 1, wherein the ceramic particles have particle size in the range of 5 nm to 30 nm.

8. A process of application of passivation film on Zn/Zn alloys using passivation formulation claimed in claim 1-7, the process comprising steps of:

   - plating zinc/zinc alloy;
   - rinsing the plated zinc/zinc alloy with water;
   - treating the rinsed zinc/zinc alloy with nitric acid for 10-60 seconds;
   - rinsing the treated zinc/zinc alloy with water;
   - applying a passivation formulation at pH 2.2 to 3.0 to the to the rinsed zinc/zinc alloy at temperatures ranging from 25°C to 40°C for about 30-90 seconds;
   - rinsing the passivated zinc/zinc alloy with water;
   - treating the rinsed zinc/zinc alloy with a top coat/sealer for about 30-90 seconds;
   - drying the coated zinc/zinc alloy; and
   - baking the dried zinc/zinc alloy at 80°C - 120°C for 15-20 minutes to obtain a corrosion resistant zinc/zinc alloy surface.
Zn/Zn alloy Plating

Water rinse

Nitric Acid (0.5%) 15s

Water Rinse

Water Rinse

Water Rinse

Passivation (30-37C), 30-90 s

Water Rinse

Water Rinse

Water Rinse

Top Coat/Sealer (30-90s)

Drying (Air dry/centrifuge)

Oven baking (80-120 C) 15-20min

Figure 1