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(54) CYANIDE-FREE PRE-TREATING SOLUTION FOR ELECTROPLATING COPPER COATING LAYER ON ZINC ALLOY SURFACE AND A PRE-TREATING METHOD THEREOF

(75) Inventors: **Ching-An Huang**, Gweishan (TW); **Jo Hsuan Chang**, Kwei-Shan (TW); **Sung-Yu Ma**, Kwei-Shan (TW)

Correspondence Address:
NIKOLAI & MERSEREAU, P.A.
900 SECOND AVENUE SOUTH, SUITE 820
MINNEAPOLIS, MN 55402

(73) Assignee: **Chang Gung University**, Kwei-Shan (TW)

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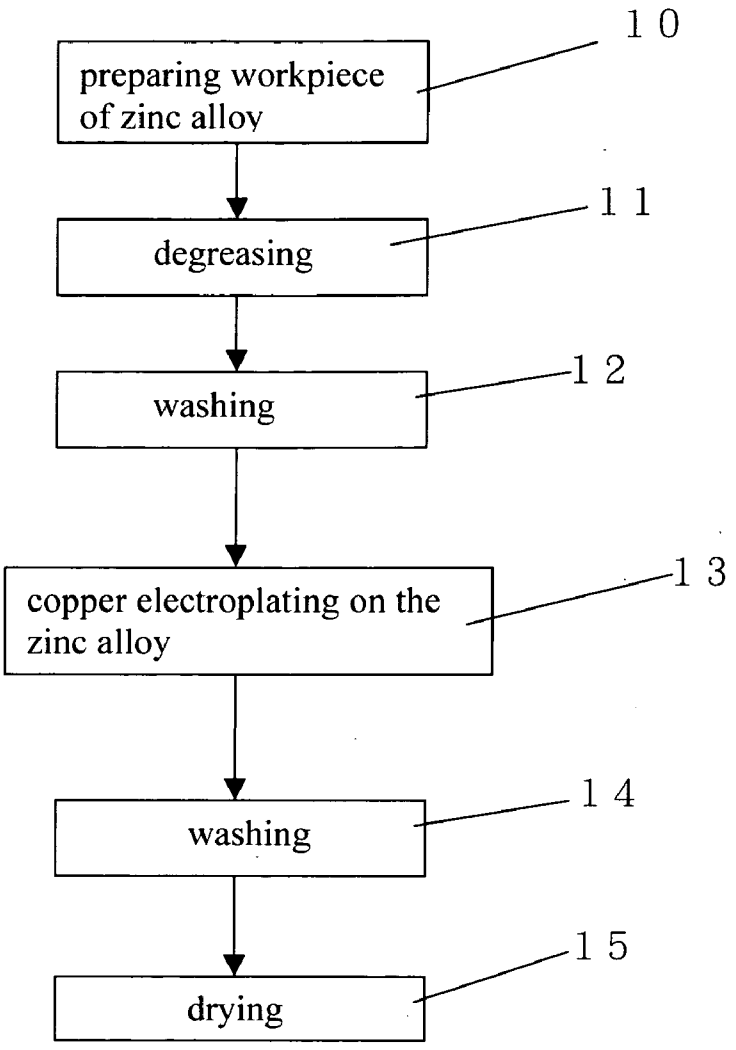
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(57) **ABSTRACT**

A pre-treating solution for electroplating zinc alloy surface contains copper ions, hydroxyl ions, a complexing agent and an additive, wherein the additive is selected from sodium phosphate, sodium hypophosphite, phosphoric acid and dissolvable salts of phosphoric acid. The zinc alloy is dipped in the pre-treating solution and electroplated with a copper coating layer. Then, the zinc alloy is further dipped in a copper sulfate solution for thickening the copper coating layer and lastly coated with an anti-corrosion metal layer. Thereby, zinc alloy has excellent anti-corrosion and anti-wearing efficiency and varnish appearance. Moreover, the pre-treating solution contains no cyanide and thus is low toxic and safe to operator during electroplating and to environment after discharging.



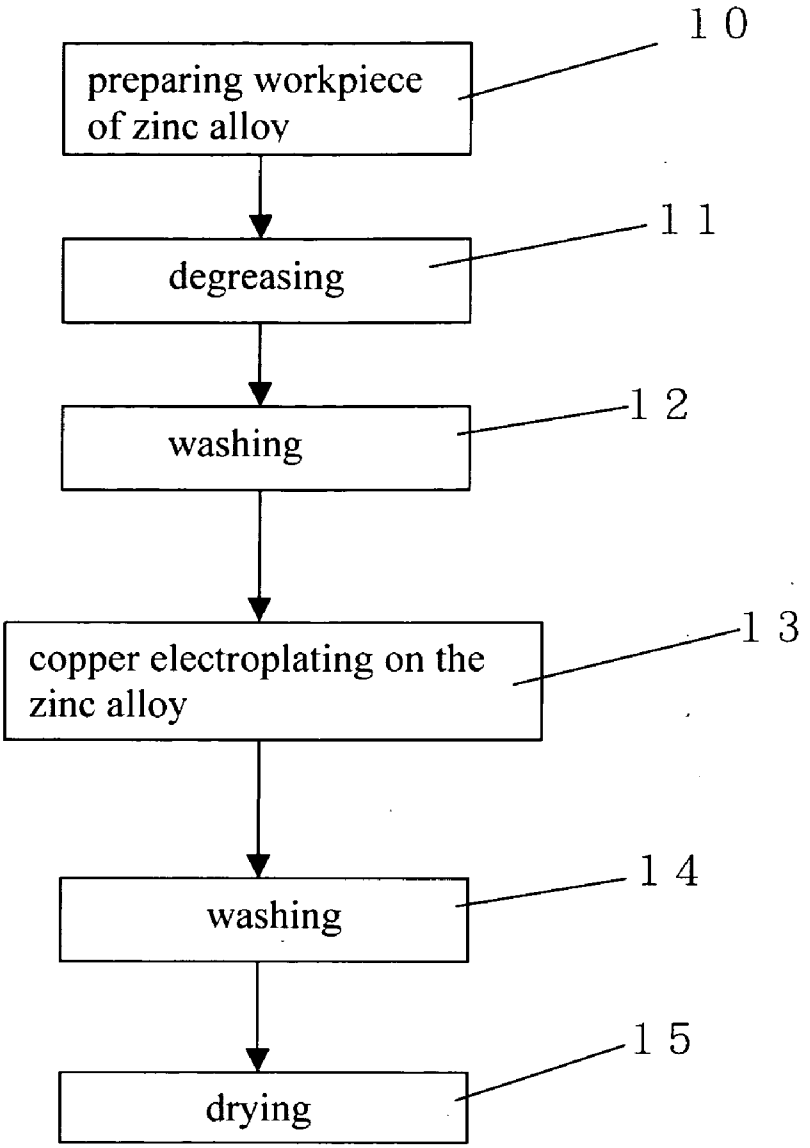

10
preparing workpiece of zinc alloy
11
degreasing
12
washing
13
copper electroplating on the zinc alloy
14
washing
15
drying

FIG 1

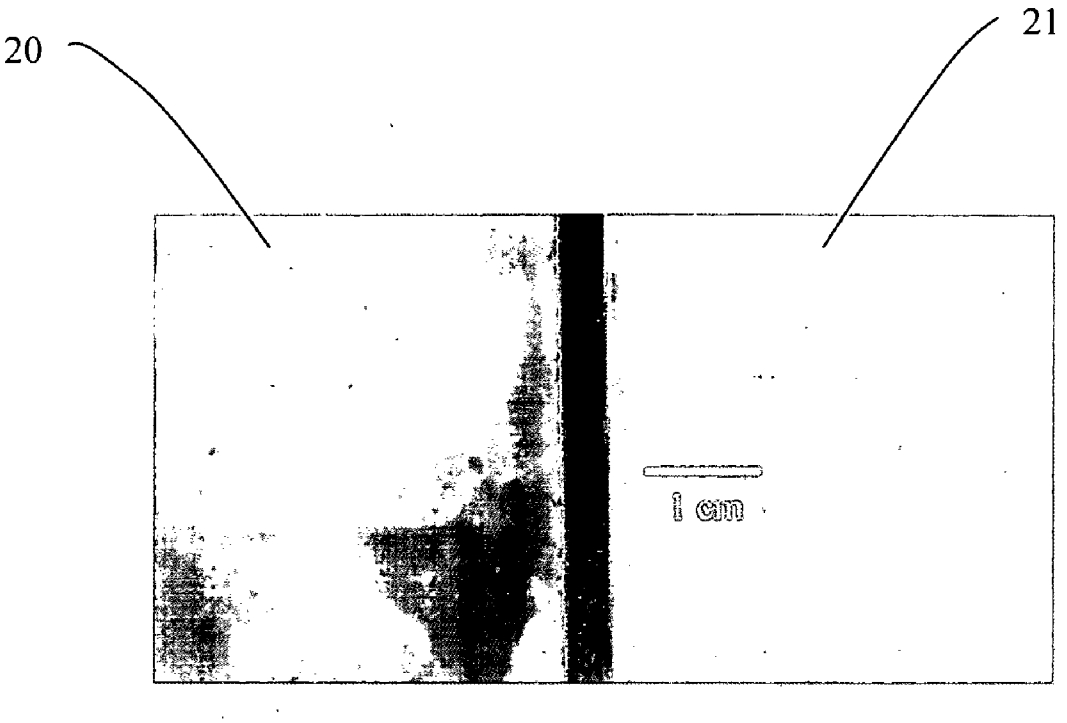


FIG 2

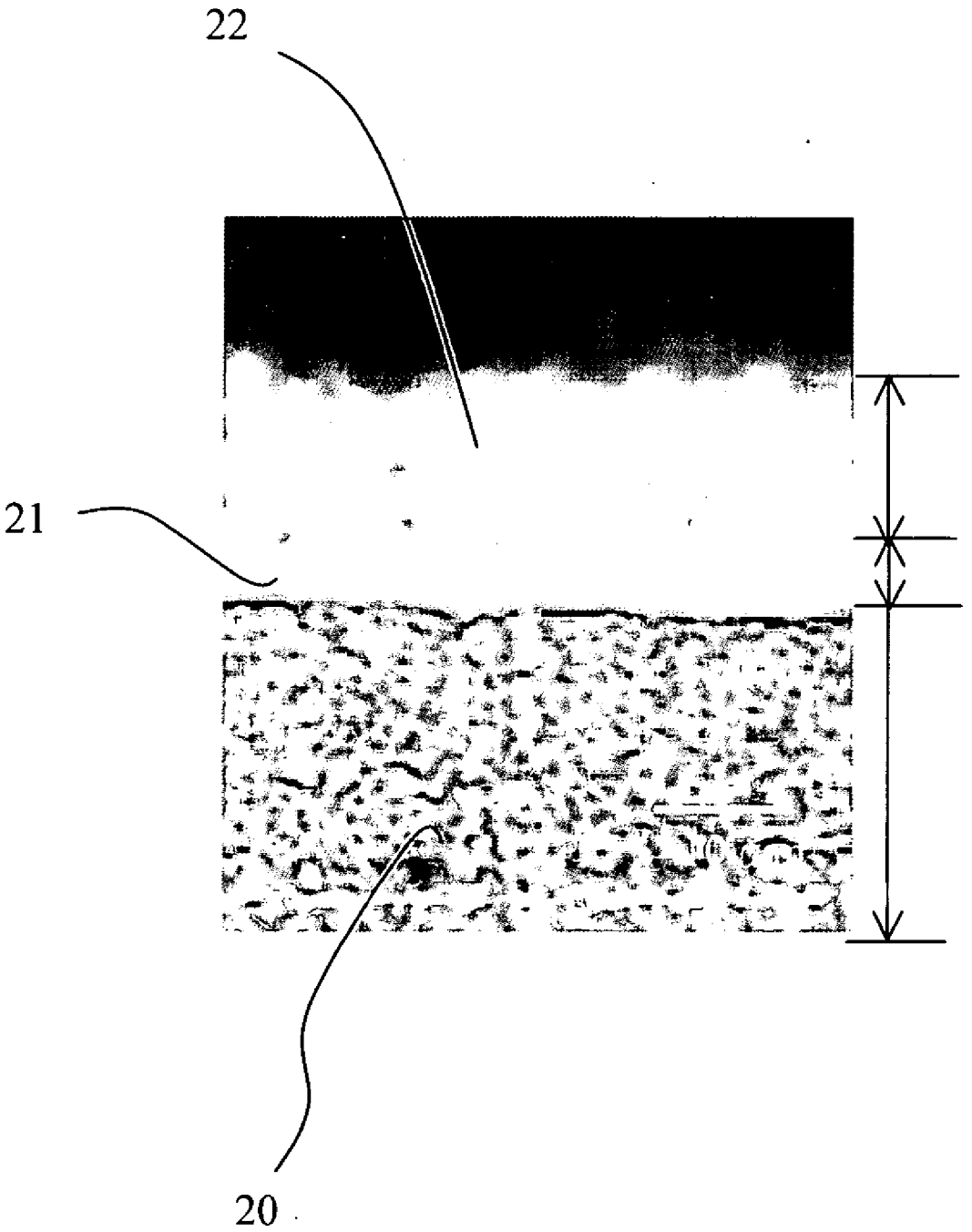


FIG 3

CYANIDE-FREE PRE-TREATING SOLUTION FOR ELECTROPLATING COPPER COATING LAYER ON ZINC ALLOY SURFACE AND A PRE-TREATING METHOD THEREOF

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a pre-treating solution, and more particularly to a pre-treating solution without toxic materials. A pre-treating method of the pre-treating solution is also disclosed.

[0003] 2. Description of Related Art

[0004] Zinc alloy is composed of zinc in majority and other additive elements and is active in chemical reacting property so that its application can not extended. Because the zinc alloy is insufficient in anti-corrosion capability, surface treatment of the zinc alloy is particularly important. Conventional surface treatment of zinc alloy includes anodic treatment, synthesizing treatment and metal-coating treatment (e.g. nickel-coating treatment) etc. Wherein, anodic treatment and synthesizing treatment are to create an anti-corrosion oxide layer on surface of the zinc alloy but the oxide layer has insufficient corrosion resistance and needs further processes such as paint-spraying to achieve anti-corrosion purposes. The metal-coating treatment not only significantly improves corrosion resistance of the zinc alloy but also increases hardness, abrasion resistance and appearance varnish.

[0005] The metal-coating treatment on the zinc alloy is carried out by electroless plating method that is time-consuming and has complex pre-treatments. Moreover, solvents used in the pre-treatments mostly contain toxic acidic materials such as hydrofluoric acid (HF) and chromium trioxide (CrO_3) and cyanide. The complex pre-treatments cause cost increment and the toxic materials may cause damage to environments and human being. Although another optional electroplating method can save more time than the electroless plating method, the electroplating method on the zinc alloy is at a developing stage and not matured enough so that yield is poor. A critical disadvantage of the electroplating method is that corrosion happens easily on surface of the zinc alloy no matter in acid or alkaline electroplating solutions. Therefore, the market-available electroplating solution can not directly use in the electroplating method of zinc alloy. Moreover, the electroless plating method generates a non-conductive layer on the surface of the zinc alloy and thus can not be applied as a pre-treatment of the electroplating method.

[0006] Additionally, two conventional electroplating methods for zinc alloy are also concerned, one is chemical electroplating that takes formaldehyde as catalyst and the other is current electroplating that applies current to reduce copper ions, wherein the copper cyanide is toxic and acidic.

[0007] Therefore, the present invention has arisen to mitigate and/or obviate the drawbacks of the conventional electroplating solutions and methods for electroplating the zinc alloy.

SUMMARY OF THE INVENTION

[0008] The main objective of the present invention is to provide a cyanide-free pre-treating solution for electroplating zinc alloy surface, wherein the pre-treating solution is non-toxic and enables its operational methods to be simplified.

[0009] Another main objection of the present invention is to provide operational methods that make use of the above pre-treating solution for electroplating zinc alloy surface.

[0010] To achieve foregoing main objectives, the cyanide-free pre-treating solution comprises an aqua solution added with copper ions, hydroxyl ions, a complexing agent and an additive, wherein the additive is selected from the group consisting of sodium phosphate, sodium hypophosphite, phosphoric acid and dissolvable salts derivative from phosphoric acid or hypophosphite acid.

[0011] The operational method comprises steps of:

[0012] (a) degreasing: a prepared workpiece made of zinc alloy is degreased with a degreasing agent to remove oil and dirt from surface of the prepared workpiece;

[0013] (b) washing: the prepared workpiece is washed to remove the degreasing agent and to keep the surface of the prepared workpiece clean;

[0014] (c) copper electroplating: the prepared workpiece is dipped into the pre-treating solution with auxiliary electrodes and electroplated to obtain a copper coating layer by applying a fixed current from an additional power supplier; and

[0015] (d) drying: the pre-treating solution residual on the prepared workpiece is removed from the surface of the workpiece to make the surface dry rapidly.

[0016] Because the pre-treating solution contains no toxic materials such as cyanide etc., the pre-treating solution is safe and environmental during treatment of the zinc alloy surface. Moreover, the pre-treating method using the pre-treating solution facilitates the further nickel-coating treatment of the zinc alloy.

[0017] Further benefits and advantages of the present invention will become apparent after a careful reading of the detailed description with appropriate reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. **1** is a flow chart of a pre-treatment of zinc alloy using a cyanide-free pre-treating solution in accordance with the present invention;

[0019] FIG. **2** is a SEM (Scanning Electronic Microscopy) picture showing a first copper coating layer on surface of the zinc alloy; and

[0020] FIG. **3** is a SEM (Scanning Electronic Microscopy) picture further showing a second copper coating layer laminated on the first copper layer in FIG. **2**.

DETAILED DESCRIPTION OF THE INVENTION

[0021] A pre-treating solution for electroplating zinc alloy surface in accordance with the present invention contains copper ions, hydroxyl ions, a complexing agent and an additive, wherein the additive is selected from sodium phosphate, sodium hypophosphite, phosphoric acid and dissolvable salts derivative from phosphoric acid or hypophosphite acid. The zinc alloy is dipped in the pre-treating solution and electroplated with a first copper coating layer. Then, the zinc alloy is further dipped in a market-available copper sulfate solution for thickening the copper coating layer (performing a second copper coating layer) and lastly coated with an anti-corrosion metal layer. Thereby, zinc alloy has excellent anti-corrosion and anti-wearing efficiency and varnish appearance. Moreover, the pre-treating solution contains no cyanide and thus is low toxic and safe to operator during electroplating and to environment after discharging.

[0022] The pre-treating solution for electroplating zinc alloy surface comprises: 3 to 50 g/L of copper ions obtained from copper chloride, copper sulfate, or copper pyrophosphate; 5 to 30 g/L of hydroxyl ions obtained from sodium hydroxide, potassium hydroxide, or ammonium hydroxide; 25 to 150 g/L of the complexing agent selected from the group consisting of potassium sodium tartrate, potassium tartrate and sodium tartrate; and 5 to 50 g/L of the additive selected from the group consisting of sodium phosphate, sodium hypophosphite and phosphoric acid. Reasonably, the pre-treating solution can be modified to have different preferred compositions as shown in following table:

	components			
Num.	Copper ion	Hydroxyl ion	complexing agent	additive
1	3.5 g/L	5 g/L	57 g/L	15 g/L
2	5.7 g/L	9.1 g/L	27.3 g/L	2 g/L
3	3.2 g/L	17.3 g/L	66.9 g/L	5 g/L
4	6.2 g/L	8 g/L	27.9 g/L	1.7 g/L
5	5.4 g/L	30 g/L	65 g/L	14.7 g/L
6	6.4 g/L	8.6 g/L	30.9 g/L	1 g/L
7	5.9 g/L	7.7 g/L	26.4 g/L	1.8 g/L
8	13.7 g/L	22.3 g/L	67.8 g/L	3.3 g/L
9	14.6 g/L	25.8 g/L	45.3 g/L	3.2 g/L
10	15.1 g/L	27.4 g/L	32.4 g/L	5 g/L
11	7.2 g/L	7.9 g/L	21.6 g/L	4.1 g/L
12	17.4 g/L	19.5 g/L	12.7 g/L	3.8 g/L
13	7.1 g/L	8.5 g/L	33 g/L	3 g/L
14	22.2 g/L	7.3 g/L	25 g/L	5 g/L
15	21.6 g/L	17.9 g/L	53 g/L	2.4 g/L
16	24.3 g/L	24.7 g/L	55 g/L	3.5 g/L
17	6.4 g/L	9 g/L	25.8 g/L	2.3 g/L
18	23.8 g/L	6.8 g/L	45 g/L	4.8 g/L
19	25 g/L	19.3 g/L	14.2 g/L	9.7 g/L
20	7.3 g/L	8.7 g/L	24.9 g/L	2.1 g/L
21	8.4 g/L	5.5 g/L	66.9 g/L	13.2 g/L
22	24.1 g/L	6.2 g/L	15.8 g/L	1.7 g/L
23	21. g/L	7.9 g/L	32.3 g/L	11.3 g/L
24	24.8 g/L	9.1 g/L	25 g/L	12.7 g/L

[0023] Compositions of the pre-treating solution in serial number of 2, 4, 6, 7, 11, 13, 17 and 20 in the table are mostly preferred.

[0024] With reference to FIG. **1**, a pre-treating operation to the zinc alloy is shown and is adapted to form a first copper coating layer on a prepared workpiece made of the zinc alloy by using the pre-treating solution in the present invention. The pre-treating operation comprises steps of:

[0025] (a). Degreasing:

[0026] The prepared workpiece is degreased with a degreasing agent to remove oil and dirt from its surface.

[0027] (b). Washing:

[0028] The prepared workpiece is washed to remove the degreasing agent and to keep the surface clean.

[0029] (c) Copper Electroplating:

[0030] The workpiece is dipped into the pre-treating solution with auxiliary electrodes and electroplated to obtain a copper coating layer (the first copper coating layer) thereon by applying a fixed current from an additional power supplier.

[0031] (d) Drying:

[0032] After electroplating, residual solution is removed from the surface of the workpiece to make the surface dry rapidly.

[0033] Moreover, a washing step is added into the pre-treating method after the (c) step of copper electroplating.

[0034] Wherein, the surface temperature of the workpiece in (c) step of copper electroplating is about 10 to 90° C.

[0035] Wherein, the fixed current provided by the additional power supplier has a range from 0.002 to 0.02 ampere per square decimeter.

[0036] Wherein, the auxiliary electrodes are made of material selected from the group comprising titanium core coated with platinum, titanium, platinum, graphite and stainless steel.

[0037] With further reference to FIG. **1**, a preferred embodiment of a pre-treating operation is shown. Before copper electroplating, the workpiece is prepared (**10**), degreased (**11**) and washed (**12**) to make its surface clean. Then, the workpiece, auxiliary electrodes, and the pre-treating solution are inputted into a tank to carry out electroplating (**13**) with mechanically stir. By applying a fixed current from an additional power supplier, the copper ions in the pre-treating solution obtain electrons to reduce and deposit on the surface of the workpiece so that the workpiece obtains a uniform copper coating layer, i.e. the first copper coating layer. After copper electroplating, the workpiece is washed (**14**) again and dried (**15**) to obtain the final product. The workpiece with the first copper coating layer is further treated with a conventional electroplating process to form a second copper coating layer on the first copper coating layer to obtain the final product. Lastly, the workpiece is further coated with an anti-corrosion metal layer to have excellent anti-corrosion and anti-wearing efficiency and varnish appearance.

[0038] With reference to FIG. **2**, the substrate (**20**) of the zinc alloy is coated with a uniform first copper layer (**21**) after inputting the substrate (**20**), the auxiliary electrodes and the pre-treating solution into the tank and carrying out electroplating with mechanically stir by applying a fixed current from the additional power supplier. Thereby, the surface of the zinc alloy substrate (**20**) becomes brownish in appearance.

[0039] With reference to FIG. **3**, the zinc alloy having the first copper layer (**21**) is further treated with conventional electroplating by use of market-available copper sulfate solution to form a second copper layer (**22**) for thickening.

[0040] Lastly, the zinc alloy is further treated with an anti-corrosion electroplating to perform a nickel coating (not shown) thereon so that the surface of the zinc alloy is corrosion-resistant and wearing-resistant and has a varnish appearance.

[0041] The cyanide-free pre-treating solution for zinc alloy surface contains an aqua solution added with copper ions, hydroxyl ions, a complexing agent and an additive, wherein the additive is selected from sodium phosphate, sodium hypophosphite, phosphoric acid and dissolvable salts derivative from phosphoric acid and hypophosphite acid.

[0042] Wherein, the copper ions are obtained from copper chloride, copper sulfate, copper pyrophosphate or hydrates of foregoing mentioned salts.

[0043] Wherein, concentration of the copper ion is 3 to 50 g/L.

[0044] Wherein, the complexing agent is selected from potassium sodium tartrate, potassium tartrate, sodium tartrate, tartaric acid, and dissolvable salts derivative from tartaric acid.

[0045] Wherein, concentration of the complexing agent is 10 to 150 g/L.

[0046] Wherein, concentration of the additive is 1 to 50 g/L.

[0047] Wherein the hydroxyl ions are obtained from sodium hydroxide, potassium hydroxide, ammonium hydroxide or dissolvable salts of alkaline.

[0048] Wherein, concentration of the hydroxyl ion is 5 to 30 g/L.

[0049] According to above description, the cyanide-free pre-treating solution for zinc alloy surface in accordance with the present invention and its operational method has the following advantages:

[0050] 1. The conventional electroless method is troublesome in pre-treatment. By using the pre-treating solution with copper ions to carry the pre-treatment out, the following nickel layer can be efficiently applied onto the copper layer so that the active zinc alloy surface is completely treated with rapidly and simply two-step electroplating procedures.

[0051] 2. The pre-treating solution in the present invention is alkaline in particular and contains no toxic cyanide, hydrofluoric acid (HF) and chromium trioxide (CrO_3) so that it is safe to human being and environment and causes no pollution during electroplating procedures.

[0052] Although the invention has been explained in relation to its preferred embodiment, it is to be understood that many other possible modifications and variations can be made without departing from the spirit and scope of the invention as hereinafter claimed.

What is claimed is:

1. A cyanide-free pre-treating solution for zinc alloy surface, the pre-treating solution comprising an aqua solution added with copper ions, hydroxyl ions, a complexing agent and an additive, wherein the additive is selected from the group consisting of sodium phosphate, sodium hypophosphite, phosphoric acid and dissolvable salts derivative from phosphoric acid or hypophosphite acid.

2. The pre-treating solution as claimed in claim **1**, wherein the additive is 1 to 50 g/L in concentration.

3. The pre-treating solution as claimed in claim **1**, wherein the hydroxyl ions are obtained from the group consisting of sodium hydroxide, potassium hydroxide, ammonium hydroxide and dissolvable salts of alkaline.

4. The pre-treating solution as claimed in claim **1**, wherein the hydroxyl ions are 5 to 30 g/L in concentration.

5. The pre-treating solution as claimed in claim **1**, wherein the complexing agent is selected from the group consisting of potassium sodium tartrate, potassium tartrate, sodium tartrate, tartaric acid, and dissolvable salts derivative from tartaric acid.

6. The pre-treating solution as claimed in claim **5**, wherein the complexing agent is 10 to 150 g/L in concentration.

7. The pre-treating solution as claimed in claim **1**, wherein the copper ions are obtained from the group consisting of copper chloride, copper sulfate, copper pyrophosphate and hydrates of foregoing motioned salts.

8. The pre-treating solution as claimed in claim **7**, wherein the copper ions are 3 to 50 g/L in concentration.

9. A pre-treating method for zinc alloy surface comprising steps of:

(a) degreasing: a prepared workpiece made of zinc alloy is degreased with a degreasing agent to remove oil and dirt from surface of the prepared workpiece;

(b) washing: the prepared workpiece is washed to remove the degreasing agent and to keep the surface of the prepared workpiece clean;

(c) copper electroplating: the prepared workpiece is dipped into the pre-treating solution with auxiliary electrodes and electroplated to obtain a copper coating layer by applying a fixed current from an additional power supplier; and

(d) drying: the pre-treating solution residual on the prepared workpiece is removed from the surface of the workpiece to make the surface dry rapidly.

10. The pre-treating method as claimed in claim **9** further comprising a washing step after (c) step of copper electroplating.

11. The pre-treating method as claimed in claim **9**, wherein the fixed current provided by the additional power supplier has a range from 0.002 to 0.02 ampere per square decimeter.

12. The pre-treating method as claimed in claim **9**, wherein the auxiliary electrodes are made of material selected from the group comprising titanium core coated with platinum, titanium, platinum, graphite and stainless steel.

13. The pre-treating method as claimed in claim **9**, wherein surface temperature of the prepared workpiece in (c) step of copper electroplating is 10 to 90° C.

14. The pre-treating method as claimed in claim **9**, wherein the workpiece is further treated with another copper electroplating process and a nickel coating process after the step of drying.

15. The pre-treating method as claimed in claim **10**, wherein, wherein the pre-treating solution comprises an aqua solution added with copper ions, hydroxyl ions, a complexing agent and an additive;

wherein the additive is selected from the group consisting of sodium phosphate, sodium hypophosphite, phosphoric acid and dissolvable salts derivative from phosphoric acid or hypophosphite acid.

* * * * *