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ELECTROLYTIC SOLUTION FOR ZINC PLATING

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ABSTRACT OF THE DISCLOSURE

An electrolytic solution for zinc plating containing zinc acetate, zinc chloride or zinc sulfate; ammonium chloride; sodium or potassium gluconate; boric acid; and glossing agents. Equal or superior uniform depositability, chromate treatability and corrosion resistance can be obtained with the use thereof.

This invention relates to an electrolytic solution for zinc plating. More particularly, it relates to a process for plating zinc on metal surfaces and an electrolytic solution therefor which contains (1) zinc acetate, zinc chloride or zinc sulfate; (2) ammonium chloride; (3) sodium or potassium gluconate, (4) boric acid and (5) glossing agents.

Acidic zinc sulfate electrolytic solutions, alkaline zinc cyanide electrolytic solutions, etc. have principally been used heretofore as electrolytic solutions for galvanic zinc plating. The alkaline zinc cyanide electrolytic solutions are considerably superior to the acidic zinc sulfate electrolytic solutions insofar as uniform depositability is concerned. Thus, when a material having a complicated shape is to be plated, alkaline zinc cyanide electrolytic solutions have usually been used. However, the alkaline zinc cyanide electrolytic solutions contain very toxic cyanides, making the disposition of the electrolytic solution a very troublesome matter. Furthermore, much expense and valuable space are required for the disposal of the waste solution.

One of the objects of the present invention is to provide an electrolytic solution which contains no toxic cyanides and is equal or superior in performance and effect to an alkaline zinc cyanide electrolytic solution.

Another object of the invention is to provide an electrolytic solution capable of giving an excellent corrosion resistance by means of a relatively simple operation and device.

A further object of the invention is to provide an electrolytic solution capable of producing a good glossy and smooth surface.

A still further object of the present invention is to provide an efficacious and advantageous process for the plating of zinc.

These and other objects and advantages of the present invention will become apparent to one skilled in the art from a consideration of the following specification and claims.

In accordance with the present invention, it has been found that the objectives outlined above are attained by using for the zinc plating an electrolytic solution comprising (1) zinc acetate, zinc chloride or zinc sulfate, (2) ammonium chloride, (3) sodium or potassium gluconate, (4) boric acid and (5) glossing agents.

The zinc ion concentration employed in the electrolytic solution of the present invention is 10–100 g./l. (grams per liter), preferably 20–50 g./l. The amount of zinc ion is closely related to the uniform depositability and cathode current efficiency which can be obtained, and when the zinc ion is used in excess, the uniformity of the deposit tends to worsen and become undesirable. As noted above, the zinc salts used in the present invention are zinc acetate, zinc chloride and zinc sulfate.

The ammonium chloride concentration used in the electrolytic solution is preferably 30–150 g./l. In this case, the ammonium chloride is used as a current-passing assistant, and when the ammonium chloride is used in excess amounts, the deposited zinc surface tends to become worse, with the result that the corrosion resistance also tends to deteriorate in quality. In addition, the adhesiveness of the deposited zinc to metal surface tends to become poor when too much or too little of an amount of ammonium chloride is used.

The concentration of potassium or sodium gluconate used in the electrolytic solution is preferably 30–300 g./l. More specifically, the concentration of sodium or potassium gluconate is preferably 180–220 g./l. in the case of zinc acetate, 80–120 g./l. in the case of zinc chloride and 100–140 g./l. in the case of zinc sulfate. The addition of sodium or potassium gluconate to the solution makes it possible to obtain a deposited zinc surface having a uniform gloss distribution. A film of chromate having a good corrosion resistance can be readily formed on the deposited zinc surface by chromate treatment. The adhesiveness of the deposited zinc to metal surface tends to become worse when too small of a quantity of gluconate is used.

The boric acid concentration is preferably 10–100 g./l. more preferably 15–25 g./l. The boric acid acts as a pH buffering agent. By adding H_3BO_3 to the electrolytic solution, the gloss of the deposited zinc can be much improved.

The pH of the solution is preferably kept at 2 to 7, more preferably 4–5. The pH is closely related to the adhesiveness of deposited zinc to metal plate. The adhesiveness tends to become poor when too high or too low of a pH is used. A too low pH increases the solution of the zinc anode, and control of the electrolytic solution becomes difficult.

Glossing agents which may be employed in the solution include, for example, gelatin, glue, dextrin, polyethylene glycol and triethanolamine.

Examples of the present invention are shown in the following table. In addition, the conventional electrolytic solution of alkaline zinc cyanide is also shown in the table as a comparison. These examples are given merely as illustrative of the present invention and are not to be considered as limiting.

TABLE

	Example 1	2	3	4	5	Alkaline zinc cyanide electrolytic solution	Remarks
Electrolytic solution—							
additives:							
$Zn(CH_3CO_2)_2$	100 g./l.	60 g./l.	120 g./l.	$ZnCl_2$, 75 g./l.	$ZnSC_4$, 150 g./l.	Metallic zinc, 45 g./l.	
$(NH_4)Cl$	70 g./l.	70 g./l.	80 g./l.	75 g./l.	75 g./l.	NaCN, 120 g./l.	
Sodium gluconate	220 g./l.	180 g./l.	Potassium gluconate, 240 g./l.	100 g./l.	120 g./l.	Free NaOH, 70 g./l.	
H_3BO_3	20 g./l.	20 g./l.	20 g./l.	25 g./l.	20 g./l.		
Glossing agent	Gelatin, 1 g./l.	$C_6H_{15}NO_3$, 10 g./l., gelatin, 1 g./l.	Glue, 1 g./l.	Gelatin, 1 g./l., polyethylene glycol, 2 g./l.	Gelatin, 0.5 g./l., polyethylene glycol, 4 g./l.		
pH	5.0	4.5	5.0	5.0	5.0		
Plating condition:							
Electrolytic solution temperature	35° C.	35° C.	35° C.	35° C.	35° C.	25° C.	
Current density of cathode	3 A./dm.^{2}	3 A./dm.^{2}	3 A./dm.^{2}	3 A./dm.^{2}	3 A./dm.^{2}	3 A./dm.^{2}	
Plating time	15 min.	15 min.	15 min.	15 min.	15 min.	15 min.	
Electrodeposition characteristics:							
Surface conditions	Glossy and smooth	Glossy and smooth	Glossy and smooth	Glossy and smooth	Glossy and smooth	Smooth	
Chromate treatability	Good	Good	Good	Good	Good	Good	
Adhesiveness	do	do	do	do	do	do	
Uniform electrodepositability	5.5	4.7	5.8	5.0	5.6	5.5	(1)
Corrosion resistance	26 hours	20 hours	23 hours	25 hours	25 hours	18 hours	(2)
Current efficiency of cathode	95%	75%	96%	95%	95%	80%	(3)

[1] Uniform depositability is represented by a ratio of A:B, where A and B are the thickness of the high current part and that of the low current part, respectively, when the plating is conducted according to the Hull cell method.

[2] Corrosion resistance is represented by the time required for the appearance of zinc flower when a 10% sodium chloride aqueous solution is sprayed at a pressure of 0.7 kg./cm.^{2} onto a zinc-deposited material in a test tank at 60° C.

[3] Current efficiency of cathode is represented by the actual amount of zinc deposited per theoretical amount of zinc deposited ×100 (%).

As is clear from the table, a zinc deposition equal or superior to that obtained by the alkaline zinc cyanide electrolytic solution can be obtained as regards deposition characteristics such as uniform depositability, cathode current efficiency and corrosion resistance. Furthermore, since no toxic cyanides are used in the present invention, the present electrolytic solution is not toxic and is easy to handle, and the waste disposal thereof is very simple.

The details of process conditions for plating zinc by means of aqueous electrolytic solution are well known in the art, and these conventional conditions may be employed with the electrolytic solution of the present invention. Illustrative thereof are the plating conditions recited in the above table. The same can be said of the metal surfaces to be plated. These are conventional and include, for example, the ferrous metals such as iron and alloys of iron such as steel.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included herein.

We claim:

1. An electrolytic aqueous solution for zinc plating comprising (1) from 10 to 100 grams per liter of zinc ion supplied by a salt selected from the group consisting of zinc acetate, zinc chloride and zinc sulfate, (2) from 30 to 150 grams per liter of ammonium chloride, (3) from 30 to 300 grams per liter of a gluconate selected from the group consisting of sodium and potassium gluconate, and from 10 to 100 grams per liter of boric acid, said solution having a pH of 2 to 7.

2. The electrolytic aqueous solution of claim 1 further including an effective amount of at least one glossing agent selected from the group consisting of gelatin, glue, dextrin, polyethylene glycol, and triethanolamine.

3. The electrolytic aqueous solution of claim 1 in which said solution has a pH of 4 to 5.

4. The electrolytic aqueous solution of claim 1 in which the concentration of zinc ion in the solution is from 20 to 50 grams per liter.

5. The electrolytic aqueous solution of claim 1 in which the concentration of gluconate in the solution is from 180 to 220 grams per liter when the zinc ion is supplied by zinc acetate, from 80 to 120 grams per liter when the zinc ion is supplied by zinc chloride and from 100 to 140 grams per liter when the zinc ion is supplied by zinc sulfate.

6. The electrolytic aqueous solution of claim 1 in which the concentration of boric acid in the solution is from 15 to 25 grams per liter.

7. An electrolytic aqueous solution for zinc plating comprising from 20 to 50 grams per liter of zinc ion supplied by a salt selected from the group consisting of zinc acetate, zinc chloride and zinc sulfate; from 30 to 150 grams per liter of ammonium chloride; a gluconate selected from the group consisting of potassium and sodium gluconate, the concentration of the gluconate being from 180 to 220 grams per liter when the zinc ion is supplied by zinc acetate, from 80 to 120 grams per liter when the zinc ion is supplied by zinc chloride, and from 100 to 120 grams per liter when the zinc ion is supplied by zinc sulfate; and from 15 to 25 grams per liter of boric acid; said solution having a pH of 2 to 7.

8. The electrolytic aqueous solution of claim 7 further including an effective amount of at least one glossing agent selected from the group consisting of gelatin, glue, dextrin, polyethylene glycol, and triethanolamine.

9. The electrolytic aqueous solution of claim 7 in which the said solution has a pH of 4 to 5.

10. A method for plating zinc on a metal surface which comprises electrolyzing an aqueous solution having a pH of from 2 to 7 and containing from 10 to 100 grams per liter of zinc ion supplied by a salt selected from the group consisting of zinc acetate, zinc chloride and zinc sulfate, from 30 to 150 grams per liter of ammonium chloride, from 30 to 300 grams per liter of a gluconate selected from the group consisting of potassium and sodium glu-

conate, and from 10 to 100 grams per liter of boric acid, for a sufficient period of time to plate zinc metal on said metal surface; said metal surface acting as a cathode.

11. The method of claim **10** in which the electrolysis is carried out at a cathode current density of about 3 amperes per square decimeter at a temperature of about 35° C.

12. The method of claim **11** in which said solution has a pH of 4 to 5.

13. The method of claim **10** in which said aqueous solution further contains an effective amount of at least one glossing agent selected from the group consisting of gelatin, glue, dextrin, polyethylene glycol and triethanolamine.

14. The method of claim **10** in which said metal surface is on a ferrous metal.

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