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ZINC PLATING SOLUTION

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15 Claims

ABSTRACT OF THE DISCLOSURE

Electrolyte solution for use in the electrodeposition of zinc comprises an aqueous solution of (A) zinc sulphamate and (B) fluoroboric acid and/or one or more soluble salts of fluoroboric acid and/or a combination of fluoroboric acid and hydrofluoric acid. Preferred solutions comprise 0.5 to 4 mols per litre zinc sulphamate and 0.01 to 0.5 mols per litre fluoroboric acid. Brightening agents, e.g. 1 to 75 gms. per litre boric acid, and levelling agents, e.g. 0.05 to 1 gm. per litre gelatin, may also be present.

This invention relates to zinc plating solutions for the electrolytic deposition of zinc.

It is known to electroplate various metallic substrates, notably continuous steel strip and wire in order to provide protection from corrosion. A zinc anode is used which dissolves as electrolysis proceeds. Very many electrolyte solutions have been suggested and used in attempts to improve the speed of deposition, homogeneity and appearance of the zinc coating and to avoid the formation of dendritic deposits. Commonly used electrolyte solutions comprise a solution of chloride, sulphate, cyanide, fluoroborate or pyrophosphate salts of zinc. A diversity of other additives is also known which modify or improve the properties of electrolyte solutions in various respects.

A limitation on electrolyte solutions is that the use of too high a current in attempts to accelerate the rate of electrodeposition leads to "burning" which is the production of a rough non-coherent deposit often containing oxides or other inclusions. The upper current density at which an electrolyte solution may be employed without giving rise to this effect is an important criterion of its utility.

We have now discovered a novel electrolyte solution for zinc plating which is capable of giving acceptable products at current densities higher than the permissible maxima for comparable previous electrolyte solutions.

Accordingly, the invention provides an electrolyte solution for use in the electrodeposition of zinc which comprises an aqueous solution of (A) zinc sulphamate and (B) fluoroboric acid and/or one or more soluble salts of fluoroboric acid and/or a combination of boric acid and hydrofluoric acid.

Best results are obtained using a solution of zinc sulphamate together with fluoroboric acid. The zinc sulphamate is preferably present in a concentration of from 0.5 to 4 molar, most preferably 1-2 molar and the fluoroboric acid is preferably present in a concentration of from 0.01 to 0.5 molar, preferably 0.025 to 0.25, most preferably 0.08 to 0.12 molar, e.g. 0.1 molar. Where alternative materials to fluoroboric acid in the category (B) above are chosen these may generally be employed in like quantities as for fluoroboric acid, i.e. to give similar fluorine concentrations (expressed as atomic fluorine) in the solution.

The fluoroborate salt or salts may be any salt or mixture of salts which are soluble and whose cations do not

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impair the zinc deposit. The incidence of such impairment may readily be ascertained by simple experiment. Suitable salts are the fluoroborates of zinc, ammonium, sodium and potassium. If desired a mixture of fluoroboric acid with one or more of such salts may be used. Combinations of boric acid and hydrofluoric acid, although offering advantages as additives to the electrolyte are less preferred but if used are preferably present in at least substantially 1:4 molar ratio boric: hydrofluoric acid, excluding any boric acid used as a brightening agent.

The novel electrolyte solutions should be an acidic solution having a pH of from 2 to 5, preferably 3 to 4, most preferably 3.6 to 3.8 e.g. 3.7 pH adjustment to the desired value may be effected for example, by addition to the electrolyte solution of zinc oxide or sulphamic acid.

Preferred novel electrolyte solutions further comprise a brightening agent, most preferably together with a levelling agent which latter helps to reduce dendritic deposits. Such brightening and levelling agents may be known materials for electroplating applications. Possible brightening agents include boric acid; sulphur-containing organic compounds such as aromatic and unsaturated aliphatic sulphonic acids and disulphonic acids such as 2-butyne-1,4-disulphonic acid and salts thereof, and the benzene, toluene or naphthalene sulphonic acids and alkali metal salts thereof; sulphonamides and sulphimides such as p-toluene-sulphonamide, benzene sulphonamide, o-benzoyl sulphonamide, alkyl sulphonic acids and alkali metal salts thereof; and O-sulpho-benzaldehyde; formaldehyde; chloral hydrate; bromal hydrate; coumarin and butyne-diol. Levelling agents include gelatin, glucose, starch, glue, goulac, polyethylene glycol, triethanolamine, gum of guar, fucula, products of the degradation of starch and fucula such as hydroxy ethyl starch, gluten, casein, albumin, carboxymethyl celluloses, polyvinyl alcohols and alkali metal silicates.

The preferred brightening agent is boric acid, which is preferably present in a concentration of from 1 to 75 g./l. more preferably 5 to 50 g./l., most preferably 15-25, e.g. 20 g./l. The aforesaid quantities exclude any additional boric acid which may be present together with hydrofluoric acid as component B of the electrolyte.

The preferred levelling agent is gelatin which is preferably present in a concentration of from 0.05 to 1 g./l., most preferably from 0.1 to 1 g./l.

The novel solutions may further comprise other known additives for electrolyte solutions used in electroplating applications.

The novel electrolyte solutions may be used according to standard techniques of zinc electroplating. Operating temperatures are not critical, being generally from room temperature to boiling point, but are preferably in the range 25-60° C. The current densities employed may be considerably higher than has hitherto been acceptable in such applications. Under static conditions a current density up to 500 amps. s.f. may be possible whilst under conditions of agitation of the electrolyte solution; such as where a mechanical agitator is provided or in a strip line application where movement of the strip through the electrolyte solution causes rapid passage of the solution over the substrate surface, a current density of up to 800-1000 amps. s.f. may be found possible in preferred cases.

Zinc electrodeposition processes wherein is used as an electrolyte solution a solution as hereinbefore defined constitute a further aspect of this invention.

The invention is illustrated by the following examples:

EXAMPLE I

A solution containing zinc sulphamate (1.5 M) and fluoroboric acid (0.1 M) having a pH of 3.7 was used as an electrolyte in a standard pull cell. The anode for the

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cell was made from thin zinc sheet and the cathode was degreased mild steel. The temperature of the cell was maintained in the range 35–40° C. and the electrolyte was essentially static. A current range of 0–20 amps. (corresponding to a current density of 0–1300 a.s.f.) was passed through the cell for 5 minutes. It was found that even at the areas where the current densities had been as high as 1300 a.s.f. no burning was apparent and an even matt grey deposit was obtained on the cathode. Only inconsiderable dendritic growth was observed in the higher current density ranges.

In a comparative experiment, a cell similar to that described was used, but with an electrolyte consisting of zinc sulphate (1.5 M) and fluoroboric acid (0.1 M). The pH and temperature control used was the same as before, but it was found that in this case, current densities in excess of 600 a.s.f. resulted in severely burnt deposits being formed.

EXAMPLE II

A solution containing zinc sulphamate (1.5 M) fluoroboric acid (0.1 M) and boric acid (20 g./l.) was used as an electrolyte in a cell of capacity of 10 lis. Two anodes made of ½" zinc plate were used and the cathode was of degreased mild steel which was anodically etched in 10% sulphuric acid prior to insertion in the bath. The electrolyte which was maintained at a pH of 3.7 and a temperature in the range 35–40° C. was maintained by continuous circulation of the solution through the cell. A current range 0–100 amps. (corresponding to a current density of 0–1450 a.s.f.) was passed through the cell and it was found that even at the higher current densities used, no burning of the deposit was apparent. Only inconsiderable dendritic growth took place, notably at the areas of high current densities. The electro deposit had a bright white lustrous finish which was not apparent when the boric acid was absent.

EXAMPLE III

An electrolyte similar to that described in Example II was used, except that gelatin (0.5 g./l.) was added. As in the preceding experiment, a bright lustrous deposit was obtained, but on this occasion dendritic growth was suppressed to such a degree as to be negligible. No burning was observed.

What I claim is:

1. An electrolyte solution for use in the electrodeposition of zinc which comprises an acidic aqueous solution of (A) zinc sulphamate in a concentration of 0.5 to 4 molar and (B) at least one additive selected from the group consisting of fluoroboric acid, soluble salts of fluoroboric acid, and a combination of boric acid and hydrofluoric acid; said additive being present in an amount such as to give a fluorine concentration as atomic fluorine corresponding to a concentration of 0.01 to 0.5 molar of fluoroboric acid.

2. A solution as claimed in claim 1 which contains zinc sulphamate in a concentration of 1–2 molar.

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3. A solution as claimed in claim 2 which contains fluoroboric acid in a concentration of 0.025 to 0.25 molar.

4. A solution as claimed in claim 3 which has a pH of from 3.6 to 3.8.

5. A solution according to claim 4 containing gelatin as a levelling agent, present in a concentration of from 0.05 to 1 gm. per litre.

6. A solution according to claim 4 which contains boric acid as a brightening agent present in a concentration of from 5 to 50 gms. per litre in addition to any boric acid present together with hydrofluoric acid in a molar ratio of substantially 1:4 as said component (B) of the solution.

7. A solution as claimed in claim 1 which contains an effective amount of a levelling agent selected from the group consisting of gelatin; glucose; starch; glue; goulac; polyethylene glycol; triethanolamine; gum of guar; fecula; products of the degradation of starch or fecula; gluten; casein; albumin; carboxymethyl cellulose; polyvinyl alcohols and alkali metal silicates.

8. A solution as claimed in claim 7 which contains an effective amount of a brightening agent selected from the group consisting of boric acid; aromatic and unsaturated aliphatic sulphonic acids and disulphonic acids and salts thereof; sulphonamides; sulphimides; alkyl sulphonic acids and alkali metal salts thereof; O-sulpho-benzaldehyde; formaldehyde; chloral hydrate; bromal hydrate; coumarin; and butyne-diol.

9. A solution as claimed in claim 1 which has a pH of from 3 to 4.

10. A solution as claimed in claim 1 which contains boric acid as a brightening agent, present in a concentration of from 5 to 50 gms. per litre in addition to any boric acid present together with hydrofluoric acid in a molar ratio of substantially 1:4 as said component (B) of the solution.

11. A process for the electrodeposition of zinc wherein zinc is electrodeposited from a solution as claimed in claim 1.

12. An electrolyte solution for use in the electrodeposition of zinc which comprises an acidic aqueous solution of from 0.5 to 4 moles per litre of zinc sulphamate; from 0.01 to 0.5 moles per litre of fluoroboric acid; from 1 to 75 gms. per litre of boric acid and from 0.1 to 1 gm. per litre of gelatin.

13. A solution as claimed in claim 12 having a pH of from 3 to 4.

14. A solution according to claim 13 containing zinc sulphamate in a concentration of 1–2 molar; and boric acid in a concentration of from 5 to 50 gms. per litre.

15. A process for the electrodeposition of zinc wherein zinc is electrodeposited from a solution as claimed in claim 12.

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