(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 492 790 A2**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **91310546.6**

(51) Int. Cl.[5]: **C25D 3/56**

(22) Date of filing: **14.11.91**

(30) Priority: **20.12.90 US 631474**

(43) Date of publication of application:
01.07.92 Bulletin 92/27

(84) Designated Contracting States:
DE ES FR GB

(71) Applicant: **MACDERMID INCORPORATED**
245 Freight Street
Waterbury, Connecticut 06702(US)

(72) Inventor: **Becking, Donald H.**
138 Tanglewood Drive
Southington, Connecticut 06489(US)

(74) Representative: **Pendlebury, Anthony et al**
PAGE, WHITE & FARRER 54 Doughty Street
London WC1N 2LS(GB)

(54) **Electroplating composition and process.**

(57) An electroplating composition for use in depositing bright zinc-cobalt alloys on a conductive substrate. 2-Naphthaldehyde or a substituted derivative thereof is incorporated in the compositions of the invention as brightening agent.

EP 0 492 790 A2

This invention relates to electroplating compositions and processes for their use and is more particularly concerned with compositions for electrodeposition of zinc-cobalt coatings on substrates and with processes employing such compositions.

The electrodeposition of zinc-cobalt alloys on metallic substrates such as iron, steel and like metals to provide increased corrosion resistance is finding increasing acceptance in the marketplace. Such alloys not only provide increased corrosion resistance compared to traditional zinc deposits, but have the additional advantage of exhibiting bright, aesthetically pleasing surfaces.

Various means of enhancing the brightness of zinc-cobalt alloys have been described in the art. Illustratively, Tremmel et al U.S. Patent No. 4,299,671 discloses the use of a complexing agent for zinc and cobalt ions. Martin U.S. Patent No. 4,401,526 discloses the use of derivatives of β -aminopropionic acid, including polymers thereof, as a brightening agent in a zinc-cobalt electrodeposition bath. Related Martin U.S. Patent No. 4,425,198 discloses the use as brightening agent of a soluble polyacrylamide, an N-substituted polyacrylamide derivative or copolymers thereof.

Verberne et al U.S. Patent No. 4,439,283 is particularly concerned with the electrodeposition of semi-bright to bright zinc-cobalt alloys on non-planar surfaces such as those of washers, screws, clips and the like. A mixture of additives such as benzylidene acetone, triethanolamine, N-allylthiourea and alkoxylated long chain acetylenic alcohols, is added to the electrodeposition bath. It has been found, however, that this process does not provide acceptable brightness to the zinc-cobalt alloy deposited in low current density areas. Further, the amount of cobalt in the deposit is limited to the order of about 1 percent by weight.

It has now been found that electrodeposits of zinc-cobalt alloys having improved brightness and having cobalt content up to about 1.5 percent by weight or higher can be provided by the use of novel additives as will be described in detail hereinafter.

According to the present invention there is provided a composition for the electrodeposition of zinc-cobalt alloy on a conductive substrate, the composition comprising a soluble source of zinc, a soluble source of cobalt, a soluble electrolyte and a brightening agent, characterised in that the brightening agent is 2-naphthaldehyde or a 2-naphthaldehyde having at least one substituent selected from hydroxy, halo, alkyl, aldehydo, sulfo (SO_3H) or dialkylamino.

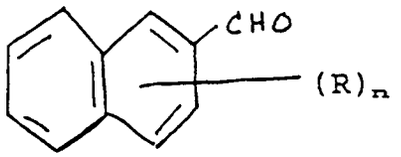
The invention also comprises a process for the electrodeposition of zinc-cobalt alloys on conductive substrates employing a composition of the invention as described above.

The term "halo" as used herein is inclusive of bromo, chloro and fluoro. The term "alkyl" as used herein is inclusive of alkyl groups having from 1 to 8 carbon atoms, inclusive of groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl and isomeric forms thereof. The term "dialkylamino" as used herein means an amino group substituted by two alkyl groups which may be the same or different and have the meaning defined above.

Electroplating baths for the electrodeposition of zinc-cobalt alloys generally comprise aqueous solutions containing a soluble source of zinc ions such as zinc chloride, zinc sulphate, zinc fluoborate, zinc acetate or mixtures of two or more of these salts, and a soluble source of cobalt ions such as cobalt sulfate, cobalt chloride, cobalt acetate, cobalt sulfamate or mixtures thereof. The baths also contain a soluble electrolyte such as ammonium chloride, potassium chloride, sodium chloride, ammonium acetate and the like. In general the amount of zinc ion present in the bath is within the range of about 10 g./liter to about 60 g./liter and, preferably, in the range of about 20 g./liter to about 50 g./liter. The amount of cobalt ion is generally within the range of about 7.5 g./liter to about 60 g./liter and, preferably in the range of about 10 g./liter to about 50 g./liter. The amount of soluble electrolyte present in the bath is generally such that the total anion electrolyte concentration is of the order of about 150 g./liter to about 300 g./liter.

In addition to the above components, the baths also generally contain a weak acid such as boric acid or an organic acid such as benzoic acid, cinnamic acid, or the like at a level of about 10 g./liter to about 25 g./liter. The baths also contain additives, such as surfactants, brightening agents and the like.

The principal feature of the present invention relates to the use of a new class of brightening agents which can be used as the sole brightening agents but are preferably employed in admixture with one or more of the brightening agents hitherto employed in the art. The novel brightening agents of the present invention comprise 2-naphthaldehyde and substituted 2-naphthaldehydes having the formula:



(I)

wherein R is selected from hydroxy, halo, alkyl, aldehydo, sulfo and dialkylamino, and n is an integer from 1 to 3. Illustrative of substituted 2-naphthaldehydes of the above formula(I) are 3-hydroxy-, 4-chloro-, 5-chloro, 7-bromo-, 6-fluoro-, 5-hydroxy, 3,4-dibromo-, 5,7-dimethyl, 7-isopropyl, 6-hexyl- and 7-octyl-, 7-sulfo- and 7-dimethylamino-2-naphthaldehyde, and the like.

When employed as the sole brightening agent the 2-naphthaldehyde or substituted derivative thereof (I) is advantageously employed in a concentration of about 0.5 mg./liter to about 20 mg./liter and preferably from about 4 mg./liter to about 12 mg./liter. When employed in admixture with one or more known brightening agents the 2-naphthaldehyde or derivative thereof (I) is advantageously employed in a concentration of at least about 0.5 mg./liter up to about 15 mg./liter and preferably in the range of about 1 mg./liter to about 5 mg./liter. The appropriate concentration to employ in any given instance can be determined readily by a process of trial and error.

Illustrative of known brightening agents which can be employed in admixture with the novel agents of the invention are benzylidene acetone, alkali metal salts of 3-(2-benzothiazolethio) propane sulfonic acid (also known as "BPS"), and aminotriglycerol [tri(2,3-dihydroxypropyl) amine]. Particularly useful combinations of brightening agents in accordance with the invention are (a) 2-naphthaldehyde and BPS, wherein the former is present in a concentration of 1 mg./liter to about 15 mg./liter and the latter in concentrations of 1 mg./liter to about 10 mg./liter; (b) 2-naphthaldehyde, BPS and benzylidene acetone, wherein the concentration of the first two named components is within the ranges given for mixture (a) and the benzylidene acetone is employed in a concentration of 10 mg./liter to 50 mg./liter; and (c) 2-naphthaldehyde and aminotriglycerol, wherein the former is present in a concentration of 1 mg./liter to 5 mg./liter and the latter is present in a concentration of 4 g./liter to 40 g./liter.

It has been found surprisingly that the isomeric 1-naphthaldehyde and substituted derivatives thereof corresponding to the compounds of formula (I) do not possess any significant properties as brightening agents in direct contrast to the compounds employed in the present invention.

The electroplating baths of the invention also contain a surfactant or mixture of surfactants which can be any of those conventionally employed in the art. Illustrative of non-ionic surfactants which are particularly useful in baths in accordance with the present invention are sulfamated alkoxylated bisphenol A which are described in U.S. 4,592,809, incorporated herein by reference. The latter surfactants are advantageously employed in concentrations of the order of about 4 to about 10 g./liter or higher and preferably from about 6 to about 8 g./liter. Other non-ionic surfactants which can be employed are inclusive of polyalkoxylated glycerols such as polyethoxylated glycerol. Mixtures of two or more non-ionic surfactants can be employed.

The electroplating baths of the invention may also comprise any of the wetting agents conventionally employed in the art. A particularly useful wetting agent is an alkali metal salt of a perfluoromethylcyclohexylsulfonic acid.

The electroplating bath compositions of the invention are employed to apply coatings of zinc-cobalt alloys to workpieces using procedures well-known in the art. Illustratively, a workpiece is made the cathode in a bath having a composition in accordance with the invention and an anode is provided which can be composed, for example, of carbon. A voltage is applied across the anode and cathode and electroplating is continued until the desired thickness of zinc-cobalt has been deposited on the workpiece. The bath is generally operated at a pH in the range of about 5 to about 6 and a temperature within the range of about 32 °C to about 40 °C. It is found that the coating of zinc-cobalt deposited on a workpiece is highly pleasing to the eye and is uniform in thickness and brightness including those portions which have been deposited in low current density areas. The latter areas have been troublesome hitherto particularly in the coating of workpieces having non-planar surfaces, for example, threaded areas of bolts, inner rims of washers and the like.

The following examples serve to illustrate the compositions and process of the invention including the best mode presently known to the inventors but are not to be construed as limited.

Example 1

An electroplating bath in accordance with the invention was prepared by dissolving the following ingredients in water in the proportions stated to provide a bath having a volume of 1 liter.

Ingredients	Pts by weight
zinc chloride	45 g.
cobalt chloride hexahydrate	37 g.
ammonium chloride	85 g.
potassium chloride	50 g.
ammonium acetate	15 g.
boric acid	20 g.
sulfamated bisphenol-A ethoxylate[1]	8 g.
sulfoalkylated polyalkoxylated naphthol[2]	0.5 g.
aminotriglycerol	4 g.
benzylidene acetone	30 mg.
BPS	3 mg.
2-naphthaldehyde	3 mg.

[1] synFAC 8118 : Milligan Chemical Company
[2] RALUFON NAT 14-90 : Raschig Chemical Company

The pH of the bath was 5.5. A Hull cell was electroplated as cathode using a zinc anode at a current density of 20 amperes per sq.ft. and a bath temperature of 35 ° C for 10 minutes. The deposit of zinc-cobalt alloy on the Hull cell had an average thickness of 0.5 mils and was uniformly bright from edge to edge. The cobalt content of the layer was determined at a series of random portions of the coating and found to range from a low of 0.6 to a high of 1.5% by weight.

Example 2

A bath was prepared exactly as described in Example 1 except that the 2-naphthaldehyde was replaced by an equal proportion of 1-naphthaldehyde. A Hull cell was plated under the same conditions and for the same time using the bath so prepared. The plating so produced was characterized by dark gray portions in the low current density areas.

Example 3

An electroplating bath in accordance with the invention was prepared by dissolving the following ingredients in water in the proportions stated to provide a bath having a volume of 1 liter and a pH of 5.3.

zinc chloride	50 g.
cobalt chloride	50 g.
ammonium chloride	85 g.
potassium chloride	50 g.
boric acid	20 g.
aminotriglycerol	10 g.
benzylidene acetone	50 mg.
2-naphthaldehyde	6 mg.

A Hull cell was electroplated in the bath so prepared using the same conditions and procedure as described in Example 1 except for the current density which was 2 amps per square foot. The coating of zinc-cobalt alloy on the Hull cell was ductile and bright in all areas except for an 1/8 inch gray band in the low current density area. An 1/8 inch burn was observed in the high current density area.

Example 4

Another electroplating bath in accordance with the invention was prepared by dissolving the following ingredients in water in the stated proportions to provide a bath having a volume of 1 liter and a pH of 5.6.

zinc sulfate	50 g.
cobalt sulfate	50 g.
ammonium chloride	85 g.
potassium chloride	50 g.
ammonium acetate	10 g.
triethanolamine	15 g.
2-naphthaldehyde	10 mg.
BPS	5 mg.

A Hull cell was electroplated in the bath so prepared using the same conditions and procedure as described in Example 1 except for the temperature (40 ° C) and current density (2 amps/sq.ft.). The zinc-alloy coating deposited on the Hull cell was ductile and of excellent brightness except for a 1/4 inch gray band in the low current density edge.

Claims

1. A composition for electrodeposition of a zinc-cobalt alloy on a conductive substrate, the composition comprising a soluble source of zinc, a soluble source of cobalt, a soluble electrolyte and a brightening agent, characterised in that the brightening agent is 2-naphthaldehyde or a 2-naphthaldehyde having at least one substituent selected from hydroxy, halo, alkyl, aldehydo, sulfo or dialkylamino.

2. A composition according to claim 1, which also comprises benzylidene acetone in an amount of from about 10 to about 50 mg/liter.

3. A composition according to claim 1 or 2, which also comprises 3-(2-benzothiazolethio) propane sulfonic acid alkali metal salt in an amount from about 1 to about 10 mg/liter.

4. A composition according to any one of the preceding claims, wherein the brightening agent comprises a mixture of 2-naphthaldehyde, benzylidene acetone, and 3-(2-benzothiazolethio) propane sulphonic acid alkali metal salt.

5. A composition according to any one of the preceding claims, which also comprises aminotriglycerol.

6. A composition according to claim 5, wherein the amount of amino-triglycerol is from about 4 to about 40g/liter.

7. A composition according to any one of claims 1 to 3, wherein the brightening agent comprises a mixture of 2-naphthaldehyde, benzylidene acetone and aminotriglycerol.

8. A composition according to any one of the preceding claims, which also comprises a surfactant.

9. A composition according to claim 8, wherein the surfactant comprises a sulfamated alkoxylated bisphenol A.

10. A composition according to claim 9, wherein the surfactant is a sulfamated ethoxylated bisphenol A.

11. A composition according to any one of claims 7 to 10, further comprising a polyethoxylated glycerol as surfactant.

12. A process for producing a zinc-cobalt electrodeposit on a conductive substrate, which process comprises the steps of immersing the substrate and an anode in a bath having a composition as claimed in any one of the preceding claims, and applying a voltage across the anode and the substrate for a period of time sufficient to deposit the desired thickness of a zinc-cobalt electrodeposit on the substrate.