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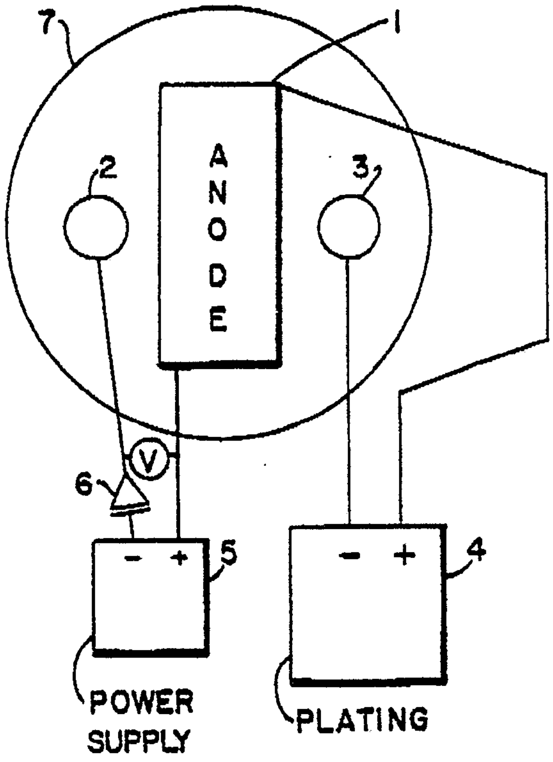
(54) Inhibiting corrosion of lead or lead-alloy anodes in a chromium electroplating bath.

(57) To inhibit anode corrosion, electroplating apparatus includes an anode protection circuit with an auxiliary power supply (5) for applying a protective potential, less than the plating potential and at a much lower current, to the anode (1). The protective potential is desirably applied through an auxiliary cathode (2) near the anode (1), and advantageously is left on when plating is not taking place.



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INHIBITING CORROSION OF LEAD OR LEAD-ALLOY ANODES IN A CHROMIUM ELECTROPLATING BATH

This invention relates to the electrodeposition of chromium, using lead or lead-alloy anodes, and, more particularly, to a chromium-plating bath apparatus and process, in which the weight loss of such lead anodes is substantially reduced.

Chromium-plating baths using chromic-acid solutions as the source of chromium almost invariably employ lead or lead-alloy anodes. However, as described in "The Electrochemistry of Lead" by A.T. Kuhn, Academic Press (1979), pages 405-407, lead and lead-alloy anodes corrode to a soluble species (leading to anode weight loss) in chromic-acid solutions. This anode dissolution proceeds at a substantial rate, the rate being proportional to the acidity of the solution. Because of this, there has been a need to find corrosion-resistant alloys for this medium. For example, alloys containing 10% tin and 0.5% cobalt appear to show good resistance. The addition of one to two grams per liter (g/l) of Co^{2+} ions also may reduce anode corrosion.

While this anode-corrosion problem is present in both conventional hexavalent chromium plating baths and in the mixed-catalyst chromium baths, it is particularly acute in high- energy-efficient baths, e.g. the so-called "HEEF-25" baths, as described in European Parent 196053. "HEEF" is a registered trademark of M & T Chemicals, Inc., Rahway, New Jersey. HEEF-25 baths comprise chromic acid, sulfate and an alkyl sulfonic acid, which, for functional chromium deposits, is preferably a non-substituted alkyl sulfonic acid, or salt thereof, wherein the ratio of sulfur to carbon is $\geqq 1/3$. Typical alkyl sulfonic acids are methyl sulfonic acid, ethyl sulfonic acid, propyl sulfonic acid, methane disulfonic acid and 1,2-ethane disulfonic acid.

Other hexavalent chromium plating baths are described in, e.g., the following U.S. Patents: 3,745,097 to Chessin et al., issued July 10, 1973; 3,654,101 to Aoun, issued April 4, 1972; 4,450,050 to Chessin et al., issued May 22, 1984; and 4,472,249 to Chessin, issued September 18, 1984. All of the foregoing patents are assigned to the present applicant.

The present invention seeks to reduce the problem of anode corrosion.

Accordingly, the invention provides a chromium-plating system which significantly reduces the conversion of a lead or lead-alloy anode used in that system to a soluble species, comprising an anode-protection circuit for applying a protective potential on said anode, the potential being less than the potential required for normal electrodeposition of chromium on said anode. The electroplating bath of this invention may be the conventional mixed-catalyst or alkyl sulfonic-acid-containing (HEEF-25) chromium-electroplating type. In one embodiment, an auxiliary cathode is provided near the anode, and the desired voltage is imposed on the anode.

Further explanation, a description of preferred features, and examples now follow with reference to the drawing which is a schematic diagram of a chromium-electroplating system embodying the present invention.

During electrodeposition of chromium, the surface of the lead or lead-alloy anode used therein is oxidized to a film of lead dioxide on the anode, which stabilizes the anode during the process. However, when the current is turned off, i.e. during periods of non-plating, this protective lead dioxide film can be reduced to a lead (II) oxide species by the lead anode, or by trivalent chromium in solution, producing chromate ions. Subsequently, the lead (II) oxide may react with the chromate ions to form insoluble lead chromate. If the lead oxide and lead chromate materials are as adherent on the lead anode as the lead dioxide film, very little corrosion of the anode will occur. However, if these species flake off the anode and fall into the bath, fresh lead-anode surface is exposed, and further corrosion can occur.

Where an alkyl sulfonic acid, e.g. methane sulfonic acid, is present in the bath, an additional solubilizing reaction can take place in which the lead (II) oxide forms a soluble species directly. These reactions occur rapidly during periods of non-plating; when the plating current is turned on, the lead (II) oxide on the anode can be reoxidized to lead (IV) dioxide, and very little corrosion will occur. It is known in the art that lead (II) species which are not in electrical contact with the anode cannot be reoxidized, and are therefore lost from the anode.

In this invention, the formation of lead (II) species is slowed by anodic protection during periods of non-plating, thereby slowing anodic solubilizing corrosion and anode-weight loss. Anodic protection is preferably achieved in the electroplating system of the invention by providing an auxiliary, or dummy, cathode positioned near the anode, and imposing a predetermined low voltage between that cathode and the anode at a low current. This voltage is less than the operational potential between the anode and the substrate cathode, which would otherwise result in electrodeposition of chromium. In this manner, an anodic or oxidizing potential is maintained around the beneficial lead (IV) dioxide film on the anode, to prevent its reduction to a lead (II) species.

In the course of investigating the parameters of the present system, it has been surprisingly discovered that anodic protection is obtained by applying a voltage of less than the plating voltage to the anode. For instance, potentials of from about 1.8 to about 2.2 volts (v.) at currents of from about 0.01 to about 0.3% of normal chromium electroplating currents were found to be useful in reducing solubilizing corrosion of lead and lead-alloy anodes. Further, the protective current can be applied both while the bath is in operation and while the plating current is off, such as overnight.

Referring now to the drawing, there is shown a conventional electrodeposition system including plating anode 1. It is seen that the auxiliary circuit of the embodiment includes an auxiliary cathode 2, which can be a chromium-plated rod, positioned near the anode 1 and connected in series therewith through an auxiliary power supply 5. A rectifier or diode 6 is included in the auxiliary circuit to permit the auxiliary circuit to be left on even during electroplating. A dummy cathode and plating rectifier, in combination, can also be used.

In operation, an anodic protection voltage of less than the normal plating potential, about 2.8 v. is applied between the auxiliary cathode and the anode. Preferably a potential of at least 2 v. is applied, at less than 0.02% of the plating current. For example, a voltage of 2.0 v. for 1500 amp-hr provides a 10-20% improvement in Pb- 7% Sn anode corrosion, as determined by weight loss, while 2.15 v. at less than 0.1% of the plating current results in a 35-55% reduction in the anode corrosion (mass loss) in a HEEF-25 chromium plating bath, as compared to 1500 amp-hr of plating without the auxiliary protection circuit.

The presence of the diode in the auxiliary circuit prevents current flow to the auxiliary cathode during the plating cycle. The following examples illustrate the efficacy of the present invention.

EXAMPLE 1

The anode-protection circuit of Figure 1 was used and the auxiliary power supply was kept on even when plating was not occurring. The diode was a three-ampere (amp) 50 peak-inverse-voltage epoxy type with a voltage drop of about 0.5 v. The power supply was about 0.5 v higher than the voltage at the voltmeter indicated as V in the drawing. A low-ripple rectifier was used for plating (Hewlett-Packard 6268B, 40 v, 30 amp) and for the auxiliary circuit (Hewlett-Packard, 6200B, 20 v, 1.5 amp).

The auxiliary voltage was controlled at 2.0 and 2.15 v. in two separate experiments. Each test lasted for 1500 amp-hr (about one month), and the anodes were weighed four times during the experiments after a plating cycle. A thin brown film wad rubbed off the anodes prior to weighing. During the day, plating was cycled on and off every 30 minutes. Plating, heating and stirring were turned off at night. Chromic acid was replenished during the tests. Seven liters of HEEF-25 plating solution (containing 250 grams/liter [g/l.] of chromic acid and 3.5 g/l. of methyl sulfonic acid and 2.5 g/l. of sulfate ion) were prepared at the start of each experiment, and the solution divided into two 4-liter beakers. The anodes were 15 centimeter [cm] x 7.6 cm x 1 cm) Pb 7% Sn, With 12.7 cm x 7.6 cm x 1 cm in the solution. About 225 cm^2 of anode were in the solution. The cathodes were 0.95-cm diameter drill rods. The auxiliary cathode was a chromium-plated rod, and was not cleaned or changed during the test. The results are shown in Tables 1 and 2.

TABLE I

0.02% OF PLATING CURRENT at 2.0 VOLTS					
Amp.Hr.	Anode Mass, g.		Mass Loss, g.		Corrosion Difference, Per Cent
	Control	Test	Control	Test	
0	1144.1	1142.8	--	--	--
572	1134.6	1135.1	9.5	7.7	18.9
896	1128.1	1129.4	16.0	13.4	12.3
1477	1115.6	1118.0	28.5	24.8	11.4

TABLE 2

0.1% OF PLATING CURRENT at 2.15 VOLTS					
Amp/Hr.	Anode Mass, g.		Mass Loss, g.		Corrosion Difference, Per Cent
	Control	Test	Control	Test	
0	1107.0	1109.2	--	--	--
508	1098.8	1103.9	8.2	5.3	35
1014	1088.5	1098.0	18.5	11.2	43
1688	1076.0	1092.4	31.0	16.8	55

Table 1 demonstrates that with anodic protection of 2.0 v. less than 0.02% of the plating current, the test anode corroded 10 to 20% less than the control anode. Table 2 shows that at 2.15 v. less than 0.1% of the plating current, the test anode corroded 35 to 55% less than the control anode. It is seen, therefore, that anodes with protection showed a mass loss of up to about half that found with anodes used without protection. In both determinations, the control anodes corroded at the same rate within 1%.

Having described preferred embodiments of the invention, those skilled in the art will realize that the present invention should not be limited only thereto.

Claims

1. Apparatus for chromium electroplating comprising a lead or lead-alloy anode (1), a cathode (3), and means (4) for applying an electroplating potential and current to an article to be plated, characterised in that it has anode protection means comprising a circuit (2,5,6) for applying a protective potential, less than the normal electroplating potential, on said anode (1) to inhibit corrosion thereof.

2. Apparatus according to claim 1 wherein the anode protection means are adapted to apply the protective potential at a low current.

3. Apparatus according to claim 2 wherein said low current is from about 0.01 to about 0.3% of the electroplating current.

4. Apparatus according to claim 3 wherein said low current is about 0.02% of the electroplating current.

5. Apparatus according to any one of the preceding claims, wherein the anode protection circuit is adapted to apply the protective potential when electroplating is not taking place.

6. Apparatus according to any one of the preceding claims wherein the anode protection circuit comprises a rectifier.

7. Apparatus according to claim 6 wherein the rectifier comprises a diode.

8. Apparatus according to any one of the preceding claims wherein the anode protection circuit was adapted to apply a protective potential of from about 1.8 to about 2.2 volts.

9. Apparatus according to claim 8 wherein the anode protection circuit is adapted to apply a protective potential of from about 2.0 to about 2.15 volts.

10. Apparatus according to any one of the preceding claims wherein the anode protection circuit is an auxiliary circuit.

11. Apparatus according to any one of the preceding claims wherein the anode protection circuit comprises an auxiliary cathode (2).

12. Apparatus according to claim 11 wherein the anode protection circuit comprises an auxiliary power supply (5) operable at low voltage and current.

13. A method of inhibiting corrosion of a lead or lead-alloy anode (2) in a chromium electroplating system, characterised by applying a protective potential, less than the normal plating potential, on the anode.

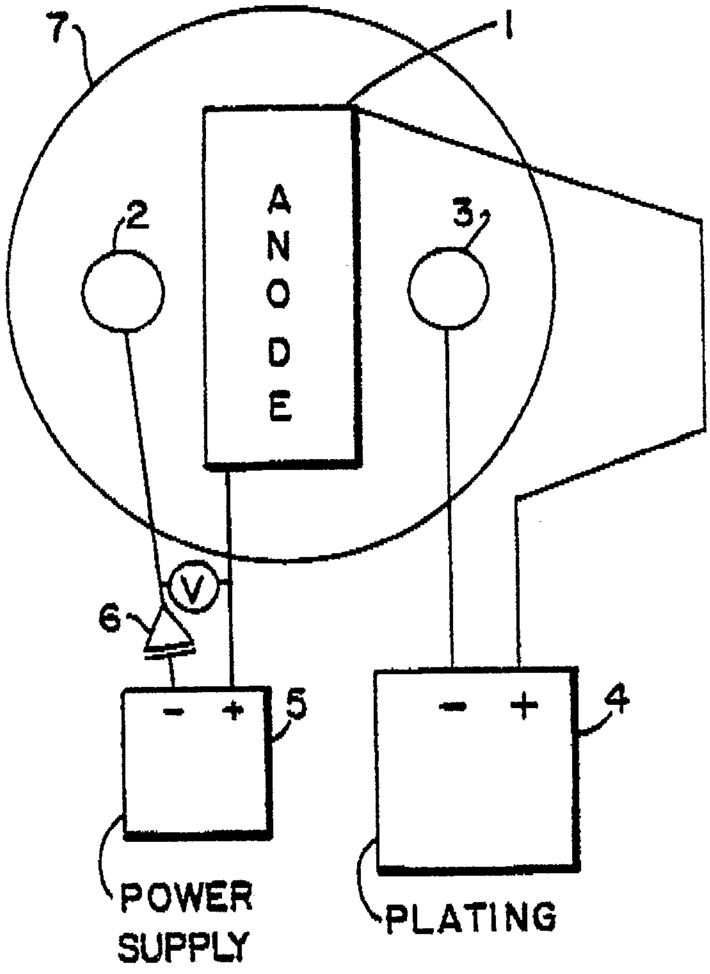
14. A method according to claim 13 in which the protective potential is supplied at a low current.

15. A method according to claim 14 in which the current is from about 0.01 to about 0.3% of the normal electroplating current.

16. A method according to any one of claims 13 to 15 in which the protective potential is from about 1.8 to about 2.2 volts.

17. A method according to any one of claims 13 to 16 wherein the protective potential is applied when electroplating is not taking place.

18. A method according to any one of claims 13 to 17 wherein the protective potential is applied between the anode (1) and an auxiliary cathode (2).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