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ELECTRODEPOSITION OF CHROMIUM

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This invention relates to electrodeposition of chromium and more specifically to the prevention of anode sludging in chromium plating processes utilizing lead anodes and an aqueous solution principally consisting of chromic acid and a catalytic agent containing an anion the lead salt of which is soluble.

It has been found in practice that catalytic agents such as acetate ions, fluosilicate ions or fluoborate ions are useful but tend to increase lead anode sludging.

It has now been discovered in accordance with the present invention that such tendency to lead anode sludging can be reduced by the inclusion of a cobaltous compound in the plating solution. The tendency to increased lead anode sludging results from the fact that the lead salts of the catalytic agents are soluble. Surprisingly, the cobalt is not deposited on the cathode in the presence of the other bath constituents, even when much larger concentrations are added than are contemplated by the present invention. Relatively small concentrations of cobalt are thus able to contact the anode and exert the beneficial effect. It is not know how the cobalt acts but it is thought probable that the cobaltous ion is oxidized at the anode and forms a protective, thin film of insoluble cobaltic compound.

The basic bath in which it is contemplated the invention will be realized is one containing in addition to water, chromic acid and the catalyst. Sulfate ion may also be present but it is not essential. Chromic acid may be present to the extent of from 100 to 700 grams per liter, the sulfate ion may be present in concentration from zero to about 1.0% preferably from 0.1% to 1.0% of the chromic acid by weight and the catalyst may be an anion whose lead salt is soluble in the bath and may be present in concentration from about 0.7% to about 40% of the weight of the chromic acid. To the basic solution is added a cobaltous compound supplying cobaltous ion in concentration from about 0.4 to about 5 grams per liter. Examples of catalyst which may be utilized are acetate ion, fluosilicate ion and fluoborate ion. These various ions may be supplied by addition of various salts. In the case of acetate, fluosilicate and fluoborate ions, the sodium salts are convenient. In the case of the cobaltous ion, it is desirable to use the cobalt salt of one of the ions already in the bath. Specific examples of cobaltous compounds which may be employed are the acetate, sulfate, fluoborate, fluosilicate and carbonate. Nickel acetate was tried and found not to be effective. The temperature of operation preferably is 60° F. to 145° F., and the cathode current density preferably is from 90 to 600 amperes per square foot.

Very excellent bath formulations are those falling in the following ranges:

CrO_3	From 200 to 400 grams per liter.
Catalyst ion[1]	From 3% to 20% of the weight of the CrO_3.
Sulfate ion	From 0.5% to 1.0% of the weight of the CrO_3.
Cobaltous ion	From 1.0 to 3.0 grams per liter.
Temperature	75° F. to 90° F.
Cathode current density	200 to 250 A. S. F.
Anode	Lead.

[1] For example, acetate, fluoborate, fluosilicate.

Specific examples of solutions in accordance with the invention are as follows:

Example I

CrO_3	g./l.	250
HBF_4 (47%)	cc./l.	6
$CoCO_3$	g./l.	2.42
H_2O		Remainder

Example II

CrO_3	g./l.	250
H_2SiF_6 (30%)	cc./l.	20
$CoCO_3$	g./l.	2.42
H_2O		Remainder

Example III

CrO_3	g./l.	250
SO_4	g./l.	1.5
$NaC_2H_3O_2$	g./l.	55
$Co(C_2H_3O_2)_2$	g./l.	5
H_2O		Remainder

Electrolyzing the above solution under the conditions indicated above, good deposits can be produced consistently and lead anode sludging is at a minimum. The term "lead anode" as used herein includes pure lead anodes and anodes principally composed of lead but containing minor quantities of other elements.

The following tests indicate the degree of reduction of sludging by the use of the invention. Using the bath of Example I and a lead alloy anode containing minor quantities of antimony, tin and tellurium which sludges less than pure lead, the amount of sludge formation per 336 ampere hours was 0.1 gram. Omitting cobalt, the amount was 1.75 grams. Utilizing the bath of Example II with the same alloy anode, the sludge formation was 0.2 gram per 336 ampere hours. Omitting the cobalt, the sludge formation was 1.7 grams per 336 ampere hours. Utilizing the bath of Example III, with the same alloy anode, the sludging was 1.6 grams per 336 ampere hours. Omitting the cobalt, it was 36.1 grams per 336 ampere hours. With a chemical (pure) lead anode, the sludging amounted to 59.3 grams per 336 ampere hours.

The standard chromium plating bath, not containing the catalysts such as acetate ion, fluosilicate ion or fluoborate ion does not sludge badly with chemical lead anodes. Omitting the cobalt and the catalyst from Example I and using a chemical lead anode, the sludging amounted to 1.1 grams per 336 ampere hours. A lead-silver anode containing 2% silver was found to be very

resistant to sludging, yielding with the bath of Example III only 0.55 gram of sludge per 336 ampere hours, but far more expensive than the use of cobalt.

The terms "catalyst" "catalytic agent" and "catalytic ion" and similar terms employed herein will be understood as having reference to acid radicals customarily employed in chromic acid plating solutions to permit the plating of chromium from the solution without themselves being consumed by the reaction.

Having thus described my invention, what I claim is:

1. In a process of chromium plating from a solution comprising water, chromic acid, sulfate ion and a catalytic ion selected from the group consisting of acetate, fluosilicate and fluoborate ions, the method of reducing the quantity of anode sludge formation when electrolyzing said solution between a lead anode and a cathode to be coated comprising incorporating cobaltous ion in said solution in concentrations from about 0.4 to about 5.0 grams per liter.

2. In a process of chromium plating from a solution comprising water, chromic acid in concentrations from about 100 to about 700 grams per liter and a catalytic ion of the class consisting of acetate, fluosilicate and fluoborate ions in concentrations from about .7% to about 40% by weight of the chromic acid, the method of reducing the quantity of anode sludge formation when electrolyzing said solution between a lead anode and a cathode to be coated comprising incorporating cobaltous ion in said solution in concentrations from about 0.4 to about 5.0 grams per liter.

3. In a process of chromium plating from a solution comprising water, chromic acid in concentrations from about 100 to about 700 grams per liter, sulfate ion in concentrations from about 0.1 to about 1.0% by weight of the chromic acid, and a catalytic ion selected from the class consisting of acetate, fluosilicate and fluoborate ions in concentrations from about .07% to about 40% by weight of the chromic acid, the method of reducing the quantity of anode sludge formation when electrolyzing said solution between a lead anode and a cathode to be coated comprising incorporating cobaltous ion in said solution in concentrations from about 0.4 to about 5.0 grams per liter.

4. In a process of chromium plating from a solution comprising water, chromic acid in concentrations from about 200 to about 400 grams per liter, sulfate ion in concentration from about 0.5% to about 1.0% by weight of the chromic acid, and a catalytic acetate ion in concentrations from about 3.0% to about 20% by weight of the chromic acid, the method of reducing the quantity of anode sludge formation when electrolyzing said solution between a lead anode and a cathode to be coated comprising incorporating cobaltous ion in said solution in concentrations from about 1.0 to about 3.0 grams per liter.

5. In a process of chromium plating from a solution comprising water, chromic acid, sulfate ion and a catalytic ion selected from the group consisting of acetate, fluosilicate and fluoborate ions, the method of reducing the quantity of anode sludge formation when electrolyzing said solution between a lead anode and a cathode to be coated comprising incorporating cobaltous ion in said solution in concentrations from about 1.0 to about 3.0 grams per liter.

6. In a process of chromium plating from a solution comprising water, chromic acid in concentrations from about 200 to about 400 grams per liter, sulfate ion in concentrations from about 0.5% to about 1.0% by weight of the chromic acid, and a catalytic ion of the class consisting of acetate, fluosilicate and fluoborate ions in concentrations from about 3% to about 20% by weight of the chromic acid, the method of reducing the anode sludge formation when electrolyzing said solution between a lead anode and a cathode to be coated comprising incorporating cobaltous ion in said solution in concentrations from about 1.0 to about 3.0 grams per liter.

7. In a process of chromium plating from a solution comprising water, chromic acid in concentrations from about 200 to about 400 grams per liter, and a catalytic ion of the class consisting of acetate, fluosilicate and fluoborate ions in concentrations from about 3% to about 20% by weight of the chromic acid, the method of reducing the quantity of anode sludge formation when electrolyzing said solution between a lead anode and a cathode to be coated comprising incorporating cobaltous ion in said solution in concentrations from about 1.0 to about 3.0 grams per liter.

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