United States Patent Office 2,737,485 Patented Mar. 6, 1956

2,737,485

ELECTRODEPOSITION OF COPPER

Dwight M. Overcash, Elyria, and Richard B. Parks, Lorain, Ohio, assignors to General Motors Corporation, Detroit, Mich., a corporation of Delaware

No Drawing. Application September 22, 1952, Serial No. 310,926

12 Claims. (Cl. 204—52)

This invention relates to improvements in the electrodeposition of metals and more particularly to the electrodeposition of copper.

Cyanide type copper plating baths are widely used in the plating industry. These baths generally comprise or are composed essentially of an aqueous solution of a free alkali metal cyanide (usually sodium cyanide or potassium cyanide), copper cyanide and an alkali metal hydroxide (usually sodium hydroxide or potassium hydroxide). During operation these baths have sodium carbonate and/or potassium carbonate formed therein.

We have now discovered that extremely smooth copper deposits having a greatly improved brightness may be electrodeposited from conventional cyanide type copper plating baths which contain as addition agents small amounts of selenium, lead and zinc.

While copper electrodeposits having an improved brightness may be obtained according to the present invention by employing an electrolyte composed essentially of a conventional cyanide type copper plating bath and small amounts of selenium, lead and zinc, very beneficial results are obtained if the bath contains, in addition, small amounts of di-potassium tartrate.

In a preferred embodiment, optimum results are obtained if the cyanide copper bath contains a small amount of a wetting agent. The presently preferred wetting agents are those of the quaternary amine type.

While such a bath, of course, may be operated satisfactorily in various ways, we have found that most satisfactory results are obtained if an electrolyte, as described above, is employed in a copper plating process which utilizes an interrupted plating current cycle wherein the plating current is applied and then interrupted periodically according to a predetermined time cycle and this cycle repeated until the desired thickness of copper has been electrodeposited.

The following is illustrative of an aqueous cyanide type copper plating bath which may be employed in the practice of the present invention:

Copper	5 to 8 ounces per gallon.
KCN (free)	0.75 to 1.5 ounces per gallon.
KOH	5 to 6 ounces per gallon.
Carbonates	Up to saturation.

It will be understood, of course, that the above quantities are illustrative of typically practicable amounts and that in certain cases it may be desirable to vary these amounts. As is well known, the potassium hydroxide in the above bath composition, may be replaced by sodium hydroxide and the potassium cyanide may be replaced by sodium cyanide. In the practice of the present invention, selenium, lead and zinc are added to a cyanide type copper plating bath, such as described above, in amounts about as follows:

	Ounces per gallon
Selenium	0.0005 to 0.002
Lead	0.0005 to 0.002
Zinc	0.05 to 0.15

It is desirable to maintain the concentrations of the selenium, lead and zinc within the above mentioned ranges. These materials may be added to the cyanide bath either as metals or, if desired, in the form of compounds of selenium, lead or zinc which are soluble in and compatible with the bath. If the materials are added to the bath in the form of compounds of selenium, lead or zinc it will be understood, of course, that the above mentioned concentrations may be supplied by using a sufficient amount of the metallic compounds to provide in solution the desired amount of metals. For example, zinc compounds which are compatible with the bath and soluble therein and may be added to provide the required amount of zinc are: Zinc oxide, zinc cyanide, zinc hydroxide and sodium zincate.

The lead may be added in the form of various lead compounds illustrative of which are lead oxide, lead carbonate or lead cyanide. We have found that the proper amount of lead is maintained in the bath when the lead is added as a solution of basic lead carbonate in caustic soda and tartaric acid so that one ounce per gallon of basic lead carbonate is added for every 3000 ampere hours of bath operation.

The selenium may be added to the bath in the form of selenium compounds such as selenium dioxide, sodium selenite or potassium selenite. Very satisfactory results have been obtained when the selenium is added to the bath, when needed, in amounts of about 0.0001 ounce per gallon.

The addition of up to about five ounces per gallon of di-potassium tartrate or a sufficient amount of tartaric acid and potassium hydroxide which will react to provide up to about five ounces per gallon of di-potassium tartrate improves the anode corrosion and provides an electrolyte which may be operated at 100% cathode efficiency to preclude the possibility of obtaining roughened electrodeposits due to gassing at lower cathode efficiencies. Most satisfactory results are obtained when the di-potassium tartrate is present in an amount within the range of about 0.1 to 3 ounces per gallon.

Optimum results are obtained when a wetting agent is employed. The presently preferred wetting agent is a quaternary amine material. Particularly good results have been obtained using a quarternary amine wetting agent such as C-decyl betaine or a mixture of C-decyl betaine and trimethyl benzyl ammonium chloride. Most satisfactory results have been obtained when a quaternary amine wetting agent is used in an amount within the range of from 1 to 10 cubic centimeters per gallon of solution.

Baths having composition as described above may be operated satisfactorily with anode of copper, copper alloys or other conventional anode materials. If desired, the bath also may be operated using inert anodes if the concentration of copper in the bath is properly maintained.

Baths embodying the present invention may be operated over a wide range of temperatures, for example, at a temperature within the range of about 70° F. to 200° F. with a temperature in the range of 145° F. to 160° F. being preferred.

Current densities up to 100 amperes per square foot are practicable in a well agitated solution with 15 amperes per square foot illustrative of an average current density.

Most satisfactory results are obtained in plating copper having a greatly improved brightness employing baths as described above when the copper is electroplated from such a bath using an interrupted plating current cycle. In such a method the plating current is caused to pass through the plating solution to the article being plated as a cathode for a time ranging from about one-fourth of a second to as high as about 30 seconds. The flow of

current is then broken or interrupted from a time ranging from about one-tenth of a second to as high as around 4 to 5 seconds. The cycle is repeated as many times as is needed to obtain the desired thickness of copper. Typical of a suitable interrupted current cycle is a cycle in which the plating current is on for 4 seconds and then off for one-half second, a cycle in which the current is on for 6 seconds and then off for one second or a cycle in which the current is on for 7 seconds and then off for 2 seconds.

The following is a specific and illustrative example of a suitable aqueous plating bath in which the quantities are in ounces per gallon of solution unless otherwise specified:

Copper	6
KCN (free)	1.4
Na_2CO_3	At least 12
KOH	6
$PbCO_3$	0.001
SeO_2	0.001
Zinc	0.1
Di-potassium tartrate	2.5
Dupont #1085 cc./gallon	8

The above bath provides a copper electrodeposit having a greatly improved brightness when operated at an average current density of about 15 amperes per square foot using copper anodes and an interrupted current cycle of, for example, 6 seconds on and 1 second off, repeating the cycle until a sufficient thickness of copper has been electrodeposited.

A plating bath embodying the present invention may be employed to produce improved electrodeposits of copper when the base member is formed of any material which is conventionally electroplated such as iron, steel, nickel, zinc,, lead, copper or alloys thereof, etc.

As is conventional in commercial copper plating practice the base articles may have an initial flash coating of copper applied thereto before the article is electroplated using a bath embodying the present invention.

The following is a specific and illustrative example of the presently preferred method of electrodepositing copper according to the present invention. A ferrous article such as a stamped metal part is first given a copper strike in a conventional copper strike solution. This article is then placed as a cathode in a cyanide type plating bath embodying the invention and copper is electrodeposited on the article, using copper anodes, in the following manner. The plating current, at an average current density of about 15 amperes per square foot, is passed through the bath from anode to cathode for 7 seconds and is then interrupted for 2 seconds. This interrupted cycle is then repeated for a sufficient number of times until the desired thickness of copper has been electrodeposited.

The specific apparatus used in carrying out the process forms no part of the present invention and any suitable equipment may be employed to provide the interrupted current cycle. For example, a suitable generator, battery or rectifier, together with a timer and means for interrupting current may be used in large scale operation. A generator is employed to supply the plating current and the field of the generator is broken periodically for the desired time interval to thereby interrupt plating current for the desired time. Any conventional equipment such as conveyors commonly used in plating on a large scale may be used in the practice of the present invention. It is generally desirable to agitate the plating bath during the plating process to provide a more uniform electrodeposit and to permit the use of higher current densities.

Various changes and modifications of the embodiments of the invention described herein may be made by those skilled in the art without departing from the spirit and principles of the invention.

We claim:

1. A copper plating electrolyte which consists essentially of an aqueous cyanide type copper plating solution to which is added zinc within the range of 0.05 to 0.15 ounce per gallon of solution, lead within the range of 0.0005 to 0.002 ounce per gallon of solution, selenium 0.0005 to 0.002 ounce per gallon of solution, di-potassium tartrate within the range of from 0.1 to 5 ounces per gallon and a quaternary amine in an amount within the range of 1 to 10 ccs. per gallon of solution.

2. The process of electroplating copper which comprises passing a plating current from an anode to the article to be plated as a cathode through an aqueous copper plating electrolyte of the cyanide type to which has been added zinc within the range of about 0.5 to 0.15 ounce per gallon of solution, selenium within the range of about 0.0005 to 0.002 ounce per gallon of solution, lead within the range of about 0.0005 to 0.002 ounce per gallon of solution, di-potassium tartrate within the range of about 0.1 to 5 ounces per gallon of solution and about 1 to 10 cubic centimeters per gallon of solution of a quaternary amine wetting agent.

3. The method of electrodepositing copper which comprises passing an electric current from an anode to the work being plated as cathode through a cyanide copper plating bath consisting essentially of an aqueous solution of alkali metal cyanide, copper cyanide and an alkali metal hydroxide to which has been added zinc within the range of 0.05 to 0.15 ounce per gallon of solution, lead within the range of 0.0005 to 0.002 ounce per gallon of solution, selenium within the range of 0.0005 to 0.002 ounce per gallon of solution, di-potassium tartrate in an amount within the range of 0.1 to 5 ounces per gallon of solution and a quaternary amine wetting agent within the range of 1 to 10 ccs. per gallon of solution, for a time ranging from about ¼ of a second to as high as about 30 seconds then interrupting the flow of current for a time ranging from about $\frac{1}{10}$ of a second to about 5 seconds and then repeating a number of times the cycle consisting of current flow and interruption thereof until the desired thickness of copper has been electrodeposited.

4. An electrolyte which consists essentially of an aqueous bath containing the following ingredients: 5 to 8 ounces per gallon of copper, 0.75 to 1.5 ounces per gallon of free KCN, 5 to 6 ounces per gallon of KOH, 12 ounces per gallon to saturation of Na_2CO_3, 0.001 ounce per gallon of lead carbonate, 0.001 ounce per gallon of SeO_2, 0.1 ounce per gallon of zinc, 2 to 5 ounces per gallon of di-potassium tartrate and 3 to 8 cc. per gallon of C-decyl betaine.

5. The process of electrodepositing copper which comprises passing an electric current through the bath of claim 1 for a period of about 7 seconds, then interrupting the flow of current for about 2 seconds, and then repeating a number of times the cycle consisting of current flow and interruption thereof until the desired thickness of copper has been deposited.

6. A copper plating electrolyte which consists essentially of an aqueous cyanide copper plating bath to which has been added the following per gallon of solution: small but effective amounts of each of selenium and lead, said small but effective amounts being not less than about 0.0005 oz., 0.05 to 0.15 oz. zinc and 1 to 10 cc. of a quaternary amine wetting agent.

7. A copper plating electrolyte which consists essentially of an aqueous cyanide copper plating bath to which has been added the following per gallon of solution: small but effective amounts of each of selenium and lead, said small but effective amounts being not less than about 0.0005 oz., 0.05 to 0.15 oz. zinc, 0.1 to 5 oz. di-potassium tartrate and 1 to 10 cc. of a quaternary amine wetting agent.

8. The method of electrodepositing copper which comprises passing an electric current from an anode to the work being plated as a cathode through the electrolyte of claim 6, for a time ranging from about ¼ of a second up to about 30 seconds, then interrupting the flow of

current for a time ranging from about 1/10 of a second to 5 seconds and then repeating a number of times the cycle consisting of current flow and interruption thereof until the desired thickness of copper has been deposited.

9. A method as in claim 8 in which the electrolyte contains about 0.1 to 5 oz. per gallon of di-potassium tartrate.

10. The process of electrodepositing copper which comprises passing an electric current from an anode to the work to be plated as a cathode through the electrolyte of claim 6.

11. The electrolyte of claim 6 which contains C-decyl betaine.

12. A copper plating electrolyte which consists essentially of a cyanide copper plating bath to which has been added the following per gallon of solution: small but effective amounts of selenium dioxide and basic lead carbonate, said small but effective amounts being not less than 0.0005 oz., 0.05 to 0.15 oz. zinc and 1 to 10 cc. of a quaternary amine wetting agent.

References Cited in the file of this patent

UNITED STATES PATENTS

1,566,265	Antisell	Dec. 22, 1925
2,451,341	Jernstedt	Oct. 12, 1948
2,541,700	Holt	Feb. 13, 1951
2,636,850	Jernstedt et al.	Apr. 28, 1953
2,694,677	Ostrow	Nov. 16, 1954
2,701,234	Wernlund	Feb. 1, 1955

OTHER REFERENCES

Meyer et al.: Transactions Electrochemical Society, vol. 73 (1938), pp. 377, 384, 392, 394, 400, 401.

Serial No. 351,241, Weiner (A. P. C.), published May 18, 1943.