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ELECTROLYTIC DEPOSITION OF GOLD AND GOLD ALLOYS

Fritz Volk, Pforzheim, Germany, assignor to Birle & Co. K. G., Pforzheim, Germany

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The present invention relates to the electrolytic deposition of gold and more particularly to the electrolytic deposition of gold and gold alloys from solutions containing the same.

The known methods of depositing more or less heavy gold or gold alloy layers on metallic or metallized surfaces utilize gold baths, which, during the running of the process and the depositing of the gold from the bath, give an alkali reaction. Besides the gold salt which is an alkali metal-gold-cyanide complex and is most usually potassium gold cyanide, the usual baths contain strongly alkaline reacting additives such as potassium or sodium cyanide, possibly even potassium hydroxide and potassium carbonate or sodium carbonate and nearly always disodium phosphate which has an alkaline reaction due to the hydrolytic splitting thereof. In addition, the known gold baths which contain potassium ferrocyanide contain as the conducting salt the alkaline-reacting sodium carbonate.

The gold baths of the prior art all have the disadvantage that upon longer plating time the operation is not "scum-free," and therefore in the event that a heavy plating is desired, often an intermediate treatment of the object to be plated by brushing, scraping or the like is necessary since a loose coating forms upon the surface of the object to be plated, which loose coating acts as a blocking layer against the metal or metals to be plated on the base material.

This intermediate treatment is of course extremely disadvantageous since it results in a loss of time and material. Attempts have been made where it is desired to obtain a strong gold plating, to limit to a minimum the amount of free potassium cyanide in the solution from the beginning, that is, before starting the electrolytic deposition, however, the alkali fluid by the electrochemical reaction still had a harmful effect.

It is therefore a primary object of the present invention to provide for solution from which gold may be electrolytically deposited in which the harmful effect of the alkali which is set free during the electrochemical reaction of deposition of the gold from the solution is rendered harmless.

It is another object of the present invention to provide for the electrolytic deposition of gold in which the object to be plated remains scum-free during the electrolytic deposition and in which in fact there is no scum formation.

It is still another object of the present invention to provide a method of electrolytically depositing gold on objects to be plated therewith whereby there is no scum formation, so that the electrolytic deposition proceeds quickly and without any intermediate treatments even when forming relatively thick layers.

It is a further object of the present invention to provide baths from which gold may be electrolytically deposited, which baths may be utilized for the deposition of gold during relatively long time periods while avoiding

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all of the above enumerated disadvantages of the known art.

It is yet a further object of the present invention to provide for the formation of relatively thick layers of gold or gold alloys of, for example, 20 or more microns in a single operation.

Other objects and advantages of the present invention will be apparent from a further reading of the specification and of the appended claims.

With the above objects in view, the present invention mainly comprises a bath from which gold may be electrolytically deposited, the bath essentially consisting of an aqueous solution of an alkali metal-gold-cyanide complex and at least one buffer substance adapted to maintain a maximum pH of 7.5 in the solution during deposition of the gold from the solution. Preferably, the buffer utilized is such as to maintain the pH at between 6.5 and 7.5 during the electrolytic deposition of the gold from the solution.

Most preferably, the alkali metal-gold-cyanide complex is potassium gold cyanide ($\text{KAu}(\text{CN})_2$), although other alkali metal-gold-cyanides such as sodium gold cyanide may also be used.

The maintaining of the pH value of the bath during the electrolytic deposition of the gold therefrom at a maximum value of 7.5 is most preferably accomplished by incorporating a primary phosphate and more particularly an alkali metal, alkaline earth metal or ammonium primary phosphate in the aqueous solution. One or more alkali metal primary phosphate such as monosodium phosphate or monopotassium phosphate may be utilized, or mono-ammonium phosphate, or one or more alkaline earth metal primary phosphate such as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ may be utilized. It is also possible to utilize a mixture of one or more alkali metal primary phosphate and ammonium primary phosphate, or ammonium primary phosphate and one or more alkaline earth metal primary phosphate, or one or more alkali metal primary phosphate and one or more alkaline earth metal primary phosphate, or one or more alkali metal primary phosphate and ammonium primary phosphate and one or more alkaline earth metal primary phosphate. Any mixture of this type may be utilized to achieve the buffering of the aqueous solution at a maximum pH of 7.5 during the deposition of the gold from the solution. Other similar acid salts or mixtures of acid salts may be utilized in place of the primary phosphates mentioned above.

The present invention is applicable not only to the deposition of pure gold from solutions, but also to the deposition of gold along with one or more alloying metals for the hardening or coloring of the gold along with the gold from the solution. Any of the usual alloying metal salts may therefore be continued in the baths in accordance with the present invention. For example, such compounds as the water soluble complexes of cyanides of silver, copper, nickel, iron and/or cobalt may be continued in the bath. These complexes are generally complexes of an alkali metal or ammonium, the metal to be alloyed and the cyanide ion.

The maintaining of the pH at a maximum of 7.5 during the electrolytic deposition of the gold from the solution may be accomplished by the incorporation of one or more of the above primary phosphate as buffer substances in the solution, or the desired primary phosphate may be formed during the deposition process, this being achieved by the incorporation of one or more secondary phosphate in the utilized bath and the addition of dilute orthophosphoric acid before and during the electrolytic deposition until a neutral or acid reaction is obtained. The orthophosphoric acid converts the secondary phosphate to the primary phosphate which buffers the solu-

tion during the deposition of the gold therefrom so that the pH does not exceed 7.5.

The buffering effect of the primary phosphate prevents the deleterious influence of the formed alkalis during prolonged plating times whereby in accordance with the present invention a practically homogeneous bath reaction is achieved even upon prolonged plating of objects with the electrolytic baths of the present invention. An additional advantage of the present invention is that the evolution of harmful and odiferous gases is prevented. Still further, the present invention has the advantage of considerably shortening the required plating times as compared to the known baths and methods of plating therewith.

The operation of the electrolytic deposition can be carried out with insoluble anodes, and the gold and the necessary alloying components can be regularly replenished as the same are used up from the original solution. It is thus possible, for example, utilizing a 20 liter bath which originally contained 80 g. of pure gold to plate 400 g. of gold therefrom, fresh gold salt being added as the gold is deposited from the solution, before a new bath must be utilized. The following are examples of bath compositions in accordance with the present invention, the scope of the invention not however, being limited to the specific details of the examples. Each example contains a primary phosphate and—put in brackets—a secondary phosphate. The addition of a secondary phosphate is necessary only in view of the impure gold cyanides as generally used in practice. In working with pure gold cyanides the addition of such secondary phosphates is not necessary. The greatness of surface of the anodes should be nearly the same as that of the wares, on which the gold shall be deposited. The bath temperature shall be held during the deposition within the limits 65°–75° C. The anodes, the wares and the bath shall move against another during the deposition process. The electrical tension between the anodes and the wares lies between 2 and 3 volts. The colour of the gold-deposit is a function of the tension.

Example 1

Into an amount of water sufficient to form a 1 liter solution is dissolved:

- 4 g. of pure gold in the form of potassium gold (I) cyanide,
- 15 g. of primary sodium phosphate
(20 g. of secondary sodium phosphate) and
- 0.5 g. of nickel in the form of potassium nickel (II) tetracyanide.

This solution may be utilized for the electrolytic deposition of gold in the usual manner with a tension of 2 volts and a current-density of 0.5 amp./dcm.², the primary sodium phosphate in the solution maintaining the pH at a maximum of 7.5 during the electrolytic deposition.

Example 2

Into an amount of water sufficient to form a 1 liter solution is dissolved:

- 6 g. of pure gold in the form of sodium gold (I) cyanide,
- 23 g. of primary potassium phosphate
(25 g. of secondary potassium phosphate) and
- 1 g. of nickel in the form of potassium nickel (II) tetracyanide.

This solution may be utilized for the electrolytic deposition of gold in the usual manner with a tension of 3 volts and a current-density of 1 amp./dcm.². The primary potassium phosphate in the solution maintaining the pH at a maximum of 7.5 during the electrolytic deposition.

Example 3

Into an amount of water sufficient to form a 1 liter solution is dissolved:

- 5 g. of pure gold in the form of potassium gold (I) cyanide,
- 16 g. of primary-ammonium phosphate
(18 g. of secondary-ammonium phosphate) and
- 0.75 g. of nickel in the form of sodium nickel (II) tetracyanide.

Example 4

Into an amount of water sufficient to form a 1 liter solution is dissolved:

- 7 g. of pure gold in the form of sodium gold (I) cyanide,
- 25 g. of primary sodium phosphate,
(28 g. of secondary sodium phosphate)
- 3 g. of iron in the form of sodium iron (II) cyanide, and
- 2 g. of copper in the form of sodium copper (I) tetracyanide.

Example 5

Into an amount of water sufficient to form a 1 liter solution is dissolved:

- 6 g. of pure gold in the form of potassium gold (I) cyanide,
- 10 g. of primary sodium phosphate,
- 5 g. of primary-ammonium phosphate,
(18 g. of secondary potassium phosphate)
- 2.5 g. of iron in the form of potassium iron (II) cyanide, and
- 0.5 g. of silver in the form of potassium silver (I) tetracyanide.

Any of the above bath solutions may be utilized in the usual manner for the electrolytic deposition of gold on a substance to be plated, the solution automatically maintaining the required pH at a maximum of 7.5 during the electrolytic deposition, due to the buffering substances contained in the solution.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. In a method of electrolytically depositing a metal selected from the group consisting of gold and gold alloys, the step of subjecting an aqueous solution containing an alkali metal-gold-cyanide complex to electrolysis in the presence of at least one buffer in an amount sufficient to maintain a pH of between 6.5 and 7.5 during electrolytic deposition of said metal from said solution.

2. In a method of electrolytically depositing a metal selected from the group consisting of gold and gold alloys, the step of subjecting an aqueous solution containing an alkali metal-gold-cyanide complex to electrolysis in the presence of at least one buffer in an amount sufficient to maintain a pH of between 6.5 and 7.5 during electrolytic deposition of said metal from said solution, said buffer being selected from the group consisting of alkali metal, alkaline earth metal and ammonium primary phosphates.

3. In a method of electrolytically depositing a metal selected from the group consisting of gold and gold alloys, the step of subjecting an aqueous solution containing an alkali metal-gold-cyanide complex and at least one secondary phosphate selected from the group consisting of alkali metal, alkaline earth metal and ammonium secondary phosphates to electrolysis; and adding dilute ortho-

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phosphoric acid to said aqueous solution so as to convert said secondary phosphate to the corresponding primary phosphate in an amount sufficient to maintain said solution at a pH between 6.5 and 7.5 during electrolytic deposition of said metal from said solution.

4. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex and at least one buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

5. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of a potassium-gold-cyanide complex and at least one buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

6. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex, a water-soluble complex salt of at least one metal adapted to alloy with gold during electrolytic deposition of said gold from said solution and at least one buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

7. A bath of pH 6.5 to 7.5 of the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex, a water-soluble complex salt of an alkali metal cyanide and a metal selected from the group consisting of silver, copper, iron, nickel and cobalt and at least one buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

8. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex and at least one buffer substance selected from the group consisting of alkali metal, alkaline earth metal and ammonium primary phosphates in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

9. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of a potassium-gold-cyanide complex and at least one buffer substance selected from the group consisting of alkali metal, alkaline earth metal and ammonium primary phosphates in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

10. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex, a water-soluble complex salt of at least one metal adapted to alloy with gold during electrolytic deposition of said gold from said solution and at least one buffer substance selected

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from the group consisting of alkali metal, alkaline earth metal and ammonium primary phosphates in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

11. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex and at least one alkali metal primary phosphate as buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

12. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex and monosodium phosphate as buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

13. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex and a plurality of alkali metal primary phosphates as buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

14. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex and ammonium primary phosphate as buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

15. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex and a mixture of at least one alkali metal primary phosphate and ammonium primary phosphate as buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

16. A bath of pH 6.5 to 7.5 for the electrolytic deposition of a metal selected from the group consisting of gold and gold-base alloys consisting essentially of an aqueous solution of an alkali metal-gold-cyanide complex and at least one alkaline earth metal primary phosphate as buffer substance in an amount sufficient to maintain the pH of the bath between 6.5 and 7.5 during deposition of the metal therefrom.

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