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3,672,969

ELECTRODEPOSITION OF GOLD AND GOLD ALLOYS

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Continuation of application Ser. No. 830,547, June 4,
1969, which is a continuation-in-part of application
Ser. No. 634,134, Apr. 27, 1967, which in turn is a
continuation-in-part of application Ser. No. 579,821,
Sept. 16, 1966. This application Oct. 26, 1970, Ser.
No. 84,228

Int. Cl. C23b 5/42, 5/28, 5/46
U.S. Cl. 204—43

21 Claims

ABSTRACT OF THE DISCLOSURE

Organo-phosphorus compounds and their water soluble salts are incorporated into aqueous soluble cyanide gold or gold alloy plating baths.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of our previously filed application Ser. No. 830,547, filed June 4, 1969, now abandoned, which in turn is a continuation-in-part of application Ser. No. 634,134, filed Apr. 27, 1967, now abandoned, which in turn is a continuation-in-part of our earlier filed application Ser. No. 579,821, filed Sept. 16, 1966, now abandoned.

SUMMARY OF THE INVENTION

This invention relates to electrodeposition of gold and gold alloys from an aqueous soluble cyanide gold plating bath in which there is dissolved an organo-phosphorus compound or its water soluble salt.

Organo phosphoric or phosphorus containing compounds can broadly be classified into two groups, namely, chelating and non-chelating. The organic-phosphorus chelating compounds can advantageously be used for the deposition of both pure gold and gold base alloys. The use of the non-chelating compounds produces good deposits of pure gold and particularly when used in combination with water soluble citrates. The use of these non-chelating organo-phosphorus compounds for electrodeposition of gold base alloys results in a bath having a limited plating range, usually around about one ampere per square foot, for bright deposits without the addition of a conventional chelating agent such as ethylene diamine tetraacetic acid.

The invention therefore broadly includes the addition of organo-phosphorus compounds to gold and gold alloy plating baths.

The invention further includes the addition of organo-phosphorus chelating agents or compounds to soluble gold plating baths for the deposition of pure gold and particularly gold alloys. The plating baths containing the organo-phosphorus chelating compounds not only provide the same operational advantages for the gold alloy plating process without the addition of the phosphates but produces gold base alloy deposits which are brighter even without the use of conventional brightening agents. To produce gold base alloys, various alloying metals as known in the art are added to the gold plating baths such as nickel, cobalt, iron, zinc and copper in the form of water soluble salts or metal chelates.

The invention further includes the addition of an organo-phosphorus compound or its water soluble salt in combination with a water soluble citrate to an aqueous gold plating bath for the electrodeposition of pure or 24

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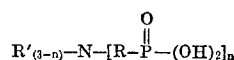
Karat gold. A synergistic reaction is obtained by use of this combination which substantially improves the plating range enabling the bath to operate at a higher rate of electrodeposition.

The plating baths of this invention may be effectively used over a wide range of pH depending upon the type of metal to be plated and the particular organo-phosphorus compound employed. If polyamine phosphonate compounds are employed [such as ethylenediaminetetra(methylphosphonic) acid or hexamethyldiaminetetra(methylphosphonic) acid] a pH of 12 or 13 and higher may be used. A pH as low as 2.5 or lower may be used with all of the organo-phosphorus compounds disclosed herein. For many plating processes, however, a pH of from 3 to 7.5 has been found to produce effective results. Operating the plating bath at a pH near neutrality or at a basic pH is advantageous for gold plating on base metals which would be affected or attacked by the acid in an acidic bath.

For particularly brilliant gold or gold alloy deposits, the organo-phosphorus compound or its salt is used in combination with an amine such as those described in our U.S. Pat. No. 2,967,135. This process, which has all the advantages described hereinabove, is particularly suitable for the electrodeposition of 24 karat mirror bright gold plate up to and exceeding 0.0005 inch thick.

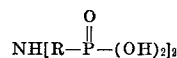
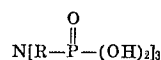
According to this invention, the process comprises electrodepositing gold or gold base alloys from an aqueous solution of at least one soluble gold cyanide salt in which there is dissolved from about 0.01 to 400 g./l. of an organo-phosphorus compound or its water soluble salt at a temperature in the range of between about 70° F. to 170° F.

Examples of chelating organo-phosphorus compounds which can be used according to this invention include those conforming to the following structural formula:

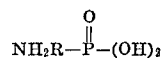


wherein R is a lower alkylidene radical and their water soluble salts, R' is hydrogen or a lower alkyl radical, and n is an integer from 1 to 3.

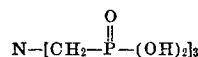
Some more specific examples of phosphonic acids coming within the above formula include those having the following structural formula:



and



wherein R contains 1 to 5 carbon atoms. We found amino-tri(methylphosphonic acid) to be eminently suitable for the present invention. This compound has the following structural formula:

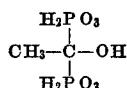


Other phosphonic acids that can be used include amino-tri(ethylidenephosphonic acid) and amino-tri(isopropylidene phosphonic acid).

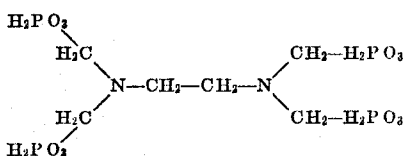
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Further examples of chelating organo-phosphorus compounds which can be used according to this invention include:

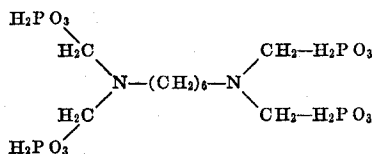
1-hydroxyethylidene-1,1 diphosphonic acid



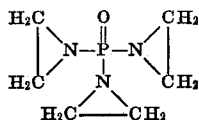
ethylenediaminetetra (methylphosphonic) acid



hexamethylenediaminetetra (methylphosphonic) acid



hexamethyl phosphonic triamide
[(CH₃)₂N]₃PO



and

Non-chelating organo-phosphorus compounds that can be used according to this invention include, benzene phosphonic acid, benzene phosphinic acid, ethyl acid phosphate-C₂H₅O-PO(OH)₂ and diethyl phosphite-(C₂H₅O)₂PHO.

The organo-phosphorus compounds can be used alone or in admixture with other organo-phosphorus compounds.

The soluble salts are the sodium salts and other alkali metal salts, such as potassium and lithium, as well as mixtures thereof. Ammonium salts and water soluble amine salts which exhibit the characteristics of the alkali metal salts may also be used.

The organo-phosphorus compounds containing —P=O can be referred to as phosphonyl compounds.

The organo-phosphorus compounds which give particularly good and improved results are the chelating compounds. The results of the non-chelating compounds tested to date can be classified as satisfactory.

The organo-phosphorus compounds, particularly the chelating compounds, when used in acidic gold plating baths substantially improve the plating characteristics of the bath. The resulting baths have excellent stability and are capable of operating at a wide temperature and pH range to provide lustrous fine grain and low porosity deposits, even for very thick deposits on the order of 0.0005 inch thick and above.

The pH of the plating bath when used without the soluble citrate is preferably maintained in the range between 3 and 5. The pH may be adjusted to the proper range by the addition of alkali metal hydroxide, preferably KOH, or an acid, preferably phosphoric acid.

The effectiveness of the organo-phosphorus compound in improving the electrodeposition of gold and gold alloys is not limited to any one particular aqueous gold plating

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bath. Suitable baths include, for example, the gold cyanide baths which have the following compositions:

	Low metal, oz./gal.	High metal, oz./gal.
5 Metallic gold, troy oz./gal. [as Kau(CN) ₂]...	0.25	3.0
Di-potassium citrate.....	1.0	30.0

The addition of the organo-phosphorus compound to these baths substantially improves the plating range due to the synergistic action of the soluble citrate and the phosphonic acid as stated hereinabove. The amount of citrate used may be varied within the range of 1 to 400 g./l. depending on the number of process variables. The pH of such baths can be extended to a wider range by the addition of the organo-phosphorus compounds according to this invention to below pH 2.5 and about pH 13.

Modification of the gold cyanide bath that are used commercially for the production of bright gold and other gold base alloys are also found to be satisfactory for the process of this invention. We found that acid-gold bath to be eminently suitable. This type of bath contains alkali metal gold cyanide, an organic acid or its soluble salts, such as citric acid, ammonium citrate, sodium malate, and so forth.

In the brilliant gold deposits, as stated previously the organo-phosphorus compound preferably is added to the plating bath in combination with an amino compound. Suitable amines as disclosed in our previous patents include:

- 30 Ethylene diamine
- Diethylene triamine
- Triethylene tetramine
- Hydroxyethyl ethylene diamine
- 35 Aminoethylethanolamine
- Monoethanolamine
- Triethanolamine
- Triisopropanoamine

40 Polymers of these compounds are also found to be eminently suitable. In general, those amines having from 1 to 2 carbon atoms and polymers thereof having molecular weights up to say 2500, and even higher, are suitable for the purpose.

45 For plating bright gold base alloys, the alloying metals that may be used are nickel, cobalt, iron, zinc, and copper. Advantageously, these alloying metals are added to the plating bath in the form of a soluble metal salt, such as nickel sulfate, nickel tartrate, cobalt sulfate, and cobalt gluconate.

50 The amount of phosphonic acid to be added to the plating bath depends on the process variables, alloying metals, gold concentrations, and others. In general, the range of 0.01 to 400 g./l. work well for the electrodeposition of gold and gold base alloys. Further to illustrate this invention, specific examples are described hereinbelow:

EXAMPLE I

24 karat lustrous gold deposits

60 A sufficient amount of water is used to form one liter of solution in which there is dissolved 8 grams of potassium gold cyanide and 50 grams amino-tri(methylphosphonic acid) N[CH₂PO(OH)₂]₃.

65 The pH of the solution is adjusted by the addition of potassium hydroxide to a pH about 4. The electrodeposition of gold is then carried out in a conventional manner at a temperature of about 100° F. and a current density of 1 to 5 amperes per square foot. A lustrous, fine grain gold plate on brass base metal is obtained.

EXAMPLE II

24 karat lustrous gold deposits

75 A sufficient amount of water is used to form one liter of solution in which there is dissolved 8 grams of potas-

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sium gold cyanide, 80 grams amino-tri(methylphosphonic acid), and 90 grams potassium citrate. The pH of the solution is adjusted by the addition of potassium hydroxide to a pH about 6.0. The electrodeposition is then carried out in a conventional manner at a temperature about 145° F. and a current density of 1 to 5 amperes per square foot. A similar lustrous gold deposit is obtained.

EXAMPLE III

Bright gold base alloy deposits

A sufficient amount of water is used to form one liter of solution in which there is dissolved 4 grams of potassium gold cyanide, 150 grams of amino-tri(methylphosphonic acid), and 0.25 gram of cobalt as a water soluble salt. The solution is adjusted by the addition of potassium hydroxide to a pH of about 4.3 and the electrodeposition is carried out at a temperature of 100° F.

The current density may be varied in the range from 1 to about 10 amperes per square foot. The resultant gold based alloy is bright and of excellent quality.

EXAMPLE IV

Brilliant 24 karat gold deposits

A gold plating bath in which there is dissolved 12 grams per liter of potassium gold cyanide, 150 grams per liter of amino-tri(methylphosphonic acid), and 25 grams per liter of tetraethylene pentamine is prepared. The pH of the solution is adjusted by the addition of potassium hydroxide to about 6 and the bath is permitted to age for approximately 10 days prior to electrodeposition. The electrodeposition of gold is carried out in a conventional manner at a temperature of about 140° F. and a current density of 1 to 2 amperes per square foot. A mirror bright 24 karat gold deposit is obtained.

The gold concentration suitable for the present application may vary from 1 gram per liter to 25 grams per liter, preferably in the range of 8 to 12 grams per liter. While the examples show the use of amino-tri(methylphosphonic acid), it is understood that other compounds falling within the scope of the claims may be used with beneficial results.

We claim:

1. A bath for producing deposits of gold or gold alloys by electrodeposition of gold or gold base alloys comprising an aqueous solution containing at least one soluble gold cyanide compound in an amount effective to produce electrodeposits of pure gold, or gold alloys when a codepositable base metal is also present, and a water soluble organo-phosphorus chelating agent or a water soluble organo-phosphorus non-chelating compound comprising phenyl phosphonic acid or phenyl phosphinic acid or ethyl acid phosphate or diethyl phosphite, or a water soluble salt of said chelating agent or non-chelating compounds in an amount above about 0.01 g./l.

2. A bath for producing deposits of gold or gold alloys by electrodeposition of gold or gold alloys comprising an aqueous solution containing at least one soluble gold cyanide compound in an amount effective to produce electrodeposits of pure gold, or gold alloys when a co-depositable base metal is also present, and an organo-phosphorus chelating agent, or a water soluble salt of said chelating agent in an amount above about 0.01 g./l.

3. The bath of claim 2 in which the chelating agent is 1-hydroxy-ethylidene-1, 1-diphosphonic acid or its water soluble salts.

4. The bath of claim 3 which also contains an amine brightening agent.

5. The bath of claim 3 which contains a water soluble citrate salt in sufficient amount to improve the gold or gold alloy plating.

6. The bath of claim 2 in which the organo-phosphorus chelating agent is a monoamine or polyamine phosphonic acid compound or a lower alkyl derivative thereof, or its water soluble salt.

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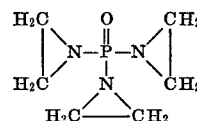
7. The bath of claim 2 in which the phosphorus chelating agent is an alkyl amine tetra (alkyl phosphonic) acid or its water soluble salt.

8. The bath of claim 2 in which the organo-phosphorus agent is ethylenediamine tetramethylphosphonic acid or its water soluble salts.

9. The bath of claim 2 in which the organo-phosphorus agent is hexamethylenediamine tetramethylphosphonic acid or its water soluble salts.

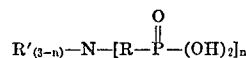
10. The bath of claim 2 in which the organo-phosphorus agent is hexamethyl phosphonic triamide or its water soluble salts.

11. The bath of claim 2 in which the organo-phosphorus agent conforms to the structural formula:



or its water soluble salts.

12. The bath of claim 2 in which the organo-phosphorus agent conforms to the structural formula:



in which R is a lower alkylidene radical, R' is hydrogen or a lower alkyl radical and n is an integer from 1 to 3 or its water soluble salts.

13. The bath of claim 2 in which the chelating agent is amino-tri (methylphosphonic acid), or its water soluble salts.

14. The bath of claim 2 which contains an amine brightening agent.

15. The bath of claim 2 which contains a water soluble citrate in sufficient amount to improve the gold or gold alloy plating.

16. A bath for producing gold or gold alloys by electrodeposition of gold or gold alloys comprising an aqueous solution containing at least one soluble gold cyanide compound in an amount effective to produce electrodeposits of pure gold, or gold alloys when a co-depositable base metal is also present, and non-chelating phenyl phosphonic acid or phenyl phosphinic acid or ethyl acid phosphate or diethyl phosphite or their water soluble salts in an amount above about 0.01 g./l.

17. The bath of claim 16 in which the non-chelating agent is ethyl acid phosphate.

18. The bath of claim 16 in which the non-chelating agent is diethyl phosphite.

19. The bath of claim 16 which contains a soluble citrate in a sufficient amount to improve the quality of the gold or gold alloy plating.

20. The bath of claim 16 which contains an amine brightening agent in a sufficient amount to improve the brightness of the gold or gold alloy plating.

21. A process for the electrodeposition of gold or gold base alloys which comprises the steps of electrolyzing said gold or gold base alloy metal from a bath containing at least one soluble gold cyanide compound in an amount sufficient to produce electrodeposits of pure gold, or gold alloys when a co-depositable base material is also present in the bath, and a water soluble organo-phosphorus chelating agent or a water soluble organo-phosphorus non-chelating compound comprising phenyl phosphonic acid or phenyl phosphinic acid or ethyl acid phosphate or di-

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ethyl phosphite, or a water soluble salt of said chelating agents or non-chelating compounds in an amount above about 0.01 g./l.

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10 GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

204—44, 46; 260—239 EP, 551 P

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

M-1667Cip3Con

Patent No. 3,672,969

Dated June 27, 1972

Inventor(s) FRED I. NOBEL and BARNET D. OSTROW

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 16 "2,5
--2,5 and above pH 13--.

pH 13" should read

Column 6, line 71 "base material" should read --base metal--.

Signed and sealed this 6th day of March 1973.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents