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ELECTRODEPOSITION OF SILVER

Donald Gardner Foulke, Watchung, N.J., assignor to Sel-Rex Corporation, Nutley, N.J., a corporation of New Jersey

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This invention relates to the electrodeposition of metals and specifically to a method of and solutions for electroplating silver. A further object of this invention is to plate silver deposits which are bright.

Silver and gold have been plated from alkaline cyanide baths since about 1800. In the late 1950's acid gold electrolytes were developed when it was discovered that alkali gold cyanide was stable at a pH as low as 3.0. Sodium and potassium silver cyanides do not have the stability of alkali metal gold cyanides in acid solutions and, consequently, no corresponding acid silver plating solutions have been developed.

Among the objects of this invention is to provide a silver plating bath useful for plating objects with a basis material or parts that are more or less sensitive to alkaline baths.

One phase of this invention is based on the discovery that potassium silver cyanide, if buffered in the region of 6.0 or 6.5 to 7 will remain reasonably stable. However, even though buffered, there is a danger in commercial practice that the pH will fall below 6.0 and in so doing silver cyanide precipitates out.

Another object of the invention is to provide silver plating baths in the acid range with exceptionally good stability.

Another phase of this invention is based on the discovery that the addition of relatively small amounts of an alkali metal or ammonium thiocyanate will stabilize silver plating baths, in the acid range so that plating can be carried out on a commercial scale.

Deposits from the acid bath just described are not bright but they are smooth and the solution is easy to rinse off the parts as compared to the conventional high cyanide baths or the high thiocyanate solutions described in copending application Ser. No. 404,518, filed Oct. 16, 1964.

Among other objects of the invention is to provide silver plating baths in the acid range which produce bright silver platings.

Still another phase of the invention is based on the discovery that the addition of even small amounts of nickel salts (the complex nickel tetraethylenepentamine compound is especially useful) as well as cobalt, copper, iron, zinc, indium, arsenic, antimony, and bismuth will refine the grain size of the deposits to give in many instances fully bright deposits. On the other hand selenium and mercaptobenzothiazole added to the bath do not brighten the deposits.

Maleic acid plus one or more salts of maleic acid (especially the potassium salt) have been found to serve as a particularly good buffer in the pH range of 6 to 7. However, any acid-salt combination buffering in this particular region will serve to stabilize the bath and at the same time maintain the cyanide build-up to a low value, minimizing rinsing and waste disposal problems.

As partially indicated above, the objects of the invention are attained by providing a bath containing the following ingredients:

	Grams per liter
Alkali metal silver cyanide (calc. as Ag.)	4-75
Acid+anionic buffering agent	2-100

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Alkali metal or ammonium thiocyanate	2-20
Additional metal (as metal ions and added as salt or complex)	0-100
Alkali to provide a pH of 6 to 7.5.	

The alkali in addition to neutralizing the acid content of the bath to the proper pH provides conductivity salts for the bath. The term alkali will be understood to include ammonia, ammonium hydroxide, the alkaline reacting amines as well as the lithium, sodium, potassium hydroxides.

It will be understood that the "additional metal" called for means a metal different from the metals already specified, namely different from silver and the alkali metals.

Any acid can be added to provide the final acidity, but there must be sufficient amount of weak acid (anionic) ions present to provide a substantial buffering action in the range of pH 6 to 7. Any of the acids known as weak acids if added as acids or as salts act as buffering agents. Thus, a weak acid to be effective at a pH of 6.5 to 7.5 should have a K (K_1 , K_2 or K_3) of approximately 2.6×10^{-8} or more. Any weak acid with a greater K constant can be neutralized to the desired pH. Typical acids with suitable ionization constants include maleic, malonic, phosphoric, phosphorous and sulfanilic.

The general features of novelty characterizing this invention having been given, specific examples hereafter set down will make for a better understanding of the invention. It will be understood, however, that the following examples are illustrative only and should not be considered as limiting the invention.

Example 1

A bath was prepared by dissolving the following ingredients in water:

	G./l.
Ammonium thiocyanate	5
Maleic acid	20
KOH to pH 6.5.	

To which was added:

Potassium silver cyanide	30
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Brass panels were plated in this bath at room temperature, at a current density of 1.0 amp./dm.². Smooth matte deposits were obtained.

Example 2

To the bath described under Example 1 was added 45 g./l. (instead of 30 g./l.) of potassium silver cyanide. Deposits were obtained similar to those described above, but the current density could be raised to 2.5 amp./dm.². The addition of 5 g./l. of methylene bis naphthalene sulfonate (Na or K) provided deposits which were semi-bright and not grainy in appearance.

Example 3

A bath was prepared by dissolving the following ingredients in water:

	G./l.
Potassium silver cyanide	30
Maleic acid	20
Potassium thiocyanate	5
Nickel tetraethylenepentamine	5
KOH to pH=6.8.	

The pH was adjusted to 6.5-6.8 before the silver salt was added to prevent precipitation of silver cyanide.

Deposits obtained from this bath on bright brass panels were fully bright at a current density of 1.0 amp./dm.².

Example 4

A bath was made by dissolving the following ingredients in water:

	G./l.
Phosphoric acid, ortho	10
Ammonium thiocyanate	10
Potassium silver cyanide	50
KOH to pH 6.5.	

Deposits obtained were similar to those obtained under Example 1 at 1.0 to 1.5 amp./dm.².

Example 5

A bath was prepared by dissolving the following ingredients in water:

	G./l.
Maleic acid, partially neutralized with KOH	40
Potassium thiocyanate	10
Nitriloacetic acid	5
Methylene bis-naphthalene-sulfonic acid	5
Antimony potassium tartrate	2
Potassium silver cyanide	60
pH 6.6.	

Panels plated in the bath were bright from 0.1 to 2.5 amp./dm.² depending upon the degree of agitation provided.

I claim:

1. Aqueous electrolyte solutions for electroplating conducting surfaces with silver comprising:

	G./l.
Alkali metal silver cyanide (calc. as Ag)	4-75
Acid plus anionic buffering agent	2-100
Thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates	2-20
Additional ionic metal	0-100
Alkali to provide a pH of 6 to 7.5.	

2. Aqueous electrolyte solutions as claimed in claim 1 in which said acid plus anionic buffering agent is a mixture of a weak acid and an alkali metal salt of a weak acid.

3. Aqueous electrolyte solutions as claimed in claim 1 in which said acid plus anionic buffering agent includes maleic acid anions.

4. Aqueous electrolyte solutions as claimed in claim 1 in which the additional ionic metal is added in sufficient quantity to produce bright deposits.

5. Aqueous electrolyte solutions as claimed in claim 1 in which ionic nickel is added as the additional ionic metal in sufficient quantity to produce bright electro-deposits.

6. Aqueous electrolyte solutions as claimed in claim 5 in which ionic nickel is added as a nickel complex.

7. A process for electrodepositing silver comprising making an object having a conducting surface the cathode in an aqueous bath comprising

	G./l.
Alkali metal silver cyanide (calc. as Ag)	4-75
Acid plus anionic buffering agent	2-100
Thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates	2-20
Additional ionic metal	0-100
Alkali to provide a pH of 6 to 7.5.	

8. A process as claimed in claim 7 in which said acid plus ionic buffering agent includes a mixture of a weak acid and an alkali metal salt of a weak acid.

9. A process as claimed in claim 7 in which said acid plus anionic buffering agent includes maleic acid anions.

10. A process as claimed in claim 7 in which the additional ionic metal is added in sufficient quantity to produce bright deposits.

11. A process as claimed in claim 7 in which ionic nickel is added as the additional ionic metal in sufficient quantity to produce bright deposits.

12. A process as claimed in claim 11 in which ionic nickel is added as a nickel complex.

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ROBERT K. MIHALEK, *Primary Examiner*.

G. KAPLAN, *Assistant Examiner*.