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"COMPOSITION AND PROCESS FOR HIGH SPEED
ELECTRODEPOSITION OF SILVER"

The present invention relates to the electrodeposition of silver.

5. Although the electrodeposition of silver from a variety of plating baths has been disclosed in the art, there is still a need for baths capable of functioning effectively for high speed bright silver plating.

10. The present invention relates to new and improved electroplating baths, utilizing an alkali metal silver cyanide as the source of the silver, for high speed silver plating. More particularly, the invention pertains to particular electroplating baths wherein mirror bright silver plating is achieved at current densities up to 5000 ASF (540 ASD).

15. As is well known in the art, silver cyanide plating baths have been employed for many years. Many efforts also have been made to develop non-cyanide or low-cyanide silver plating baths. See, for example, U.S. Patents 4,155,817 (Fletcher) and 4,024,031 (Lerner); where the latter patent is directed to an
20. electroplating bath with a low silver content, which is essentially at a neutral pH and operates substantially without free cyanides.

The patent to Fletcher (No. 4,155,817) also contains a detailed description of silver plating; and
25. when this is considered along with disclosures in the prior art cited in this patent as well as in the Lerner patent, one obtains an excellent background to the historical silver plating art as well as the numerous endeavours to develop improved electroplating baths
30. for a variety of commercial advantages such as high

speed deposition and high quality, bright silver deposits.

5. The patent to Fletcher discloses, inter alia, the use of a divalent (-2) selenium complex together with an electrolyte bath having a free cyanide content of less than 1.5 g/l. The use of alkali metal selenium compounds as brighteners is also disclosed in U.S. Patent No. 2,613,179 (Wolfson) and U.S. Patent No. 4,121,982 (Fletcher). Wolfson discloses, inter alia,
10. that the use of a selenite of an alkali metal together with alkali metal cyanides and nitrates results in the formation of a high speed bright silver deposit because of the presence of nitrate (100-150 g/l) and potassium selenite up to 1.0 g/l. Wolfson states that
15. the presence of the nitrates permits him to plate at up to 100 ASF (10 ASD) and that without the nitrates this current density could not be achieved.

- Another relevant patent for the present purposes is U.S. Patent No. 2,735,808 (Greenspan) which teaches
20. that the use of a glycerol complex and potassium cyanide are necessary to obtain bright silver deposits from an electroplating bath, which is tartrate-free. Greenspan states that his baths must be tartrate-free when using the glycerol complex of antimony.

25. Furthermore, in U.S. Patent No. 2,777,810 (Ostrow) there is a disclosure that divalent (-2) selenium compounds in the presence of antimony compounds and free cyanide gives bright deposits at up to 100 ASF (10.8 ASD).

30. It should further be noted that when divalent or

hexavalent selenium compounds are used, either by themselves or in combination with antimony, they do not give bright deposits over a wide current density range, i.e. over the range 200 to 5000 ASF (21.6 to 540 ASD).

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- The present invention relates to a particular electroplating bath for producing mirror bright silver deposits. More particularly selenium, or combinations of selenium and antimony, are added as additives. The selenium component may be any bath soluble selenium compound in which the selenium is tetravalent, i.e. is in a valency state of 4, and in which the anions and/or cations associated with the tetravalent selenium do not have an adverse effect on either the electroplating bath or the silver electrodeposit produced. Generally, the selenium (IV) is added as either selenious acid or as an alkali metal or ammonium selenite. Similarly, the antimony component may be any bath soluble compound or complex of antimony in which the anions and/or cations associated with the antimony do not have an adverse effect on either the electroplating bath or the silver electrodeposit produced. Desirably, the antimony component is employed in the form of its complex with an alkali metal carboxylic acid salt.
10. With selenium or both antimony and selenium present a mirror bright silver deposit results.
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- The source of silver may be an alkali metal or ammonium or amine silver cyanide. Other essential components are boric acid or citric acid or mixtures thereof, or the alkali metal or ammonium salts of
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such acids. Preferably, for operations at current densities above about 500 ASF (54 ASD), both boric acid and citric acid are employed; and most preferably the acids are utilized in the form of their alkali metal salts.

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The electroplating bath is substantially free of free cyanide. It is preferably formulated to have a pH within the range of about 7.0 to about 9.0; and it is preferably operated within a temperature range of about 20° to about 80°C and at a high current density of up to about 5000 ASF (540 ASD).

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The silver will be present in the bath in an amount which is at least sufficient to produce a smooth electrodeposit of silver on the substrate. The citrate and borate will be present in amounts which are at least sufficient, either alone or in combination, to effect buffering of the bath to maintain it within the desired operable pH range. The selenium or selenium and antimony will be present in amounts which are at least sufficient to produce a bright electrodeposit of silver.

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As previously set forth, the goal of the present invention is to provide an electroplating bath, which can be operated at high speed up to 5000 ASF (540 ASD) to produce a mirror bright silver deposit on various substrates or workpieces such as copper alloys or nickel alloys.

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The source of the silver in the bath is desirably an alkali metal or ammonium silver cyanide. Although ammonium, potassium, sodium, and lithium silver

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cyanides may be employed, the most preferred material is potassium silver cyanide. It will be further understood that for most purposes of the present invention wherever the use of an alkali metal is prescribed,

5. potassium is especially preferred unless otherwise indicated.

The amount of silver, derived from the potassium silver cyanide, is preferably in the range from about 20 to 120 g/l, more preferably from 30 to 100 g/l.

10. The citric acid or its alkali metal or ammonium salt, preferably potassium citrate, is preferably employed in amounts ranging from about 50 to 200 g/l, more preferably 75 to 140 g/l.

15. The boric acid or its alkali metal or ammonium salt, which for operations at current densities above about 500 ASF (54 ASD), will be employed not in place of the citric acid or its alkali metal salt but rather in conjunction with the citric acid, is preferably utilized in amounts ranging from about 10 to 50 g/l, preferably 20 to 40 g/l. Again, the preferred boric acid component will be its potassium metal salt, namely potassium borate.

25. The selenium component is desirably selenious acid (H_2SeO_3) or an alkali metal or ammonium selenium salt wherein the valence is 4 (i.e. tetravalent) rather than divalent as prescribed in the prior art teaching described above. The selenium component is preferably utilized in the bath in amounts ranging from about 2.0 to 5 g/l, and preferably 2.5 to 5 g/l. In forming
30. the alkali metal salt, the selenious acid need merely be

neutralized with an alkali metal material such as the hydroxide. Thus, for example, potassium hydroxide may be readily employed to neutralize the selenious acid. Based on selenium metal alone, the bath will preferably contain 1 to 3 g/l, and more preferably 1.5 to 3 g/l.

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For certain purposes of this invention an antimony component is also employed in the bath to ensure the deposition of mirror bright silver deposits. Preferably the antimony is used in the form of an alkali metal

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carboxylic acid complex, and most preferably as potassium antimony tartrate. Other complexes that could be employed in the present invention include antimony potassium glycerate, or antimony oxide dissolved in other carboxylic acids. The amount of

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antimony metal used in the bath will preferably range from about 0.5 to 2.5 g/l, more preferably 1.0 to 1.5 g/l.

It is an important feature of the present invention that the resulting electroplating bath be

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substantially free of free cyanide, which is another distinction between the present invention and the known baths of the prior art. By substantially free of free cyanide one means a cyanide ion content of less than 1.5 g/l, and preferably less than 0.25 g/l. Further-

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more, the electroplating bath is preferably also free of nitrate ions.

One of the preferred class of bath compositions in accordance with the present invention is set forth below:

	<u>Component</u>	<u>Concentration</u> <u>g/l</u>
	Silver as potassium silver cyanide	30-100
	Potassium Citrate	75-140
	Potassium Borate	20- 40
5.	H ₂ SeO ₃ (neutralized with KOH)	2- 5
	Antimony (as potassium antimony tartrate)	1-1.5

- The pH of the bath may range from about 7.0 to 9.0 and preferably is 7.5 to 8.5; while the temperature is maintained with the range of 20 to 80°C, preferably about 40 to 70°C. As described above the current density may be relatively high, i.e. up to 5000 ASF (540 ASD). Although the current density employed may be as low as 100 ASF (10.8 ASD), in order to ensure the production of mirror bright silver deposits the densities will preferably range from about 200 to 5000 ASF, i.e. about 20 to 540 A/dm² (ASD).

- The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying Examples.

EXAMPLE 1

An electrolytic bath was prepared having the following composition:

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|-----|------------------------------------|-----------|
| | Silver as potassium silver cyanide | - 60 g/l |
| 25. | Potassium citrate | - 100 g/l |
| | Boric Acid | - 30 g/l |
| | Selenium as Selenious acid | - 2.0 g/l |

- This electrolyte at 70°C deposited mirror bright plates when selectively plated at current densities between 1000 and 4000 ASF (108 to 423 ASD) on copper alloys. The pH of the bath was 8.

EXAMPLE 2

Example 1 was repeated but at 50°C, and plated selectively mirror bright deposits at current densities between 400 and 1500 ASF (43.2 and 162 ASD).

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EXAMPLE 3

Example 1 was repeated at 30°C, and plated selectively mirror bright deposits between 200 and 400 ASF (21.6 and 43.2 ASD).

EXAMPLE 4

10. Example 3 was repeated except that the potassium citrate was omitted from the bath and similar results were obtained.

EXAMPLE 5

15. Example 3 was repeated except that the boric acid was omitted from the bath and similar results were obtained.

EXAMPLE 6

An electrolytic bath was prepared having the following composition:

20.	Silver as potassium silver cyanide	- 80 g/l
	Potassium citrate	- 75 g/l
	Boric acid	- 20 g/l
	Selenium as selenious acid	- 2.0 g/l
	Antimony as potassium antimony tartrate	- 1.5 g/l

25. This electrolyte when operated at 60°C selectively plated mirror bright silver deposits at current densities from 1000 to 5000 ASF (108 to 540 ASD).

The above Examples demonstrate that the electrolytic baths of the present invention give outstanding silver deposits.

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EXAMPLES 7 and 8

5. By way of comparison, it was found that when the selenious acid or salt of the illustrative embodiment was substituted with a selenide (where the selenium is divalent) (Example 7) or selenate (where the selenium is ~~hexavalent~~) (Example 8) the thus formed electrolytes did not give mirror bright or bright silver deposits when plated selectively at current densities in excess of 500ASF (54 ASD).



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CLAIMS

1. An aqueous, stable electroplating bath substantially free of free cyanide, the bath comprising:
 - a) an alkali metal, ammonium or amine silver cyanide;
 - b) citric acid, boric acid, an alkali metal salt of citric acid or of boric acid, or an ammonium salt of citric acid or boric acid, or mixtures thereof; and
 - c) a bath soluble selenium compound in which the selenium has a valence of 4.
2. An electroplating bath as claimed in Claim 1 or Claim 2 which also contains a bath soluble compound or complex of antimony.
3. An electroplating bath as claimed in Claim 2 in which the antimony is present in the form of an alkali metal carboxylic acid complex.
4. An electroplating bath as claimed in Claim 1, 2 or 3 which contains potassium silver cyanide.
5. An electroplating bath as claimed in any one of Claims 1 to 4, which contains both alkali metal citrate and borate.

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6. An electroplating bath as claimed in Claim 5 which contains potassium citrate and potassium borate.

7. An electroplating bath as claimed in any one of Claims 1 to 6 in which the selenium compound comprises selenious acid, or an alkali metal or ammonium salt of selenious acid.

8. An electroplating bath as claimed in any one of Claims 1 to 7 in which the selenium compound is selenious acid.

9. An electroplating bath as claimed in Claim 7 in which the selenium compound is an alkali metal selenite.

10. An electroplating bath as claimed in any one of Claims 2 to 9 in which the antimony is present in the form of a potassium carboxylic acid salt complex.

11. An electroplating bath as claimed in Claim 10 in which the antimony complex is potassium antimony tartrate.

12. An electroplating bath as claimed in any one of Claims 1 to 11 having a pH of from about 7.0 to 9.0.

13. An electroplating bath as claimed in Claim 1 substantially as specifically described herein with reference to any one of Examples 1 to 6.



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14. A method of electrodepositing bright silver on a substrate which comprises passing an electric current between a cathode and an anode through an electroplating bath as claimed in any one of Claims 1 to 13 at a current density of from about 200 to about 5000 ASF (20 to 540 ASD) for a period of time sufficient to deposit the desired thickness of silver.

15 A substrate carrying an electrodeposit of silver whenever made by a method as claimed in Claim 14.

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