

(15)

1.

SILVER ELECTRODEPOSITION
PROCESS

This invention relates to the electrolytic deposition of silver on metal surfaces.

5. In conventional methods of electrolytically depositing silver, cyanide is commonly used as an electrolyte or as an additive to the bath. Such baths tend to be unstable unless soluble silver electrodes are used, and when operated at high current densities especially, for example above 800 amperes per square foot (80 amperes per square metre (ASD),
10. the resulting silver deposit usually lacks sufficient smoothness.

15. In certain procedures where silver is electrodeposited at higher current densities, for example, in the manufacture of miniature components for electronic circuitry, substantially insoluble, non-silver electrodes are required and silver electrodes are precluded. In such procedures, the bath tends to be unstable and the smoothness and evenness of the silver deposit is usually adversely affected.

20. It is an object of this invention to provide stable processes for electrodepositing metallic silver while avoiding the need for soluble silver electrodes.

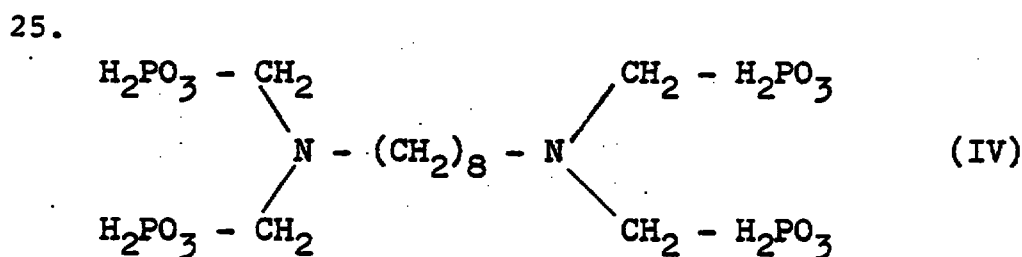
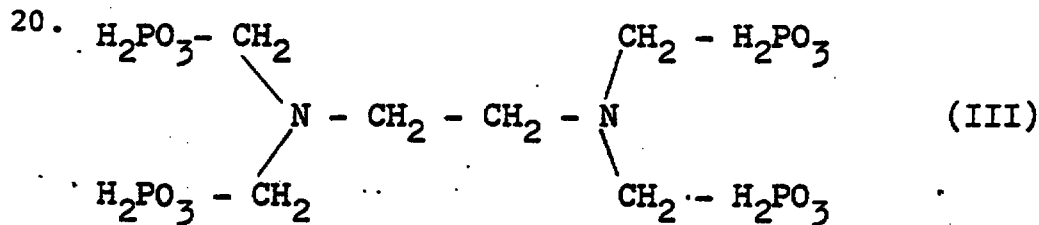
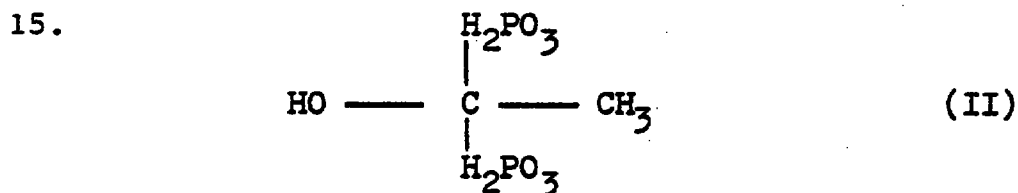
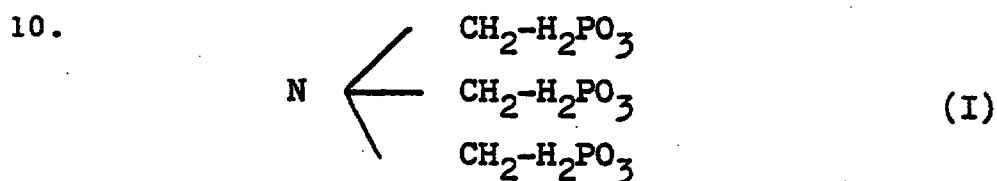
25. It is another object of this invention to provide processes for depositing metallic silver without dependence on cyanide as an electrolyte.

In accordance with the invention, there is provided a method for electrodepositing metallic silver which comprises immersing as the cathode the substrate which is to be silver plated in a bath composition comprising:-

(a) a bath soluble source of silver ions and first anions other than cyanide;

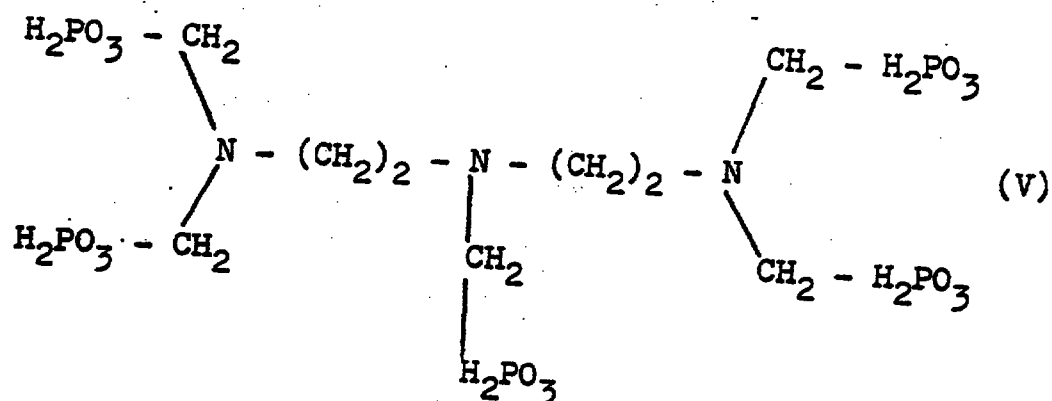
(b) a bath soluble source of second anions other than cyanide, the said second anions being different from the said first anions;

(c) an effective amount of an organic phosphonate compound selected from the following or mixtures thereof:-



30.

or



the composition being at a temperature at which it will produce galvanic deposits, and passing a current through the bath at a current density of at least 800 amperes/square foot (80 ASD) of the cathode surface.

The ingredients may be added separately to water to form a bath or the ingredients may be mixed together to form a saleable article of commerce which is then added to water. The pH is preferably adjusted to be above 7.

The bath composition is stabilized and the smoothness of the silver deposit is enhanced when the bath is operated at current densities above 800 amperes per square foot (80 ASD).

The organic phosphonate compounds (I) to (V) are commercially available from Monsanto Company, Inc., under the name "Dequest" (Registered Trade Mark), or they can be prepared by following known procedures described in the chemical literature.

The electrolyte for the bath is selected from among non-cyanide compounds capable of dissolving in water to form ions. Usually, these are soluble alkali metal compounds, and preferably, are phosphates,

citrates, nitrates or carbonates, for example of potassium or sodium.

5. The silver compound is preferably a water soluble inorganic compound capable of being dissolved in the bath at room or slightly elevated temperatures within the operating range of the bath. Examples of such compounds include potassium silver cyanide, silver chloride, silver nitrate, silver nitrite and silver bromide.

10. The compositions useful in the method of the invention are preferably formulated within the following ranges shown in Table 1 and the bath is preferably operated under the conditions of pH and temperature shown in Table 1.

Table 1

15.	<u>INGREDIENTS</u>	<u>AMOUNT</u>
	Soluble silver compound, preferably potassium silver cyanide (source of first anions other than cyanide - namely complex cyanide)	30-90 e.g. 50-90 g/l as silver
20.	Soluble non-cyanide compound, preferably potassium citrate (source of second anions other than cyanide namely citrate)	90-110 g/l
	Organic phosphonate compound	10-500 e.g. 20-40 g/l
	pH	7-10
	Temperature	50-70°C
25.	The pH is adjusted by adding suitable amounts of a weak acid, preferably citric acid or phosphoric acid, or a base, preferably potassium hydroxide or potassium carbonate.	
	The bath is operated at current densities	
30.	above 800 amperes per square foot (80 ASD), and more usually	

(19)

5.

between about 1,000 and 2,000 amperes per square foot (100-200 ASD), using conventional non-silver electrodes which are substantially insoluble in the bath, for example solid platinum wire or mesh, or platinum coated
5 tantalum or columbium.

Plating is conducted for a period sufficient to obtain a silver deposit of the desired thickness. In general, at the indicated conditions of temperature and current density, a period of about 3 seconds or
10 less is sufficient to deposit a layer of silver having a thickness of 130-150 micro-inches, 3.3×10^{-4} to 4.1×10^{-4} cms (3.3 to 4.1 microns). The plating period may be shortened or extended accordingly to achieve any other desired thickness.

15 Using this invention, substantially smooth, adherent silver deposits may be produced, with suitable preparation, on virtually any metal surface, such as copper, nickel, silver, steel or alloys thereof, such as stainless steel or alloys such as brass or bronze.

20 Other ingredients conventionally used in silver electrodeposition baths may also be included, especially brightening agents for enhancing the brightness of the silver deposit. Any conventional brightening agents used in silver plating processes can be employed.

25 Preferred for such purposes are water soluble salts of a metal or metals selected from among arsenic, for example, arsenic trioxide: lead, for example, lead citrate: thallium, for example, thallium chloride, bismuth, for example, bismuth molybdate and antimony, for example,
30 antimony chloride (SbCl_3 or SbCl_5). These are usually

added in small amounts, for example from about 1 to about 10 parts (as metal) per million parts by weight of the total composition.

Other conventional inorganic or organic brightening agents, such as mercaptobenzothiazole, thiazole or thio cyanate, may be used in place of, or together with, the foregoing brighteners.

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.

EXAMPLES 1A and 1B

EXAMPLE 1A

In accordance with the present invention, a copper strip, suitably cleaned to remove any surface dirt or grease, was mechanically masked to allow the area for deposition to be exposed in a selective plating head commercially available from the Dynacraft Corp. to a silver bath having the following composition:

20	Potassium silver cyanide	60 g/l
	(source of first anions other than cyanide - namely complex cyanide)	

25	Potassium citrate	100 g/l
	(source of second anions other than cyanide - namely citrate)	

	Organic phosphonate compound I	30 g/l
	pH	7-10

The anode consisted of pure platinum wire. The current source was an 8-volt d.c. power supply. The current density was maintained at 1500 amperes per square foot (150 ASD) during the plating period. The temperature was maintained between 65°C and 70°C while plating took place.

After 3 seconds the copper strip was removed from exposure to the bath. A metal deposit having a thickness of 150 micro-inches, 4.1×10^{-4} cms (4.1 microns)

was obtained. The semi-bright silver deposit was substantially smooth and even, and displayed good adhesion to the substrate even when rubbed.

EXAMPLE 1B

5 This is a comparison example.

The procedure of Example 1A was repeated but without the organic phosphonate present. This led to a rough, uneven silver deposit which had poor adhesion to the substrate.

10

EXAMPLE 2

The procedure of Example 1A was repeated, except that trivalent arsenic ions, As (III), were included in the bath at a concentration of 0.005 g/l.

15 The resulting silver deposit, in addition to being substantially smooth and even, had better surface brightness than the product of Example 1A.

EXAMPLE 3

The procedure of Example 1A was repeated, using a deposition bath having the following composition:

20 Potassium silver cyanide 60 g/l

(source of first anions other than cyanide - namely complex cyanide)

25 Potassium citrate 100 g/l

(source of second anions other than cyanide - namely citrate)

Organic phosphonate compound (I) 30 g/l

30 Organic brightening agent,
Silverex II, Sel-Rex Co. 8 ml/l

pH 7-10

This produced a bright, adherent silver deposit.

Substantially the same results as in the foregoing examples were obtained when the other organic phosphonate compounds useful in this invention were used in the baths.

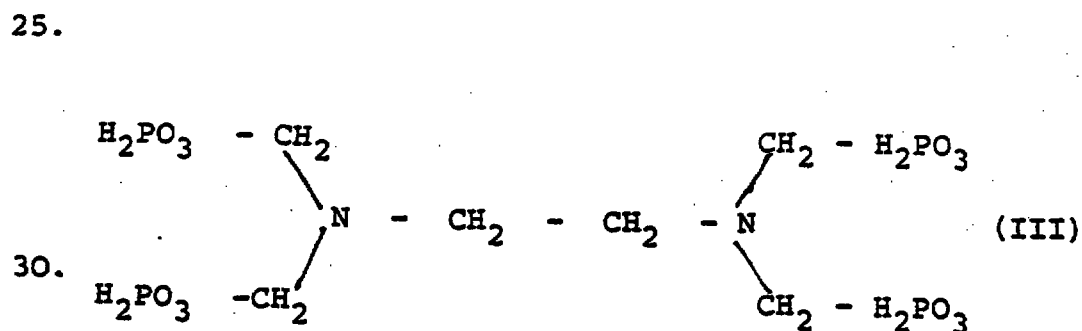
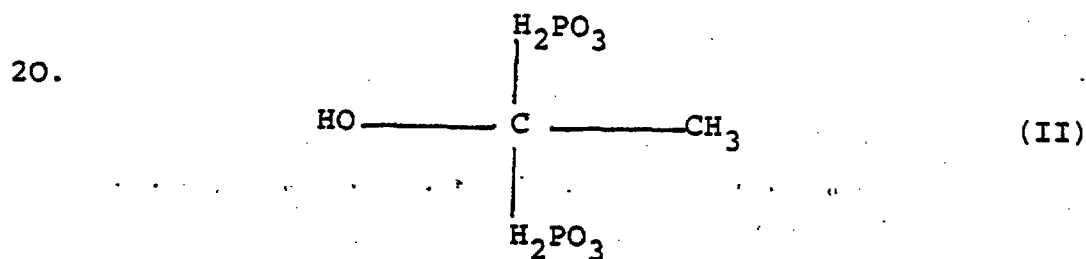
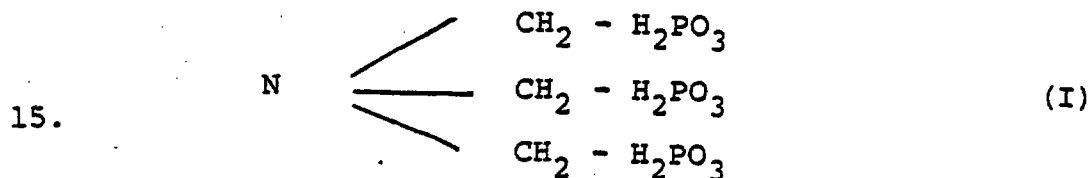


22

CLAIMS:

1. A method for electrodepositing metallic silver which comprises immersing as the cathode the substrate which is to be silver plated in a bath composition comprising

5. (a) a bath soluble source of silver ions and first anions other than cyanide;
- (b) a bath soluble source of second anions other than cyanide, the said second anions being different from the said first anions; and
10. (c) at least one of the organic phosphonate compounds identified by the formulae I, II, III, IV or V given below.





15.

20.

25.

30.

5. A method as claimed in any one of Claims 1 to 4 in which the first anions other than cyanide comprise complex cyanide anions, or chloride, nitrate, nitrite or bromide anions.



6. A method as claimed in Claims 1,2,3,4 or 5 in which an effective amount of brightening agent effective to brighten the silver deposit is included in the composition.

5. 7. A method as claimed in any one of Claims 1 to 6 in which the composition has a pH of 7 to 10.

8. A method as claimed in any one of Claims 1 to 7 in which silver ions in the composition are provided by silver chloride, silver nitrate, silver nitrite or silver Bromide.

9. A method as claimed in any one of Claims 1 to 8, in which anions other than cyanide ions in the composition are provided by alkali metal phosphates, citrates, nitrates or carbonates.

15. 10. A method as claimed in any one of Claims 1 to 9 containing 30-90 g/l of silver.

20. 11. A method as claimed in Claim 1, wherein the bath consists essentially of 50 - 90 g/l of the soluble silver compound having a first anion other than cyanide, 90-110 g/l of an electrolyte compound providing the second anion other than cyanide different to the first anion other than cyanide, optionally a brightening agent for silver and 10 to 500 grams of a single one of the organic phosphonate compound which is one of those identified by the formulae I, II, III, IV and V.

25. 12. A method as claimed in any one of Claims 1 to 11, wherein the composition contains 90-110 g/l of potassium citrate as a source of the second anion other than cyanide.

30. 13. A method as claimed in any one of Claims 1 to 12 wherein the composition contains 20-40 g/l



* C L H S *

26

11.



of phosponate compound.

14. A method as claimed in Claim 1 in which the silver in the composition is provided by potassium silver cyanide and the anions other than cyanide are provided by potassium citrate.
5. 15. A method as claimed in Claim 1 substantially as specifically described herein with reference to Examples 1A, 2 or 3.
10. 16. An article whenever provided with a silver electrodeposit by a method as claimed in any one of Claims 1 to 15.

The text of the specification has been reproduced by photocopying the applicants original typescript. It may contain a few amendments which are difficult to read. The original typescript containing these amendments may be inspected on the premises of the Patent Office