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SILVER-PALLADIUM IMMERSION PLATING COMPOSITION AND PROCESS

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This invention is concerned with the deposition of silver and specifically with the deposition of silver without the use of applied electric current.

The electroless or chemical method for depositing metals permits the deposition of heavy coatings as opposed to simple replacement or immersion technique because the electrons necessary for reduction of the metal are supplied by a reducing agent which is in turn oxidized. For example, hypophosphites are widely used as reducing agents in chemical plating processes.

Among the objects of the invention is to provide an electroless method of depositing silver.

This invention is based on the discovery that an entirely different system from any in common usage is effective to deposit silver from an aqueous solution thereof. Thus, it has been discovered that when palladous ions are added to a bath containing a soluble silver cyanide at a suitable temperature, silver rapidly deposits on metals or suitably activated non-conductors.

The bath of this invention, therefore, comprises a potassium silver cyanide solution to which is added 0.1–30 g./l. of a soluble palladous salt (calculated as Pd). Suitable palladous salts include palladium "P" salt, $(NH_3)_2Pd(NO_2)_2$, disodium palladium tetrachloride, Na_2PdCl_4, palladous chloride and sulfate.

The mechanism of this reduction is not fully understood, but it is known that silver can be deposited to considerable thickness, i.e., much thicker than immersion deposits which are limited to ⅛ to ¼ of a micron. Furthermore, the rate of deposition depends upon the base metal being plated. Deposition of silver on gold is of the order of 10 microns per 6.45 cm.²/per hour, on copper 6 microns/6.45 cm.²/hour at 80° C.

In practicing this invention, a bath of the compositions shown in Table I may be used.

TABLE I

Constituent	Optimum, g./l.[1]	Range, g./l.[1]
Soluble silver cyanide	8	0.5–30
Alkali salt of weak acid	25	up to 200
Weak Acid	12	up to 100
Soluble palladous salt	2	0.01–30
Ammonium hydroxide	pH 10	pH 8–10
Temperature	80° C.	50–100° C.

[1] G./l.=grams per liter.

The weak acid salts as well as the acids, which, of course, exist in the bath as salts at the pH specified, are optional. Effective salts include, the organic acids such as acetic, propionic, citric, tartaric, etc., as well as the inorganic phosphorous acids.

The hydroxy polybasic acids salts such as citrates and the salts of polybasic amino acids such as ethylene diamine tetraacetic acid are particularly desirable, apparently because of their complexing ability.

Example No. 1

A bath was made up as follows:

	G./l.
$KAg(CN)_2$	8
Palladium "P" salt	2
Ammonium citrate	15.0
Disodium EDTA	37.5

NH_4OH, to pH 10.0.

At 80° C. 5 microns of silver plated out on a gold plated panel 6.45 cm.² in half an hour.

The rate of deposition on a brass panel 6.45 cm.² in size was 3 microns per half hour and the rate on a nickel panel was 1.1 micron per half an hour.

Example No. 2

A bath was made up similar to the bath in Example 1, except that disodium palladium tetrachloride was substituted for the diamino-dinitro palladium salt.

The results were similar to those obtained in Example 1.

Example No. 3

A bath was made up to contain

	G./l.
$KAg(CN)_2$	8.0
Palladium "P" salt	2.0

NH_4CH, to pH 10.0.

A gold plated brass panel immersed in this bath received a deposit of 1.7 microns in 15 minutes at 80° C.

When K_2HPO_4 was added to this bath in the amount of 20 g./l., the rate of deposition on gold was 1½ microns per 6.45 cm.² per 15 minutes at 80° C.

We claim:

1. As a composition for chemically depositing silver an aqueous solution having a pH of 8–10 and comprising 0.5–30 g./l. of a soluble silver cyanide and 0.01 to 30 g./l. of a soluble palladous salt.

2. As a composition for chemically depositing silver, an aqueous solution containing

	G./l.
Alkali silver cyanide (calc. as Ag)	0.5–30
Alkali salt of a weak acid	Up to 300
Weak acid	Up to 100
Palladous salt (calc. as Pd)	0.01–30

Ammonia, sufficient to provide a pH of 8 to 10.

3. As a composition for chemically depositing silver, an aqueous solution containing

	G./l.
Potassium silver cyanide	About 4
Trialkali citrate	About 25
Citric acid	About 12
Palladous salt	About 2

Ammonia, sufficient to provide a pH of about 10.

4. The composition as claimed in claim 2 in which the palladous salt is $(NH_3)_2Pd(NO_2)_2$.

5. The composition as claimed in claim 2 in which the palladous salt is disodium palladium tetrachloride.

6. A process for depositing silver on a workpiece hav-

ing a surface layer of metal comprising immersing the workpiece in an aqueous solution at a temperature of 50 to 100° C. containing 0.5–30 g./l. of a soluble silver cyanide in the presence of 0.01 to 30 g./l. of palladous ions until the desired amount of silver is deposited.

7. A process according to claim 6 wherein the palladous ions are obtained from $(NH_3)_2Pd(NO_2)_2$.

8. A process according to claim 6 wherein the palladous ions are obtained from disodium palladium tetrachloride.

9. A process according to claim 6 wherein the palladous ions are obtained from palladous chloride.

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