United States Patent Office 3,396,042
Patented Aug. 6, 1968

3,396,042

CHEMICAL GOLD PLATING COMPOSITION

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No Drawing. Filed Aug. 28, 1961, Ser. No. 134,106
9 Claims. (Cl. 106—1)

This invention is concerned with the deposition of gold. More particularly, the invention relates to the deposition of gold without the use of applied current.

The chemical reduction and the immersion deposition of many metals upon basis metals are widely practiced. In the latter process, it is possible to obtain deposit thicknesses of the order of ⅛ to ¼ of a micron and only on basis metals less noble in the electrolyte than the metal being plated out.

On the other hand, the chemical reduction (electroless) process is not so limited in application as the immersion method, in that the metal will be continually deposited by chemical reduction to substantial thicknesses, although deposition generally is limited to certain "catalytic" basis metals which effectively accept the deposit. In addition, suitably activated non-conductors can be plated by electroless chemical reduction.

The most common method of electroless chemical reduction employs a solution of the ions of the metal to be deposited and a reducing agent. Most commercial processes employ the hypophosphite ion as the reductant; the bath is operated at about 90° C. and certain buffers are added to prevent wide pH fluctuation. However, gold is a highly electronegative element, i.e., it is easily reduced, and the system containing hypophosphite is unstable with the result that spontaneous decomposition occurs and the bath has to be refined.

This invention is based on the discovery of an entirely different system that will produce gold deposits at the rate of 2 to 2½ microns per hour at a temperature substantially below that ordinarily used for either immersion or electroless gold. Furthermore, the bath or baths of the invention are stable for long periods of time under production conditions. Thus, it has been found that gold deposits from a solution thereof in the presence of palladous ions. The palladous ion may be present in the bath containing the gold salt or may be applied to the work to be plated from a separate bath.

The bath of the invention is made up of potassium gold cyanide to which is added 0.01–30 g./l. of a soluble palladous salt calculated as Pd. Suitable soluble palladous salts include palladium "P" salt, $(NH_3)_2Pd(NO_2)_2$, disodium palladium tetrachloride, Na_2PdCl_4, palladous chloride and sulfate.

It is to be understood that the invention is not limited in scope by explaining a theory upon which the operation is believed to depend. It is believed that when the simpler soluble Pd salts such as palladous chloride or sulfate are employed in the bath of the invention, a complex palladous salt (providing Pd^{++} ions) is formed in said bath which may be similar in structure to the "P" salt, for example. In the event that a great excess of free CN ions exists in said bath no deposition takes place. It is believed that this effect is due to the formation of a very stable Pd complex which does not provide Pd^{++} ions. The ratio of the Pd salt to free CN^- ions should therefore be maintained high enough to provide Pd^{++} ions which are necessary for the deposition of the gold. An exact measurement of the working ratio of Pd salt/CN^- is not possible but it is very simple to test a given solution to see if gold deposits therefrom. It is understood that the palladium of the "P" salt and of disodium palladium tetrachloride provides Pd^{++} ions in the gold cyanide bath.

In practicing this invention a bath of the following composition was provided:

TABLE I

Constituent	Optimum, g./l.	Range, g./l.
Soluble gold cyanide	4	0.5-30.
Alkali salt of a weak acid	25	Up to 300.
Weak acid	12	Up to 100.
Soluble palladous salt	2	0.01-30.
Ammonium hydroxide to pH=	10	pH 8-11.

As indicated in the broad range of the table above, the alkali salts of weak acids and the weak acid, per se, are optional constituents which, however, improve the stability of the bath. Weak acids are specified because of their buffering and/or complexing properties. Satisfactory weak acids include the phosphoric acids, and substantially all of the organic acids such as acetic, propionic, kojic, maleic, tartaric, citric, etc. Hydroxy polybasic acids such as citric and polybasic amino acids such as ethylenediamintetraacetic acid (EDTA) are especially desirable because they have a high degree of complexing activity.

The method of plating out the gold is simple in that the bath is heated to about 65°–75° C. and the clean metal workpiece is inserted for sufficient time to obtain the desired thickness of gold.

With the bath comprising 4 g./l. of potassium gold cyanide, 25 g./l. of tripotassium citrate, 12 g./l. of citric acid, 2 g./l. of palladium "P" salt and sufficient ammonia to produce a pH of 10, there was obtained a gold thickness of ¼ micron in one hour, 2½ microns in 2 hours, and 3⅓ microns in three hours. In other experiments satisfactory deposits were obtained at the high and low ranges listed in Table I.

To show that the addition of salts of organic acids are not necessary, a bath was made up as follows:

	G./l.
$KAu(CN)_2$	4.0
Palladium "P" salt	1.5
NH_4OH to pH=10.0.	

A copper panel immersed in this bath at 65° C. received a deposit of 18 mg. in 15 minutes, the deposition being matte to semi-bright.

Although satisfactory deposits can be obtained from the basic bath containing only a soluble gold cyanide and palladium "P" salt, $(NH_3)_2Pd(NO_2)_2$, the addition of the salts of organic acids such as citric, glycollic, tartaric which are capable of complexing any base metals present in the system and thus maintain the bath in good operating condition for a longer period of time, is very desirable. The sodium salts of citric, glycollic, acetic and tartaric acids have been found to produce satisfactory deposits and to improve the operation of the bath similar to the way the citric acid salt additions do.

As further examples, a bath was made up containing:

	G./l.
$KAu(CN)_2$	4
K_2HPO_4	20
Palladium "P" salt	1
NH_4OH to adjust to pH=10.0.	

Satisfactory deposits were obtained at the rate of 17½ mg./in.^{2} in 15 minutes. The sodium salt Na_2HPO_4 was substituted for the diposattisum phosphate and the equivalent results were obtained.

A solution was made up containing:

	G./l.
$KAu(CN)_2$	4
Na_2PdCl_4	1
NH_4OH to pH 10.	

A brass panel immersed in this bath received a gold deposit at the rate of 14 mg./in.^{2} in 15 minutes.

The process works as well for a properly sensitized non-conductor. Thus, a printed plastic board with copper circuit elements including holes therein was cleaned, etched in cuprous chloride, treated in 50% HCl, sensitized in stannous chloride solution and then catalyzed by immersing in $PdCl_2$ solution. The board was then immersed in a solution of 4 g./l. of $KAu(CN)_2$, 1 g./l. of Na_2PdCl_4 and 40 g./l. of the disodium salt of EDTA neutralized with NH_3 to pH 10. A satisfactory gold deposit was obtained on the plastic board and through the holes.

The features and principles underlying the invention described above in connection with specific exemplifications will suggest to those skilled in the art many other modifications thereof. It is accordingly desired that the appended claims shall not be limited to any specific feature or details thereof.

I claim:

1. As a composition for chemically depositing gold an aqueous solution consisting essentially of 0.5–30 g./l. of a soluble gold cyanide, 0.01 to 30 g./l. of a soluble palladous salt, absent sufficient CN ions to prevent deposition induced by said palladous salt, and sufficient alkali to provide a pH of 8–11.

2. As a composition for chemically depositing gold, an aqueous solution consisting essentially of

	G./l.
Alkali gold cyanide (calc. as Au)	0.5–30
Alkali salt of a weak acid selected from the class consisting of the phosphoric acids and organic acids	Up to 300
Weak acid selected from the class consisting of the phosphoric acids and organic acids	Up to 100
Palladous salt (calc. as Pd)	0.01–30
Ammonia to pH 8–11.	

the CN^-/Pd^{++} ratio being below that at which the chemical deposition induced by Pd^{++} is prevented from taking place by CN ions.

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

	G./l.
Potassium gold cyanide	About 4.
Trialkali citrate	About 25.
Citric acid	About 12.
Palladous salt	About 2.
Ammonia to approx. pH 10.	

the CN^-/Pd^{++} ratio being below that at which the chemical deposition induced by Pd^{++} is prevented from taking place by CN ions.

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 palladous tetrachloride.

6. A process for depositing gold on a workpiece having a conducting surface comprising immersing the workpiece in an aqueous solution consisting essentially of 0.5–30 g./l. of a soluble gold cyanide, sufficient alkali to provide a pH of 8–11, in the presence of 0.01 to 30 g./l. of a soluble palladous salt, and in the absence of sufficient CN ions to prevent deposition induced by said palladous salt whereupon gold is deposited on said conducting surface by the chemical reduction process.

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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