

# United States Patent

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[54] **METHOD FOR ELECTROPLATING GOLD**

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[51] Int. Cl. .... **C23b 5/28, B01k 3/00**

[58] Field of Search ..... **210/38; 204/232, 233, 234, 204/235, 46, 110, 236, 237, 238, 239, 240**

[56] **References Cited**

**FOREIGN PATENTS OR APPLICATIONS**

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[57] **ABSTRACT**

In an improved gold plating process the alkali metal concentration in the bath is maintained substantially constant during the plating operation by contacting the plating bath with an ammoniated cation exchange resin to replace alkali metal ions with ammonium ions and operating the ion exchanged plating bath at 60°–90° C. This process is particularly applicable when heavy coatings are desired, for example, in electroforming processes.

**10 Claims, 3 Drawing Figures**

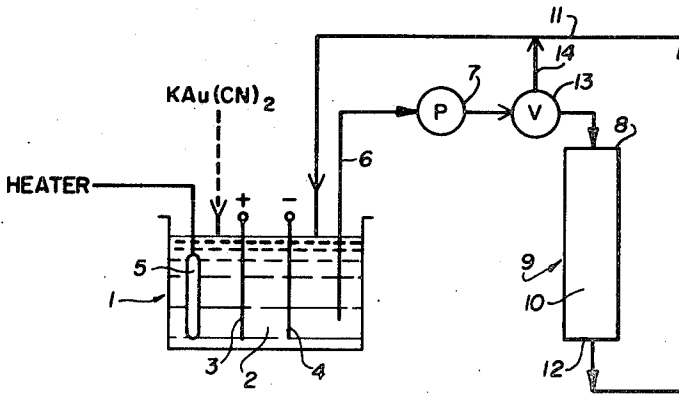


FIG. 1

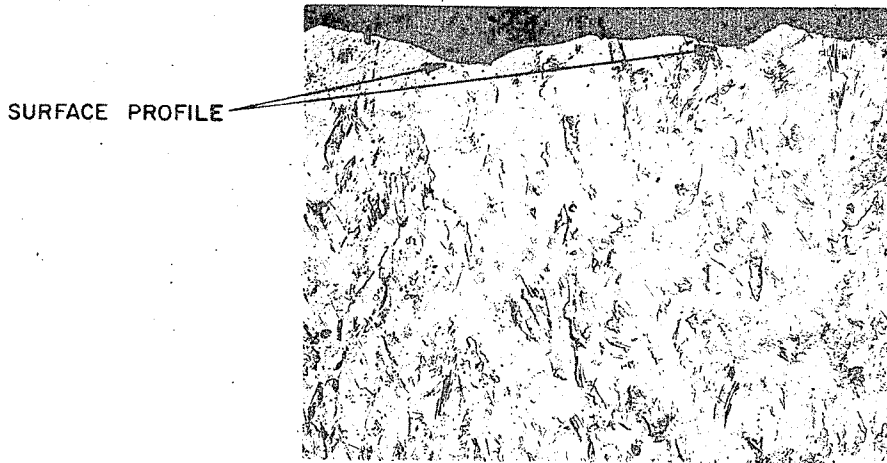


FIG. 2

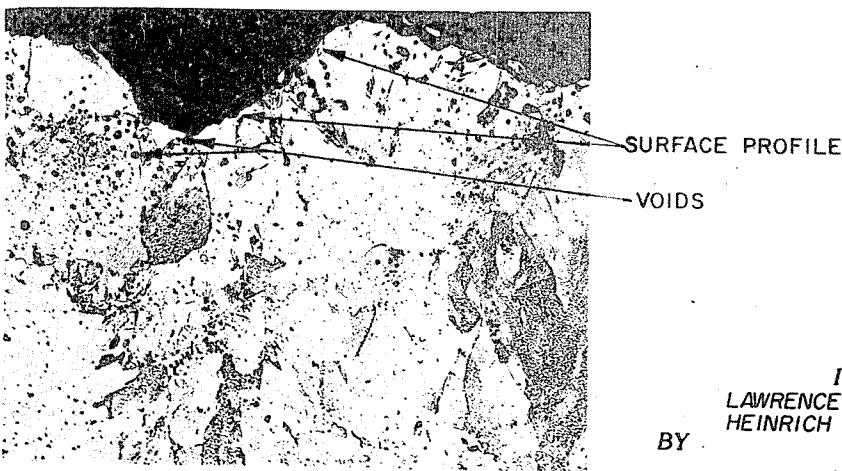


FIG. 3

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## METHOD FOR ELECTROPLATING GOLD

## BACKGROUND OF THE INVENTION

The present process relates to an improved method of electroplating gold in processes which use baths containing complex salts of gold and which operate at a pH in the range of about 5.5 to 7.5. Such gold electroplating processes are well known and widely used commercially.

Since most of the commercial gold-electroplating processes, especially those requiring heavy coats, use gold cyanide baths, the invention will be discussed with particular reference to such baths. It will be understood, however, that the present process applies generally to gold-plating baths wherein the source of gold is a complex salt containing the gold in the anion. For example, alkali gold sulfites have also been used in plating baths.

The gold cyanide baths are generally aqueous solutions containing an alkali metal or ammonium gold cyanide. Potassium gold cyanide,  $\text{KAu}(\text{CN})_2$ , has proved to be particularly effective and is readily available. The conventional baths also contain various salts which serve as buffers and improve the conductivity and throwing power of the solution. Examples of compounds used for such purposes are water soluble phosphates, sulfamates, borates, tartrates, citrates, acetates, formates, and the like. The effective baths usually contain these compounds as sodium, potassium or ammonium salts. During the electrodeposition of gold from the alkali metal gold cyanide bath, alkali metal cyanides, hydroxides, and salts of buffering agents are formed and there is a tendency for the pH of the bath to rise. As the plating process continues, the gold deposited from the bath is usually replenished by the addition of alkali metal gold cyanide and the pH is usually adjusted by the addition of an acid such as phosphoric, polyphosphoric, sulfamic, citric, or tartaric acid. The net effect of repeated additions of alkali metal gold salts with subsequent deposition of gold therefrom and additions of pH adjusting materials to bath is a buildup in the bath of nongold containing alkali metal salts.

One of the major problems in operating such plating processes is the maintenance of substantially uniform or constant plating values in the bath. A principal unbalancing factor is the buildup of alkali metal salts. This buildup lowers the plating quality and current efficiency, and the adverse effects become more marked as the solution approaches saturation and crystallization occurs. At or near the saturation point of the alkali metal salt, a gold plate of gross roughness is produced.

One of the convenient methods of monitoring the bath is to measure the density of the solution. For each process the density of the most effective plating bath can be established empirically. In plating the density is usually given in the Baume scale, and, for example, where potassium gold cyanide is the source of gold the most effective bath may have an initial Baume within the range of about 8 to 20, measured at 65° C. Once the effective operating conditions are established it is highly desirable to keep these conditions constant. However in conventional processes the steady buildup of alkali metal salts in the plating bath is reflected in the constantly increasing density.

It will be appreciated that the problems usually associated with gold plating are intensified and become increasingly more difficult to overcome as the thickness of the desired coating increases, and they are particularly significant when relatively heavy gold plate, e.g., of the order of 3 mils and higher are required. For thin coatings, there is usually sufficient removal or "dragout" of the plating solution to retard the salt buildup. However, ultimate deterioration of the bath does occur even in baths for thin coatings. The problem is of major proportions for very heavy gold deposits required in electroforming since the baths are more concentrated, electroforming processes are operated at the highest possible current densities and the parts are kept in the bath for a longer time, measured in hours or even days rather than minutes.

During this time, the gold deposited from the bath is replenished and the pH is maintained by constantly adding alkali metal gold cyanides and pH adjusting acids without any removal of the concomitant salt buildup by "dragout." Generally, electroforming baths are continuously operated to form gold coatings of about 3 to 100 mils in thickness. And, as noted previously, with the buildup of alkali metal salts in the bath the plate tends to become rough and unacceptable.

It has now been found that by the use of the process of the present invention, the gold plating bath can be operated continuously and with long life, producing smooth gold coatings.

## INVENTION

In accordance with the present invention, electroplating processes in which gold is plated from an aqueous bath having an acid or neutral pH and containing gold as a soluble complex gold are improved by replenishing the gold deposited from the bath with an alkali metal free soluble gold salt, whereby the alkali metal concentration of the bath is maintained substantially constant during the plating operation.

In a specific embodiment of this invention, wherein the gold deposited from the bath is replenished by the addition of a soluble alkali metal salt, the improvement comprises passing the plating bath into contact with an ammoniated cation exchange resin to replace alkali metal ions with ammonium ions and operating the ion exchanged plating bath at a temperature of 60°-90° C. In this way sufficient alkali metal ions are removed and a buildup of such ions in the bath is avoided.

As noted above, the present process is applicable to gold-plating processes in which the source of the gold is a complex salt of gold and the gold is complexed in the anion. Potassium and sodium gold cyanide complex salts are most commonly used, and the potassium gold cyanide is usually preferred for its greater solubility. The gold content of the bath varies depending on the process, e.g., the gold content of conventional potassium gold cyanide baths varies from 1 g./liter to 40 g./liter and higher. The baths may contain other metals, e.g., Ag, Cu, Ni, Fe, Co, As, which may or may not alloy with the gold deposit, so long as such metals are not present as cations which will interfere with the ion exchange procedure. For example, the metals may be present as part of a complex anion such as in an alkali metal (or ammonium) heavy metal cyanide. The agents added to buffer, improve the conductivity, brighten, or otherwise improve the bath are well known and may be present, for example, as the alkali metal or ammonium salts. In such bath, the alkali metal salts remaining after deposition of gold from the plating bath buildup with subsequent additions to the bath of the gold replenishing salt and continued removal of gold from solution as gold plate. On contacting the plating solution with the ammoniated ion exchange resin, alkali metal salts in the bath are converted to ammonium salts and the alkali metal salts in the bath can thus be maintained substantially constant during the plating operation.

For the cation exchange resins which replace the alkali metal ions in the bath with ammonium, any ammoniated cation exchange resin which is stable at temperatures from ambient to about 95° C. in the presence of the plating solution can be used. Preferably the resin is entirely in the ammonium form. However, equilibrated resins, i.e., resins containing acid and ammonium, can be employed. The equilibrated resins are not preferred because of the problems of obtaining a proper balance of pH control and alkali ion removal. Acid resins cannot be employed since they drop the pH rapidly with precipitation of gold cyanide in the ion exchange resin column. Examples of suitable cation exchange resins are the ammonium forms of highly sulfonated polystyrene type cation exchange resins and sulfonated copolymers of styrene-divinyl benzene-type resins. Suitable cation exchange resins are commercially available, e.g., under the names Amberlite IR-120, Amberlite IR-200, Decolite C-20, Dowex 50 and Ionac C-250.

The resins generally are prepared or are available commercially in the sodium form. The sodium form of the resin is converted to the ammoniated form by methods well known in the art. For example, the resin usually is first washed with aqueous acid to remove sodium ions and the acid washed resin is then treated, for example, with ammonium hydroxide to provide the ammoniated form.

In operation of the process of this invention the plating bath containing alkali metal ions is contacted with the ammoniated cation exchange resin, e.g., by passing it through a cation exchange column and alkali metal ions are replaced by ammonium ions. There can be an intermittent or continuous passage of the plating solution into contact with the ion exchange resin and the alkali metals need not be replaced entirely. All that is required is that sufficient alkali metals are removed to prevent a harmful buildup in the bath. It is within the skill of the art to control the rate and extent of ion exchange.

When the ion exchange resin has been depleted of ammonium ions it must be regenerated. Generally, it is preferred to regenerate the resin when it is only partially depleted, for example, when about 70 percent of the exchange capacity has been utilized. More than one column may be provided in the plating system so that while one column is replaced or regenerated the other may be used and the process can be operated continuously.

The solution which has been contacted with the cation exchange resin is circulated back to the plating bath, which is maintained at a temperature in the range of about 60° to 90° C. and preferably 65° to 70° C. and at a pH of about 5.5 to 7.5, preferably 6.0-6.5.

At about 60° to 90° C., good plating quality is achieved and the ammonium salts, e.g.,  $\text{NH}_4\text{CN}$ , tend to decompose with the liberation of  $\text{NH}_3$  and an equilibrium is established giving a solution having a minimum pH of about 5.5. The pH of the solution should be no higher than about 7.5, since any carbonates present in the bath would otherwise remain in the solution at above the pH of about 7.5 to the detriment of the plating process. Well-known buffering agents, such as phosphates, citrates or tartrates are employed to maintain the pH within the desired range. Preferably a certain proportion of the buffering compounds are added as the ammonium salts to facilitate elimination of ammonia, however it will be appreciated that if used as alkali metal salts they may be converted to the ammonium salts on contact with the cation exchange resin.

When operated according to the above-described procedure the bath operates with substantially constant plating values as evidenced by the uniform Baume maintained therein. For any given bath the most effective Baume, i.e., one which gives the greatest current efficiency at the operating conditions, can be established empirically. In accordance with this invention the effective Baume is maintained within  $\pm 2^\circ$ .

The nature of the invention will be more fully understood by reference to the Figures in which

FIG. 1 is a diagrammatic representation of gold plating apparatus adapted to carry out this process.

FIG. 2 is a photomicrograph at a magnification of about 200 times of a section gold plate prepared by a method of this invention.

FIG. 3 is a photomicrograph at a magnification of about 200 times of a section of gold plate prepared by a prior art method.

In FIG. 1 the plating tank 1 contains a gold plating bath 2 comprised of an aqueous solution of an alkali metal gold cyanide, e.g.,  $\text{KAu}(\text{CN})_2$ . The insoluble anode 3 is composed of platinized titanium and the part to be plated, for example, a mandrel suitably prepared for plating, serves as the cathode 4. When the call is in operation these electrodes are connected to a source of electric power (not shown). A heater 5 maintains bath 2 at a temperature suitable for producing a good gold plate and also suitable for liberating ammonia from the bath, e.g., within a range of 60°-90° C. Conduit 6 provided with pump 7 is positioned with one end in bath 2 and extends

into the inlet end 8 of cation exchange column 9, which contains an ammoniated cation exchange resin 10, e.g., a highly sulfonated polystyrene cation exchange resin in ammoniated form. Conduit 11 extends from the outlet 12 of the cation exchange column 9 into the tank 1. Valve 13 is used to regulate the rate of flow through conduit 6 and optionally to divert the flow through bypass line 14 to conduit 11.

For heavy gold plate deposit, e.g., of the order of 40 mils thickness the bath may contain, for example 36 g./l.,  $\text{KAu}(\text{CN})_2$ , 50 g./l. dipotassium hydrogen phosphate, 15 g./l. dibasic potassium citrate and 15 g./l. ammonium citrate. The bath has an initial pH of about 6.3 and a Baume, measured at 65° C., of about 11.

In the operation of the plating process the plating bath is maintained, for example, at 65° C. A current of about 1-10 amperes per square foot is applied to the bath. As the gold is deposited, the bath is constantly replenished with gold by adding a solution of  $\text{KAu}(\text{CN})_2$  to the solution. The replenishing salt may be added directly to the solution of circulated first through the cation exchange resin. During the operation, pump 7 controlled by valve 13 circulates a portion of the plating bath 2 through conduit 6 into contact with cation exchange resin 10 and back through conduit 11 to the bath 2. In the cation exchange resin, potassium ions are exchanged for ammonium ions. The alkali metal can be partially or entirely exchanged for ammonium ions. Such regulation is within the skill of the art. Preferably sufficient alkali metal ions are exchanged to maintain the desired Baume of the bath constant. The cation exchange-treated solution is circulated back to the plating tank wherein the ammonium ion concentration of the recirculated solution and the buffering salts maintain the bath at a pH in the range of about 5.5 to 7.5. The gold plate deposited under these conditions is of exceptionally good quality. It is smooth and dense and plates of heavy thickness, of the order of 40 mils and higher and high quality can be produced.

FIGS. 2 and 3 are photomicrographs at about 200 times magnification of etched sections of gold plate. The samples of gold plate were prepared substantially as described in the example below. FIG. 2 is a sample of the gold plate prepared in accordance with this invention and FIG. 3 is the sample of gold plate produced by the prior art technique. FIG. 2 shows that the plate obtained by the method of this invention has a smooth surface, as evidenced by the even profile and a fine grain structure. These characteristics are highly desirable. For example, with respect to the smooth surface, it can be noted that gold plate formed in an electroforming process is often machined, to obtain the required surface finish and the more uneven the surface, the more expensive gold must be machined off to obtain the desired surface finish. Contrastingly, in the prior art coating of FIG. 3 the markedly uneven profile, coarser grain structure and voids (indicating porosity) are clearly evident.

#### EXAMPLE

The following example will further illustrate the invention. In this example a generally recognized gold-plating process of the prior art is compared with the improved method of this invention.

In the comparative tests, the gold-plating bath was an aqueous solution having pH of 6.0, an initial gold concentration of 24.6 g./l., and the following composition:

Compound	Weight, g./l.
Potassium gold cyanide	36.0
Monobasic potassium phosphate	50.0
Dibasic potassium citrate	14.5

The general conditions of the tests were as follows:

Temperature	65° C.
pH	6.0-6.6

Agitation

rotating cylinder cathode

150	85.5	80.8	XS
190	77.7	72.8	XS
20	91.8	89.8	11.0

In order to accelerate the plating process, the tests were operated at a current density of 10 amperes per square foot (ASF) for a period of roughly 6 hours per day and maintained at 65° C. each night and over the weekends. At the end of the running time each day cathode efficiency measurements were made at 5 ASF and 7 ASF, the Baume and pH were recorded, and the cathode was weighed to determine the amount of gold electrodeposited. Additions of  $\text{KAu}(\text{CN})_2$  were made to replenish the gold-plated out.

a. Prior Art Plating Method

Employing one liter of the solution and the general conditions and procedure outlined above a bath was operated until about 240 grams of gold deposited. The pH of the solution was adjusted daily by the addition of phosphoric acid.

Table I records the measurements of cathode efficiency at 5 ASF and 7 ASF and the Baume after the given amounts of gold were plated in the test using the prior art method.

b. The Method of this Invention

Employing 1 liter of the solution and general plating conditions outlined above, a gold-plating cell was operated in accordance with this invention by circulating the gold bath during plating through a column containing an ammoniated cation exchange resin. The bath was operated until about 200 grams of gold was deposited.

The ammoniated resin was prepared by charging the column (2 feet high by 1 inch in diameter) with 240 grams of Amberlite IR-120, a highly sulfonated polystyrene type cation exchange resin sold by Rohm and Haas Company. The resin was first acid exchanged by passing 1.23 liters of 10%  $\text{H}_2\text{SO}_4$  through the column. Next the resin was converted to the ammonia form by passing 1.25 liters of 4%  $\text{NH}_4\text{OH}$  through the acid treated resin. During operation of this test the resin was periodically regenerated when about 70 percent of the capacity of the resin was used. The resin was regenerated by the same procedure used to convert it to the ammonia form in the first instance.

Table II records the measurements of cathode efficiency at 5 ASF and 7 ASF and the Baume after the given amounts of gold were plated in the test using the method of this invention.

TABLE—I PRIOR ART

Total Amt. Au-plated (Grams ± 5%)	Efficiency at 5 ASF (%)	Efficiency at 7 ASF (%)	Baume at 65° C.
0	N.M.	N.M.	11.0
25	72.5	78.8	12.0
50	73.3	68.8	14.0
100	71.2	68.4	17.0
150	61.4	56.0	N.D.
190	42.6	37.4	22.0
200	42.7	38.5	23.0
240	30.0	33.4	26

N.D.: not determined

N.M.: The starting composition of the bath was known to have current efficiency greater than 90 percent for the first 8 hours of use and hence the efficiency was not measured at this point.

TABLE—II PROCESS OF THIS INVENTION

Total Amt. Au-plated (Grams ± 5%)	Efficiency at 5 ASF (%)	Efficiency at 7 ASF (%)	Baume at 65° C.
0	N.M.	N.M.	11.0
25	93.3	90.5	XS
50	79.7	77.0	XS
100	94.2	83.4	11.0

N.M.: The starting composition of the bath was known to have current efficiency greater than 90 percent for the first 8 hours of use and hence the efficiency was not measured at this point.

XS: Excessive sampling was avoided to preclude even the remote possibility of "dragout."

Reference to table I shows that in prior art method the Baume of the solution rose progressively from 11 to 26 at which point the solution became saturated with potassium phosphate and crystallization occurred. Also, the current efficiency decreased from an initial value of about 90 percent to about 30 percent. The results in table II show that in the process of the present invention, the Baume of the bath remained relatively constant throughout the run and that the cathode efficiency remained at relatively high levels. In contrast to the prior art method the pH in the process of this invention remained relatively constant throughout the test and no phosphoric acid was added.

On comparing the samples plated by the two methods it was found that the quality of the plate deposited by the method of this invention was superior, in that it was a markedly smoother and more uniform deposit. The above-mentioned photomicrographs show, for example, the finer grain structure and the smoother surface of the plate prepared by the present method (FIG. 2) compared with the plate prepared by the prior art (FIG. 3).

Although the invention has been described with reference to specific embodiments, it will be appreciated that it includes all the modifications and variations that come within the spirit of this disclosure.

We claim:

1. In a process of electroplating gold from an aqueous plating bath having an acid or neutral pH wherein the source of gold is a soluble alkali metal complex salt containing the gold complex in the anion and wherein the gold deposited from the bath is replenished by the addition of a soluble alkali metal gold salt containing said complexed gold anion, the improvement which comprises passing the plating bath into contact with an ammoniated cation exchange resin to replace alkali metal ions with ammonium ion and operating the ion exchanged plating bath at a temperature in the range of 60° to 90° C.; whereby the alkali metal concentration of the bath is maintained substantially constant during the plating operation.

2. A process of electroplating gold according to claim 1 wherein the pH is maintained at 5.5 to 7.5.

3. A process of electroplating gold according to claim 2 wherein the process is continuously operated to form a gold coating of about 3 to 100 mils in thickness.

4. A process of electroplating old according to claim 3 wherein the Baume of the plating bath is maintained within ±2°.

5. A process of claim 1 wherein the gold-replenishing salt is an alkali metal gold cyanide.

6. A process of claim 5 wherein the alkali metal gold cyanide is  $\text{KAu}(\text{CN})_2$ .

7. A process of claim 5 wherein the alkali metal gold cyanide is  $\text{NaAu}(\text{CN})_2$ .

8. A process of electroplating gold according to claim 1 wherein the cation exchange resin is an ammoniated form of a highly sulfonated divinylbenzenepolystyrene copolymer or a highly sulfonated polystyrene polymer.

9. A process of electroplating gold according to claim 1 wherein the ammoniated cation exchange resin is regenerated after about 70 percent of the exchange capacity is used.

10. A process of electroplating gold according to claim 1 wherein the bath is maintained at 65° to 75° C.

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