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# ACID GOLD PLATING BATHS

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## ABSTRACT OF THE DISCLOSURE

The invention relates to gold cyanide plating baths that are operational at relatively low to very low pH values. The baths disclosed are stable and free from AuCN precipitates at pH values as low as 0.1. This advantageous result is obtained by utilizing in the acid plating baths gold (III) cyanide compounds in which the gold content consists essentially of gold in its three valence form. Especially advantageous results are realized when the plating compound is cyanoauric (III) acid. Novel methods for producing gold (III) cyanide compounds generally and cyanoauric (III) acid specifically also forms part of the invention.

## BACKGROUND OF THE INVENTION

This invention pertains to acid plating baths for the electrodeposition of gold. More specifically, the invention is concerned with providing highly acidic gold plating baths capable of efficient, stable operation at pH values heretofore found commercially impractical in this art.

The electrodeposition of gold has been practiced for many centuries in substantially the same manner. Until fairly recently, practically all gold plating was performed from an alkali gold cyanide solution. These alkali baths were stable and relatively clean during operation, but had to be aged before uniform plating resulted and varied in coverage, uniformity and throwing power. However, for most common applications requiring a relatively thin gold plate, such as gold plating costume jewelry, the alkali baths were satisfactory.

The development of sophisticated technologies, such as the aerospace and electronic industries, has created a need for heavy gold plate that can not be easily satisfied by the alkali plating baths. This need for heavy gold plate led to the use of acid gold cyanide plating baths, which gave less porous, smoother and more uniform heavy gold plate than the alkali baths then available. However, the use of acid baths created numerous problems, many of which are solved by the present invention.

The typical acid gold plating bath in use today usually consists of a mineral acid-water solution having a pH in the range 3.5–6.0, and containing gold in the form of an alkali metalgold cyanide. Additives such as weak organic acids, citrates, phosphates, tartrates and metallic compounds are also selectively included to obtain special effects or to improve certain properties of the gold plate, depending on the ultimate use for the plated article. Because conventional acid gold plating baths are very sensitive to changes in current density, operating temperatures, and, in particular, pH, the plating characteristics of these baths are highly variable and good plating characteristics are very difficult to maintain. For example, current density limits for achieving a bright plate, without undesirable soft brown depositions, varies considerably from bath to bath, and many baths are practical for use only after substantial periods of break-in. Further, if the plating solution is operated at a pH less than about 3, a yellow precipitate, identified as AuCN, develops in the bath and deposits on the anode, resulting in decreased



bath efficiency and plating quality. To maintain a prior art acid gold plating bath operational over a period of time at low pH, it is necessary, among other things, to remove the AuCN precipitates. This is done by filtering the bath periodically, with the attendant, unavoidable, loss of considerable amounts of gold, which, of course, raises the plating cost substantially.

It is also known that if the pH of the bath exceeds about 4, a soft, brown undesirable plate results. It is therefore necessary to maintain the pH of the plating bath between about 3 and 4. This maintenance requires the full time attention of a workman and even then is difficult to accomplish, since alkali hydroxides typically are formed during operation of the bath, resulting in a constantly increasing bath pH. In other words, a typical acid gold cyanide plating bath inherently tends to increase in pH during operation and therefore requires close control and tends to produce gold plate of variable quality.

It has also been noted that, for unexplained reasons, numerous plating solutions available to the trade vary tremendously in their plating rates and quality. These variations are not only evident in baths from different manufacturers, but are also present in baths of the same type from the same manufacturer.

Observations in the laboratory and in the field indicated that the efficiency of acid gold plating baths, as determined by Faraday's Law of Electrochemical Equivalents, varied greatly. If it was assumed that the gold present in the gold cyanide compound was in the III valence state (auric), efficiencies of over 100% were obtained, and if the I (auro) valence state of the gold was assumed, efficiencies of only 25–50% were obtained.

Experiments performed in our laboratories showed that alkali metal auric and auro cyanides exist in equilibrium and that this equilibrium can and does change with variations in the plating bath conditions, particularly pH. Similar indications subsequently were given in the article "Gold Electrodeposits From Cyanoaurate (III) Solutions and Some Characteristics of the Cyanoaurate Complex" Plating, June 1966, p. 765.

Our findings indicated that this equilibrium moves from the III valence state compound toward the I valence state compound as the pH of the plaating bath is increased and in the opposite direction as the pH is decreased. However, it was determined that the gold in the bath could not be converted exclusively or substantially exclusivelly to either valence state by variation of pH alone. A maximum proportion of the auro (I) compound was obtained in the pH 11–12 range and a maximum of the auric (III) compound in the pH 1–3 range. However, when operating in the pH 1–3 range, an undesirable yellow precipitate of AuCN invariably appeared in the bath and on the anode.

The above results were obtained regardless of the specific alkali metal gold cyanide used, although most of this experimental work was done with sodium and potassium gold cyanide, with a particular emphasis on the potassium compound, since it is most often used in acid gold plating baths. Our findings indicated that potassium gold cyanide used in acid gold plating baths was chiefly in the III valence state, but always contained a variable amount of the I valence compound. This was true no matter what method for producing the potassium gold cyanide was used.

## SUMMARY OF THE INVENTION

The present invention provides a gold cyanide plating bath that is stable and free from AuCN precipitates at pH values as low as 0.10. The plating baths of the invention give excellent plating characteristics at pH values from 0.1 to 5.0 and give optimum performance in the pH range from 1.0 to 3.0. The excellent plating characteristics of these baths are reliably predictable and do not radically

change with variations in the plating parameters of current density, pH, temperature and cyanide salt concentration.

Excellent bright plating can be obtained with the plating baths of the invention at operating conditions of pH as low as 1.0 and current densities as high as 50–80 amperes per square foot. Plating rates under these conditions can be as high as 10–15 micro inches per minute.

The low pH of the new plating baths also minimizes the production of cyanide contaminates in the plating solution. The presence of these contaminates results in yellow, oily, and unclean plating solutions which in turn produce dirty, fogged and matte plated areas. The baths of the invention therefore require less maintenance and produce a higher quality plate than those presently in use.

An important aspect of the invention is the production of gold cyanide compounds wherein the gold is present virtually exclusively in the III (auric) valence state, and the use of these compounds as the gold source in acid gold plating baths. This results in an AuCN precipitate-free plating bath, having the advantageous characteristics noted above. The absence of AuCN precipitates in the baths of the invention is explained by the absence of the I valence state gold cyanide compound, which is believed to be the source of the AuCN precipitates in the acid baths presently in use at pH values of less than about 3. The incorporation of substantially exclusively gold (III) cyanide compounds in the plating baths of the invention eliminates the I–III valence equilibrium conditions found in the baths presently in use and therefore eliminates most of the operational problems associated with acid gold plating baths.

The advantageous results of the invention can be obtained by producing a gold cyanide compound in such a manner as to exclude the presence of gold (I) cyanide. This can be accomplished by reacting a gold (III) salt such as gold (III) oxide, with an alkali metal cyanide such as potassium or sodium cyanide to form a mixture of the auric and auro gold cyanide compound. The auric species can then be separated from the auro species, typically, by dissolving the mixture in an acid solution having a pH of from 0.1 to 6 and aging the solution to form a gold (I) cyanide precipitate. The precipitate can then be removed from the solution by filtration and gold (III) cyanide crystals can be obtained from the filtered solution by crystallization. The gold (III) cyanide crystals can then be incorporated in an acid plating bath. The resultant plating bath has the advantageous characteristics previously described and forms a significant part of this invention.

Particularly advantageous results can be obtained by producing the desired gold cyanide compound in an acid environment having a pH of less than 6 and most advantageously less than 3. The gold cyanide compound, produced in this manner, is then incorporated in an acid gold plating bath also having a pH of less than 6 and most advantageously less than 3. It was discovered that by producing the gold cyanide compound at a pH less than 6 and maintaining the low pH environment during bath operation, the familiar but undesirable AuCN precipitate is eliminated.

Based on the previously discussed observations and experiments, it appears that the production of gold cyanide compounds by the method of this invention prevents an equilibrium between the I and III valence states of the gold compound from arising by producing and using the auric compound exclusively. By maintaining a low pH environment in the plating bath (less than about 6), gold cyanide in the I valence state does not appear and is not present. The absence of gold (I) cyanide accounts for the absence of AuCN precipitates in the baths of the invention. The gold content in crystals of the gold cyanide compounds produced by the method of the invention is reliably constant as opposed to crystals of gold cyanide compounds produced by other methods which vary substantially in gold content from batch to batch.



In accordance with another significant aspect of the invention, an acid gold plating bath is provided that does not inherently increase in pH during operation. This is accomplished by utilizing cyanoauric (III) acid, $HAu(CN)_4$, in the plating bath instead of alkali metal gold cyanides. During operation of the gold plating bath, alkali metal gold cyanides form alkali metal hydroxides which increase the bath pH during the plating operation. As previously explained, this inherently increasing bath pH can lead to very undesirable plating results and requires constant attention to keep the bath operational. By utilizing cyanoauric (III) acid as the gold source in acid gold plating baths, in accordance with this aspect of the invention, a bath is provided that produces water instead of an alkali hydroxide compound during operation with no significant increase in pH. This innovation results in a plating bath that is substantially easier to maintain and less costly to operate than those presently in use.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred gold (III) cyanide compound produced by the method of the invention is cyanoauric acid, $HAu(CN)_4$, since its use in gold plating baths eliminates the presence of potassium and sodium salts and produces a stable pH plating bath as previously discussed. The following detailed description, specifically pertaining to the production of cyanoauric acid, can, of course, be adapted by known chemical principles, to produce other gold (III) cyanide compounds, such as potassium and sodium gold cyanide, which are useful to advantage in acid gold plating baths where pH stability is considered less important.

Cyanoauric acid, $HAu(CN)_4$, was produced in accordance with the method of the invention by first dissolving 10 ounces of gold foil in 1,000 cubic centimeters of aqua regia. This solution was diluted with water, and gold (III) oxide $Au_2O_3$ was precipitated by the addition of ammonium hydroxide to a pH of 7. The gold (III) oxide was then filtered off and washed with water to get rid of excess acid. The gold (III) oxide is then heated in an acid solution of, for instance, phosphoric, nitric, or acetic acid. In this example, the gold (III) oxide was heated in a solution of 750 cubic centimeters of phosphoric acid and 500 cubic centimeters of water. This solution was brought to a boil and boiled for approximately one hour. Thereafter the solution was cooled to approximately room temperature. Sufficient KCN to react with all of the gold oxide present is then dissolved in water and added to the cooled solution. In this example, 550 grams of KCN was dissolved in 1,000 cubic centimeters of water and slowly added to the cooled gold (III) oxide-phosphoric acid solution. During this procedure HCN gas is evolved. Adequate venting provision should therefore be provided to remove this gas. After the reaction of KCN with the gold (III) oxide, the solution was cooled to approximately 50° F., and the gold bearing reaction product, which included potassium gold (III) cyanide and cyanoauric acid, was reclaimed by decanting and then reprecipitated from 500 cubic centimeters of water to separate the cyanoauric acid from the alkali metal gold salt. The cyanoauric acid was then dissolved in water and analyzed for gold content in preparation for incorporation in an acid gold plating bath. It should be noted that the potassium gold (III) cyanide compound produced by the preceding procedure and separated from the cyanoauric acid is also suitable for use in the acid gold plating baths of the invention. The relative proportions of the alkali metal gold cyanide compound and cyanoauric acid produced by this procedure can be adjusted by varying the process conditions.

The cyanide gold plating baths of the invention are characterized by being substantially completely free from

AuCN precipitates at pH values as low as 0.1. This freedom from AuCN precipitates at low pH values permits the bath to be operated for relatively long periods of time with a minimum of maintenance and to be used to produce less porous and brighter gold plating.

From the tests and experiments previously referred to, it has been theorized that the absence of AuCN precipitates in the baths of the invention is due to the absence of gold cyanide compounds wherein gold is in the I (auro) valence state. This conclusion is supported by the stability of the baths of the invention. The use of an acid plating bath, in which the gold metal source consists essentially of gold (III) cyanide compound, is therefore a significant aspect of this invention.

The composition of plating baths, in accordance with this aspect of the invention, that produce satisfactory plating results and are economical to operate, typically, are as follows: Values are given in grams/liter of bath (g./l.) or cubic centimeter/liter of bath (cc./l.)

| | G./l. |
|---|---|
| Au as metal (from a gold (II) cyanide compound) | 4–20 |
| A citrate, phosphate or tartrate compound | 30–150 |
| A weak organic acid | 3–150 |

and a mineral acid—30–150 cc./l.

Advantageously, though not necessarily, the citrate, phosphate or tartrate compound is diammonium citrate or potassium or ammonium monobasic phosphate; the weak organic acid is citric acid and the mineral acid is 85% phosphoric. These baths are intended for 24 K gold plating. For 18 K plating, from 0.005 to 3.0 g./l. of a suitable metallic compound typically nickel carbonate is added to the plating bath.

It is strongly preferred and most advantageous to utilize cyanoauric (III) acid in the plating baths of the invention as the gold (III) cyanide compound. As previously mentioned, the use of cyanoauric (III) acid, as opposed to, for instance, potassium (III) or sodium (III) gold cyanide, has the additional important advantage of not producing alkali metal hydroxide during operation of the plating bath. This last mentioned characteristic eliminates the necessity for continually adjusting the bath pH during operation, because of the formation of hydroxides which, of course, tend to increase the pH of the bath as plating progresses. The use of cyanoauric (III) acid in the advantageous plating baths of the invention results in very stable bath pH, thereby producing very consistent plating results and minimizing bath maintenance.

The preferred composition of an acid gold plating bath in accordance with the last mentioned aspect of the invention is as follows:

| | G./l. |
|---|---|
| Au as metal (from cyanoauric (III) acid) | 8 |
| Diammonium citrate | 50 |
| Citric acid | 50 |

85% phosphoric acid—50 cc./l.

The pH of this bath is about 1.5 and should be operated at from 95° F. to 125° F. Current density should be 20–80 ASF. The resultant plating rate is from 8 to $12\times16^{-6}$ inches per minute. For an 18 K plating bath, 1.5 g./l. of a suitable metallic compound such as Ni carbonate should be added.

Advantageously, the cyanoauric (III) acid used in this bath is obtained by the previously described process for producing gold III cyanide compounds.

A significant aspect of the invention is the use, in acid gold plating baths, of gold cyanide compounds wherein the gold content consists essentially of gold in the three valence form. This results in a plating bath far superior to those presently available, in relation to stability at low pH, consistency, and quality of plate. The methods of the invention for producing gold (III) cyanides and the baths of the invention incorporating gold (III) cyanides can, of course, be adapted to produce or operate with a variety of gold cyanide compounds, as for instance potassium and sodium gold cyanides. Thus, the particular gold (III) cyanide compound to be used in a particular bath may be selected as a function of the specific final result desired.

The invention provides a method for producing gold (III) cyanide compounds that are particularly useful in acid gold plating baths. The method of the invention includes the conversion of a gold (III) salt, typically gold III oxide, obtained by dissolving elemental gold in aqua regia and precipitating with a hydroxide, exclusively to the desired gold (III) cyanide compound. According to the invention, the gold (III) oxide solution is maintained at a pH lower than 6, preferably less than about 3, during the reaction with cyanide to form the gold cyanide compound. While in solution, the gold cyanide compound is also maintained continuously in an acid environment. Apparently, the maintenance of these pH conditions during the preparation of the gold cyanide salts and during plating insures the absence of gold cyanide in the I valence state.

In accordance with one aspect of the invention, gold (III) cyanide compounds can be produced by reacting a gold (III) salt with an alkali metal cyanide to produce a mixture of the auro and auric compounds and subsequently recovering the auric species in a concentrated (advantageously crystalline) form by separation techniques.

It should be realized by those skilled in this art that variations in the make-up of the plating baths of the invention may be made to obtain specific plating effects without departing from the spirit of the invention. Similarly, variations in the method of the invention for producing gold (III) cyanides may be made, depending on the particular application for the gold cyanide compound, without departing from the teachings of this specification. Accordingly, reference should be made to the appended claims in determining the full scope of the invention.

We claim:

1. The method of preparing an acid gold cyanide plating bath which comprises
   (a) reacting a gold (III) salt with an alkali metal cyanide compound chosen from the group consisting of potassium and sodium cyanide to form a reaction product including cyanoauric acid,
   (b) said reacting step taking place in an acid solution consisting essentially of phosphoric acid,
   (c) reclaiming the reaction product from the gold bearing solution,
   (d) separating the cyanoauric acid from the remainder of said reaction product,
   (e) incorporating from 4–20 grams/liter of gold metal in the form of the cyanoauric acid obtained in step (d) in an aqueous solution comprising 30–150 cc./liter of phosphoric acid, 3–150 grams/liter of citric acid and 30–150 grams/liter of a compound chosen from the group consisting of citrates, phosphates and tartrates, and
   (f) maintaining of pH of less than about 3 during steps (a), (c), and (e).

2. The method of preparing an acid gold cyanide plating bath, which comprises
   (a) reacting a gold (III) salt with an alkali metal cyanide compound chosen from the group consisting of potassium and sodium cyanide in an acid environment to produce a gold (III) cyanide reaction product including cyanoauric acid,
   (b) said reacting step taking place in an acid environment having a pH less than about 3,
   (c) separating said cyanoauric acid from said reaction product,
   (d) incorporating from 4–20 grams per liter of gold metal in the form of cyanoauric acid in an aqueous

solution including approximately 30–150 cc./liter of phosphoric acid and having a pH of less than about 3.

3. An aqueous gold plating bath comprising, approximately

(a) 4 to 20 grams per liter of gold (III) metal in the form of cyanoauric acid,
(b) 30 to 150 cc./liter of phosphoric acid,
(c) 3 to 150 grams/liter of citric acid, and
(d) 30 to 150 grams/liter of a compound chosen from the group consisting of citrates, phosphates, and tartrates,
(e) said plating having a pH of about 1.5
(f) said plating bath being free of AuCN precipitates.


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