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# ELECTROPLATING BATHS FOR HARD BRIGHT GOLD DEPOSITS

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The present invention is directed to electroplating baths and more particularly to baths for depositing hard, bright gold deposits. This application is a continuation-in-part of application Serial No. 776,681, filed November 28, 1958, now abandoned.

Baths for this general purpose are known as in U.S. Patent No. 2,660,554, entitled "Bright Gold and Gold Alloy Plating Baths." This patent describes a composition which is intended to produce a heavy plate from a bath containing aurous cyanide, an alkylene-, alkylol- or alkanol-amine at a pH of 8.0 to 11.5, together with a theoretical free alkali metal cyanide of 1.2 to 2.0 grams per liter. While this bath was satisfactory for commercial operation, there were some defects which lessened its applicability. The pH of the solution tended to rise and as such pH increase occurred, it became more difficult to secure a wide, bright plating range, particularly with baths which had been in operation for some time. Another defect of such baths was the difficulty in depositing alloys containing a large percentage of nickel. Since it is known in the art that nickel-gold alloys are hard and therefore show excellent wear resistance the ability to readily deposit high nickel alloys is very desirable.

With the baths made in accordance with the above patent, it was not possible to plate gold-nickel alloys of low gold content and high nickel content, since the deposition potential of the nickel ion in the above described system at the recommended pH was too high. Even if the concentration of the nickel ion was greatly increased, it was still difficult to obtain high nickel containing alloys.

Another difficulty was in maintaining the life of the bath. When the amount of gold replenished and deposited was three or four times the amount used in making a fresh bath, harmful breakdown products reduced the overall bright plating range. This made it necessary to discard the solution and make up a new bath. Naturally, this necessity unduly increased the cost of operation.

Prior art plating baths incorporating proprietary addition agents deposited gold layers which were passive and would not accept another subsequent layer of gold deposit. This made it impractical to deposit a layer of gold, and interrupt the plating to measure the thickness or the weight of the deposit.

Prior art acid bright gold plating baths were not capable of producing bright gold deposits over a wide range of pH, temperatures and current densities. For instance, such a bath was operable only within a limited pH range of 3.0 to 5.0. Also, for successful operation, trace alloying metals were incorporated in the bath. Although pure 24 carat (100%) gold deposits were obtainable the plate was not bright. Such prior art gold deposits had a tendency toward porosity, particularly in deposits of the 30–40 millionth range.

Furthermore, such acid baths showed poor metal distribution. It is desirable that when gold is deposited, the tips or high current density areas have a thickness of gold deposit the same as in the low current density areas, and this was not obtainable in the prior acid gold baths.



The present invention is intended and adapted to overcome the difficulties and disadvantages of the prior art, it being among the objects thereof to provide a bath composition which is capable of obtaining not only bright, but also hard, yet ductile, deposits of gold or gold alloys.

It is also among the objects of the invention to produce such a plating bath which will permit production of the desired hard deposits over a wide range of metal concentrations.

It is further among the objects of the invention to provide a bath which is completely stable and simple to control and to operate.

Still another object of the invention is to provide a bath which deposits layers of gold or its alloys which are not passive and can be plated with another adherent gold layer, without any danger that the upper layers will peel off.

In the practice of the invention, it has been found that by lowering the pH of the bath of Patent No, 2,660,554 to a value below 7 and specifically within the range of 2.5 to 6.5, the above disadvantages of the alkylene-, alkanol- and alkylol-amine baths are overcome, and that the bright plating range, as well as the life of the bath, is improved in a most important degree. With the low and acid pH values, it becomes very simple to deposit higher nickel-containing gold alloys. A further advantage is that the control of the bath becomes particularly simple. In addition thereto, the hardness of the deposits is two to three times that obtained from the prior baths. At the lower pH values, because of the inclusion of nickel in the deposit, the stated amines become more active brighteners and therefore, less of these compounds are required to give the desired brightness.

Not only these amines having 1–12 carbon atoms may be used but also polymerized polyamines, such as the residues of high molecular weight resulting from the manufacture of polyamines.

The amines tend to make the bath less sensitive to variations in concentration of the base metal present. For instance, large concentrations of nickel are tolerated in the presence of the amines; while the concentrations of the base metal in the gold deposit remains substantially constant. The amines also permit securing a wide bright plating range even at elevated temperature; whereas in prior acid baths, increasing the temperature tended to reduce the brightness of the deposit. Also, the amines make possible the deposit of bright nickel-gold and other base metal-gold alloys having extremely low base metal contents.

As the operation with the baths of the present invention proceeds, in some cases there may be a tendency for the pH to rise. To overcome this, some form of buffering compounds are added to the bath, whereby this tendency is prevented and the pH is constant within the optimum operating ranges. Among such compounds are water soluble tartrates, citrates, glycollates gluconates, borates, itaconates, formates, phosphates, malates, oxalates, and the like. These buffers also act to improve the conductivity of the bath and so permit the use of lower operating voltages. These beneficial effects are particularly pronounced when the bath contains soluble nickel or cobalt, plus the alkanol or alkylene or alkylol amines. Therefore, it is desirable to include in the bath one of these base metals in addition to any other alloying meals which are used.

It becomes possible by the present invention to plate a 100% pure bright gold deposit without any alloying elements. Also, the physical properties of the deposited gold may be altered by varying the alloying metals. For example, silver may be added as the double alkali metal

cyanide, the amine cyanide or the hydrocyanide. Tin may be added as the citrate, gluconate and as a similar complex. Cobalt may be added as the amine, sulfate or the like.

The present baths have indefinite life, are simple to control, operate with no or at the worst with a minimum of pH adjustment, and give brilliant, hard, and ductile gold and gold alloy deposits. The following examples are illustrative of the invention, and they should not be considered to limit it.

*Example 1*

A bath containing only gold as the soluble cyanide, as well as nickel as the sulfate, plus an amine, when adjusted to a pH of 3.0–4.0, has a tendency to increase in pH value. Such a bath in aqueous solution is as follows:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 4.0 |
| Nickel—in the form of $NiSO_4$ | 1.0 |
| Triethylene tetramine | 10.0 |

The pH is adjusted to a value of 3.0–4.0 with sulfuric acid. While the bath is commercially operable, the tendency of the pH to increase may become troublesome. The addition to this bath of a buffer compound stabilizes it so that it operates continuously. Plating is conducted at a temperature of 115° F. at a current density of 15 amperes per square foot.

*Example 2*

An aqueous solution is made of the following ingredients:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 4.0 |
| Nickel—in the form of $NiSO_4$ | 1.0 |
| Citric acid | 60.0 |
| Triethylene tetramine | 10.0 |

The conditions of the plating operation are those usually employed in the industry. For instance, the bath may be held at about 125° F. at a current density of about 20 amperes per square foot, with a pH adjusted to about 4.0. The resulting deposit has all of the favorable characteristics set forth above.

*Example 3*

A bath is prepared having the following ingredients in aqueous solution:

| | G./l. |
|---|---|
| Gold—in the form of $NaAu(CN)_2$ | 7.5 |
| Nickel—in the form of Ni tartrate | 20.0 |
| Tartaric acid | 40.0 |
| Tetraethylene pentamine | 5.0 |

The pH is adjusted at the beginning of the operation to 3.5. The plating is conducted as usual.

*Example 4*

The following bath is prepared:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 5.0 |
| Cobalt—in the form of $CoSO_4$ | 2.0 |
| Nickel—in the form of $NiSO_4$ | 1.5 |
| Boric acid | 35.0 |
| Ethylene diamine | 2.0 |
| Diethylene triamine | 3.0 |

By the use of borax, the pH is adjusted to a value of 3.8.

*Example 5*

The gold need not be introduced as the alkali metal-gold cyanide, but the constituents may be used, as in the following bath:

| | G./l. |
|---|---|
| Gold—in the form of AuCN | 4.5 |
| KCN | 1.3 |
| Nickel—in the form of $NiSO_4$ | 0.5 |
| Triethylene tetramine | 35.0 |

The bath is prepared by dissolving the aurous cyanide and the potassium cyanide in water, then adding the amine, and finally the nickel sulfate. The pH is adjusted to 3.0–5.0 with sulfuric acid. Plating is conducted at a temperature of 110° F. with a current density of 10 amperes per square foot.

*Example 6*

The base metal may be introduced in the form of a salt of an organic acid as in the following bath:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 5.0 |
| Cobalt—in the form of gluconate | 2.0 |
| Boric acid | 35.0 |
| Ethylene diamine | 2.0 |
| Diethylene triamine | 3.0 |

The pH is adjusted to 4.5 and the plating is conducted at 130° F. with a current density of 20 amperes per square foot.

*Example 7*

The base metal and the amine may be added in the form of a complex compound as in the following bath composition:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 10.0 |
| Nickel—in the form of a complex with tetraethylene pentamine | 5.0 |
| Hydroxy-acetic acid | 60.0 |

The pH is adjusted to 4.0. A temperature of 115° F. and a current density of 15 amperes per square foot is used in the plating.

*Example 8*

The presence of silver with the other metals is illustrated in the following bath.

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 7.5 |
| Nickel—in the form of formate | 1.0 |
| Silver—in the form of double cyanide | .05 |
| Potassium formate | 50.0 |
| Tetraethylene pentamine | 5.0 |

Formic acid is used to adjust the pH to 3.5. Plating is at a temperature of 120° F. with a current density of 20 amperes per square foot.

*Example 9*

To obtain a gold-silver deposit the following bath is used.

| | G./l. |
|---|---|
| Gold—in the form of $NaAu(CN)_2$ | 8.0 |
| Silver—in the form of $KAg(CN)_2$ | 0.1 |
| Tartaric acid | 50.0 |
| Triethylene tetramine | 25.0 |

The conditions of operations include a pH of 6.5, a temperature of 115° F. and a current density of 1–40 amperes per square foot. The tartaric acid is neutralized with sodium hydroxide.

Silver may be introduced as the amine cyanide. The amounts of gold and silver in the bath may be varied as for example there may be present 15.0 g./l. of gold and .3 g./l. of silver, and the polyamine may vary from about 1 to 100 g./l.

*Example 10*

The following bath is prepared:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 4.0 |
| Nickel—in the form of $NiSO_4$ | 0.2 |
| Tetraethylene pentamine | 60.0 |

The pH is adjusted to a pH of 4.5 with sulfuric acid. While the bath is commercially operable, it is desirable to introduce a buffer compound to help stabilize the bath

to minimize fluctuation in pH. Plating is conducted at 115° F. with a current density of 15 amperes per square foot.

*Example 11*

Another gold-nickel bath has the following composition:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 4.0 |
| Nickel—in the form of citrate | 2.5 |
| Citric acid | 120 |
| Tetraethylene pentamine | 20 |

The bath is held at 120° F. with a current density of 20 amperes per square foot, and a pH adjusted to 4.0.

*Example 12*

A bath which also includes cobalt is as follows:

| | G./l. |
|---|---|
| Gold—in the form of R—AuCN | 8.0 |
| Cobalt—in the form of gluconate | 0.5 |
| Nickel—in the form of gluconate | 1.2 |
| Boric acid | 15.0 |
| Ethylene diamine | 10.0 |
| Diethylene triamine | 15.0 |

The pH is adjusted to 5.8 and the usual plating conditions are employed. R is the radical of alkanol-, alkylene-, or polyamine.

*Example 13*

To deposit a pure bright gold the following bath is utilized:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 4.0 |
| Sulfamic acid | 60 |
| Tetraethylene pentamine | 40 |

The sulfamic acid is partially neutralized by the amine and boric acid may be added to act as a buffer. The pH is adjusted to 5.0. Plating is conducted at 15 amperes per square foot at a temperature of 80° F. A pure bright 24 carat gold is deposited.

*Example 14*

The following bath is provided:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 8.0 |
| Nickel—in the form of citrate | 12 |
| Citric acid | 120 |
| Tetraethylene pentamine | 15 |
| Triethylene tetramine | 10 |

A pH of 4.5 is utilized and the operating conditions as set forth herein are followed.

*Example 15*

Higher polyamines may be used, such as the residues from the manufacture of amines and having high molecular weights as shown in the following composition:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 4.0 |
| Sulfamic acid and K sulfamate | 60 |
| Boric acid | 25 |
| Polyamine residue (mol. wt. 1700) | 30 |

A pH of 5.0 is maintained. Plating is at a current density of 15 amperes per square foot at a temperature of 80° F.

*Example 16*

A gold-silver alloy is deposited from a bath, containing polymerized polyamines, having the following composition:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 8.0 |
| Silver—in the form of $KAg(CN)_2$ | 0.1 |
| Citric acid | 50 |
| Polymerized tetraethylene pentamine (average mol. wt. 1800) | 20 |



The temperature of operation may vary from 70° F. to 120° F. with current densities of 1 to 20 amperes per square foot, at a pH of 6.0.

*Example 17*

A bath is provided having the following composition:

| | G./l. |
|---|---|
| Gold—in the form of $KAu(CN)_2$ | 8.0 |
| Nickel—in the form of acetate | 4.0 |
| Hydroxyacetic acid | 100 |
| Polymerized tetraethylene pentamine (average mol. wt. 1200) | 30 |

The pH is adjusted to 4.0, a current density of 15 amperes per square foot is employed, and a temperature of 120° F. is maintained.

It is to be understood that various other amino compounds may be used, as for instance the following:

Hydroxyethyl ethylenediamine
Aminoethyl ethanolamine
Monoethanolamine
Triethanolamine
Triisopropanolamine

and others, including high molecular weight polyamines. In general, those amines having from 1 to 12 carbon atoms and polymers thereof having molecular weights up to say 2500 and even higher are suitable for the purpose. The baths may vary greatly in overall composition and the following proportions have been found to be fully operative:

| | G./l. |
|---|---|
| Gold | 0.5 –40.0 |
| Nickel | 0.1 –70.0 |
| Cobalt | 0.1 –50.0 |
| Silver | .02– 1.0 |

The baths are characterized by the absence of free alkali metal cyanides.

As buffer substances there may be used any acid or acid salt which does not adversely affect the plating operation. Inert anodes, such as of carbon, platinum or others may be used.

What is claimed is:

1. An electroplating bath for producing hard and bright deposits of a metal selected from the group consisting of gold and gold-base alloys comprising an aqueous solution of a soluble gold-alkali metal cyanide, a sufficient amount of a substance taken from the class consisting of alkylol-, alkylene- and alkanol-amines having 1 to 12 carbon atoms and polymers thereof to produce a brighter deposit than is obtained in the absence thereof, said bath having a pH of about 2.5 to 6.5.

2. An electroplating bath according to claim 1 in which there is present a sufficient amount of a buffer to maintain a stable pH.

3. An electroplating bath according to claim 1 in which there is present in soluble form a metal taken from the class consisting of cobalt and nickel.

4. An electroplating bath according to claim 1 in which the alloying metal is small relative to the gold present.

5. An electroplating bath according to claim 1 in which there is present silver in soluble form.

6. An electroplating bath according to claim 1 in which there is present silver in the form of double alkali metal cyanide.

7. An electroplating bath according to claim 1 in which there is present silver in the form of amine cyanide.

8. An electroplating bath according to claim 1 in which the relative proportions of the active ingredients in grams per liter are as follows:

Gold—in the form of double cyanide, 0.5 to 40
Amine—sufficient amount to brighten the deposit.

9. An electroplating bath according to claim 8 in which

there is present nickel in the form of a soluble salt to the extent of 0.1 to 70 grams per liter.

10. An electroplating bath according to claim 8 in which there is present cobalt in the form of a soluble salt to the extent of 0.1 to 50 grams per liter.

11. An electroplating bath according to claim 9 in which sulfamic acid is present.

12. An electroplating bath according to claim 9 in which said amines have average molecular weights of 1200 to 2500.



13. An electroplating bath according to claim 9 in which said amines are polymerized polyamines.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,660,554 | Ostrow | Nov. 24, 1953 |
| 2,812,299 | Volk | Nov. 5, 1957 |
| 2,905,601 | Rinker et al. | Sept. 22, 1959 |