# United States Patent [19]

**Weisberg et al.**

[11] **3,870,619**

[45] **Mar. 11, 1975**


[54] **PROCESS FOR PRODUCING BRIGHT ELECTRODEPOSITS OF GOLD AND ITS ALLOYS**


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[21] Appl. No.: **327,681**

[52] **U.S. Cl.**..... **204/43 G,** 204/46 G, 260/502.5

[51] **Int. Cl.** ..... **C23b 5/28,** C23b 5/42

[58] **Field of Search** ..... 204/43 G, 46; 106/1; 260/502.5



[56] **References Cited**

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| | | | |
|---|---|---|---|
| 3,507,937 | 4/1970 | Zimmerer | 260/502.5 X |
| 3,617,343 | 11/1971 | Kandler et al. | 106/1 X |
| 3,672,969 | 6/1972 | Nobel et al. | 204/43 G |



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[57] **ABSTRACT**

This invention discloses a process for producing bright electrodeposits of gold or gold alloys from solutions containing aminomethylene phosphinic acids.


**6 Claims, No Drawings**

# PROCESS FOR PRODUCING BRIGHT ELECTRODEPOSITS OF GOLD AND ITS ALLOYS

## BACKGROUND OF THE INVENTION

Aminomethylene phosphinic acids are of interest as metal chelating agents. Several of these are described by Motekaitis, Murose and Martell in the Journal Inorg. Nucl. Chem. 33,3353 (1971). These compounds are of further interest in that they can be converted to the corresponding phosphonic acids by an oxidation process described in U.S. Pat. No. 3,160,632. In a corresponding application, the aminemethylene phosphonic acids were found to have utility in electroplating baths. We have found that the aminomethylene phosphonic acids can be synthesized by reacting hypophosphorous acid, formaldehyde and a nitrogen compound containing replaceable hydrogen in the presence of a mineral acid. The mineral acid may be any strong acid but hydrochloric acid is preferred since it can be removed by distillation.

The preparation of these compounds is the subject of our co-pending application Ser. No. 327,690 filed of even date herewith.

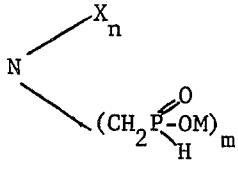
## DESCRIPTION OF THE INVENTION

We have found that the addition of aminomethylene phosphinic acids, or their water soluble salts, to gold plating baths improves the performance of the baths over conventional plating baths. The improvements are seen as more evenly distributed, brighter yellow gold deposits at higher limiting current densities. Furthermore, these new chelating agents are such effective regulators of alloying metal ions, such as copper, cobalt and nickel, that bright yellow gold is deposited from baths containing these compounds and the alloying metals. Furthermore, the deposits from these baths are brighter at higher current densities and are deposited at higher plating efficiencies than deposits from the conventional baths.

The compounds which fall within the scope of this invention may be divided into two groups, those based on a single nitrogen atom and those based on more than a single nitrogen atom.

### GROUP I

Nitrilomethylene Phosphinic Acids.



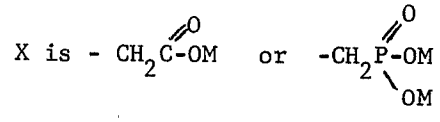
wherein

*m* is 1, 2 or 3,

*n* is 0, 1 or 2,

*n* + *m* is 3;

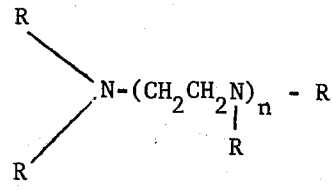
M is H or an alkali metal cation, such as, potassium or sodium; and





### GROUP II

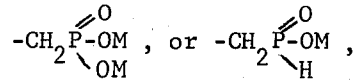
Alkylene Polyaminomethylene Phosphinic Acids



wherein

*n* is 1, 2 or 3 and

R may be H,



or —$CH_2COOM$, but at least one R group must be a methylene phosphinic acid; and

M is hydrogen or an alkali metal cation, such as sodium or potassium. Examples of these compounds are:

Nitrilotrimethylene phosphinic acid

Nitrilodimethylene phosphinic acid monoacetic acid

Nitrilo mono methylene phosphinic acid diacetic acid

Ethylenediamine tetramethylene phosphinic acid

Ethylenediamine trimethyl phosphinic acid monoacetic acid

Ethylenediamine dimethyl phosphinic acid diacetic acid

Ethylenediamine monomethylene phosphinic acid triacetic acid

The methylene phosphinic acids can be used in conventional gold plating baths as brighteners to produce bright gold or gold alloy deposits. They are especially effective in baths containing organic acids, such as citric or malic acid, or their water soluble salts. Inorganic salts, such as phosphates, polyphosphates, sulfamates, fluoroborates, etc. may also be used together with the additives. By conventional baths we mean generally those in which gold is present as a complex cyanide as a source of gold. Organic acid buffers useful with this invention are: (but others can be used)

1. Citric acid/potassium (or sodium) citrate (1:1 molar ratio) 10–150 grams/liter
2. Malic acid/potassium malate (1:1 molar ratio) 10–150 grams/liter
3. Citric acid/monopotassium dihydrogenphosphate (1:1 molar ratio) 10–150 grams/liter

Inorganic buffers useful in these plating baths are:

1. Monopotassium dihydrogen/dipotassium hydrogen phosphate (1:1 molar ratio) 40–100 grams/liter
2. Phosphoric acid/disodium hydrogen phosphate (1:2 molar ratio) 5–100 grams/liter
3. Monopotassium hydrogen phosphate/boric acid (1:1 molar ratio) 10–60 grams/liter

Generally any materials used in conventional gold plating baths as buffers are useful in our formulations.

The amount of phosphinic acid complexing agent brightener used in the plating bath depends on the specific use. The concentration may range from 0.5 gram/liter to 400 grams/liter. In those baths containing alloying metals, the molar concentration of the phosphinic acid should be equal to or greater than the concentra-

tion of the alloying metal. The invention may be illustrated by the following examples:

## EXAMPLE 1

Twelve grams of potassium gold cyanide, 58.4 grams of potassium citrate and 41.6 grams of citric acid are dissolved in water. To this solution is added 100 grams of ethylenediamine tetramethylene phosphinic acid and enough 45 percent potassium hydroxide solution to adjust the pH to 4.8. Brass test pieces were electroplated at 100°–130°F. at a current density of 5 amperes/square foot, for a period of ten minutes.

A brilliant, yellow gold deposit was obtained.

## EXAMPLE 2

A gold plating bath was prepared having the following composition:

| | |
|---|---|
| Potassium gold cyanide | 12 grams/liter |
| Cobalt sulfate | 10 grams/liter |
| Citric acid | 31 grams/liter |
| Potassium citrate | 44 grams/liter |
| Ethylenediamine tetramethylene phosphinic acid | 60 grams/liter |
| pH | 4.4 |
| Temperature | 65–130°F. |
| Current density | 10–20 amps/sq. ft. |

A bright, yellow gold deposit was obtained.

## EXAMPLE 3

The following gold plating bath was prepared:

| | |
|---|---|
| Potassium gold cyanide | 12 grams/liter |
| Cobalt sulfate | 10 grams/liter |
| Citric acid | 37 grams/liter |
| Potassium citrate | 53 grams/liter |
| Ethylenediamine tetramethylene phosphinic acid | 13.4 grams/liter |
| Potassium dihydrogen phosphate | 30 grams/liter |

The bath was used in the pH range 3.7–5.0 at 130°F and 3.7–6.6 at 75°F. The plating was carried out at a current density of 10 amperes per square foot and the resulting deposit was a bright, yellow gold.

## EXAMPLE 4

| | |
|---|---|
| Potassium gold cyanide | 12 grams/liter |
| Nickel sulfate | 10 grams/liter |
| Citric acid | 31 grams/liter |
| Potassium citrate | 44 grams/liter |
| Ethylenediamine tetramethylene phosphinic acid | 60 grams/liter |
| pH | 4.4 |
| Temperature | 120°F. |
| Current density | 10 amps/sq. ft. |

A lustrous gold deposit was obtained.

## EXAMPLE 5

| | |
|---|---|
| Potassium gold cyanide | 12 grams/liter |
| Cobaltous sulfate | 10 grams/liter |
| Citric acid | 31 grams/liter |
| Potassium citrate | 44 grams/liter |
| Nitrilotrimethylene phosphinic acid | 60 grams/liter |

The bath was used at pH 3.7–5.0. The plating was carried out at 120°F. at a current density of 10 amperes per square foot.

A highly reflective, yellow gold deposit was obtained.

## EXAMPLE 6

Using the basic formulation of Example 5, but with 40 grams per liter of ethylene diamine trimethylene phosphinic acid monoacetic acid, and plating under conditions of about the same pH level and temperature and current density, highly reflective yellow gold deposits are obtained.

## EXAMPLE 7

Using the same basic formulation as appears in Example 2, but with 50 grams per liter of ethylene diamine dimethylene phosphinic acid diacetic acid and plating under conditions of pH 5, temperature 65 at 130° in current density, 10–20 amperes per square foot, good bright yellow adherent gold deposits are obtained.

## EXAMPLE 8

Using the same basic formulation as shown in Example 3, but with 30 grams of ethylene diamine trimethylene phosphinic acid, monoacetic acid, and pH conditions of 3.7 to 5 at about 30°F. at 10 amperes per square foot, a bright yellow gold deposit is obtained.

Similar variations of the formulae using nitrilo monoacetic acid dimethylene phosphinic acid and nitrilo diacetic acid, monomethylene phosphinic acid and employing virtually any of the formulations shown in the examples, comparable results in the deposit of bright yellow gold deposits are obtained.

It is to be understood that in Examples 1–8, we have used exemplary concentrations of 12 grams per liter of gold cyanide and other specifically designated numerical concentrations with remaining balancing ingredients. These, however, are to be considered merely illustrative of what is to be used and actually, the gold concentration may vary in any of the examples, from 5 to 25 grams per liter as the complex potassium cyanide, the citric acid and citrate or buffering ingredient will be approximately in the amount shown to obtain the pH indicated, but is variable in the range from 10 to 50 grams per liter to develop the desired pH.

## EXAMPLE 9

In the production of alloy plates, any one of the formulations given in Examples 1–8 can be considered adequate and there need be added to the formulation merely a water soluble salt, generally the chloride or the sulfate, of the alloying metal. For alloying the gold, copper is commonly used to produce the red gold, nickel to produce white gold or pale golds, cobalt to produce pinkish golds, etc. An amount of the alloying metal from a fraction of a gram to about 25 grams per liter is useful but inasmuch as the general effect of tinting the gold is obtained with relatively small amounts of the alloying metal the lower concentrations are indicated, that is, only a few grams per liter of the alloy metal. Thus 0.01 to 25 grams per liter is a useful working range.

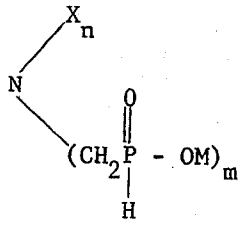
Though the invention has been described in terms of only a relatively few specific examples, it is to be understood that variations thereof may be made without departing from its spirit or scope.

What is claimed is:

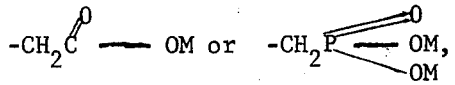
**1.** In an electroplating bath for producing bright gold or gold-base alloy deposits, in a pH range between 3.7 and 6.6, from an aqueous solution containing as the

gold source, a water soluble gold cyanide, the improvement comprising, including

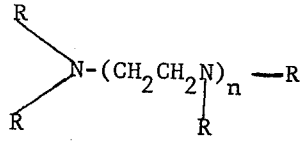
a small but useful amount in the range from about 0.5 gram to 400 grams per liter of a chelating agent selected from the group consisting of those compounds represented by the formula;



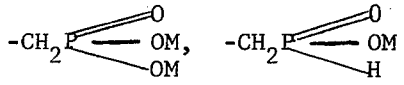
where $m$, is 1, 2, or 3, $n$ is 0, 1, or 2, $n + m$ is 3; M is H or an alkali metal cation; and X is



and those represented by the formula:



where n is 1, 2, or 3 and R is H,



or $-CH_2COOM$, but at least one R group must be a methylene phosphinic acid and M is hydrogen or an alkali metal cation.

**2.** An electroplating bath in accordance with claim **1** for producing bright gold deposits in a pH range of 3.7 to 6.6, from an aqueous solution containing

1. a water soluble gold cyanide
2. an organic or inorganic acid or alkali metal salt selected from the group citric, malic, phosphate, polyphosphate, sulfamate, fluoborate in amount from 10 to 150 grams per liter
3. 0.5 to 150 grams per liter of ethylenediamine tetramethylene phosphinic acid.

**3.** An electroplating bath for producing bright gold or gold-base alloy deposits, in a pH range between 3.7 and 6.6, from an aqueous solution containing

1. a water soluble gold cyanid,
2. a salt of an alloy metal in amount up to 25 grams per liter of alloy metal 3. an organic acid or inorganic acid, or alkali metal salt selected from the group citric, malic, phosphate, polyphosphate, sulfamate, fluoborate, in amount from 10 to 150 grams per liter, and 4. 0.5 to 150 grams per liter of nitrilotrimethylene phosphinic acid.

**4.** A bath in accordance with claim **3** wherein the bath contains a cobalt salt as a source of alloying metal in the amount of 0.01 to 25 grams per liter.

**5.** A bath in accordance with claim **3** wherein the bath contains a nickel salt as a source of alloying metal in the amount of 0.01 to 25 grams per liter.

**6.** A bath in accordance with claim **3** wherein the bath contains a nickel and a cobalt salt as alloying metals in the total amount of 0.01 to 25 grams per liter.

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