

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Gold Electro-plating

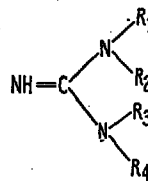
We, KABUSHIKI KAISHA SUWA SEIKOSHA, a Japanese company, of 4—5, Ginza-Nishi, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the electrodeposition of gold, herein referred to, for brevity, as gold plating.

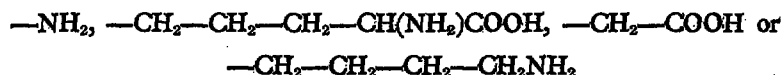
There are some cases, however, where a thickness of this order is not sufficient to resist corrosion and climatic effects. Unfortunately, as the thickness of electroplated films increases, the brightness of the plated surface generally decreases. Moreover, internal warps of the plating films increase, which result in band adhesion of and cracks in the plated films. This tendency is particularly marked where a bright plating bath is used. Use may be made of supplementary means such as buffing, annealing and so on to increase the brightness of the deposit, but such means are not only expensive but inapplicable to a great many goods such as delicate electronic parts and jewellery.

An object of this invention is to provide a method for gold plating which enables a gold plate of satisfactory thickness and brightness to be obtained.

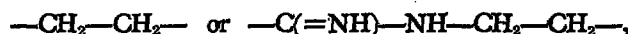
According to the present invention there is provided a process for the electrodeposition of gold which comprises electrodepositing gold by the passage of an electric current through an aqueous solution of a cyano complex salt of gold comprising between 5 and 25 gram per litre of gold, calculated as metal, the said solution containing guanidine or a derivative thereof of the formula



wherein the groups R_1 , R_2 , R_3 and R_4 are the same or different and are hydrogen atoms or alkyl groups, or three of them are hydrogen atoms and the fourth is a



groups or R_1 and R_3 are hydrogen and R_2 and R_4 together constitute a chain of the structure



the pH of the said solution being controlled to lie between pH 4 and pH 6.

[Price 4s. 6d.]

Suitable compounds of the foregoing formula are the following:—

17 SEP 1969

Amino-guanidine carbonate	$\text{NH}_2\text{NH}-\text{C}(\text{NH})-\text{NH}_2 \cdot \text{H}_2\text{CO}_3$
L-arginine	$\text{NH}_2-\text{C}(\text{NH})-\text{NH}-(\text{CH}_2)_3-\text{CH}(\text{NH}_2)-\text{COOH}$
Creatine	$\text{NH}_2-\text{C}(\text{NH})-\text{N}(\text{CH}_3)-\text{CH}_2-\text{COOH} \cdot \text{H}_2\text{O}$
Agmatine	$\text{NH}_2-\text{C}(\text{NH})-\text{NH}(\text{CH}_2)_4-\text{NH}_2$
5 Monomethyl guanidine	$\text{CH}_3-\text{NH}-\text{C}(\text{NH})-\text{NH}_2$
Tetramethyl guanidine	$(\text{CH}_3)_2\text{N}-\text{C}(\text{NH})-\text{N}(\text{CH}_3)_2$
Ethylene biguanide	$\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}(\text{NH})-\text{NH}-\text{C}(\text{NH})-\text{NH}_2$
Ethylene guanidine hydrochloride	$\text{CH}_2-\text{CH}_2-\text{NH}-\text{C}(\text{NH})-\text{NH} \cdot \text{HCl}$

10 Using the aforesaid compounds bright gold platings may be obtained, depending on the particular compound used, at thickness up to 10×10^{-4} cm. and platings of thickness up to 30×10^{-4} cm. are found to have good adhesion and to be substantially free from cracks.

15 According to a particular feature of the invention there may be included in the plating bath, to increase plating speed, a nickel salt of an organic or inorganic acid. Generally, when a nickel salt is added to an acidic cyanide gold bath, the current efficiency in the cathode becomes extremely bad, so that the plating takes a relatively long time. On the other hand, it is a well-known fact that if the plating current density is increased in an attempt to increase the plating speed, hydrogen brittleness of the deposit, leading to cracks and bad adhesion will tend to occur. The aqueous solution used according to the present invention suffers also a certain fall in the current efficiency when a nickel salt is added, but is not as prone to hydrogen brittleness of the electrochemical deposit when the current density is increased. In this case, the deposit is a gold alloy film comprising 1 to 3% nickel.

35 Although it is not exactly clear how the guanidine compounds and the nickel salts act in the plating process, it seems that the principal cause of brightness in the resultant deposit originates from the guanidine compound.

40 Preferably the plating bath is maintained at a temperature from 10 to 70°C. A cathode current density from 0.1 to 3.0 A/dm² may be employed.

45 When applying the invention to a practical plating process, it is desirable to counteract the tendency of the guanidine compounds to decompose rapidly due to electrolytic oxidation during plating, a tendency which is enhanced as the anode current density increases. For this reason there is preferably added to the bath a large quantity of a reducing agent to act as a depolariser and counteract the above-mentioned tendency.

50 This reducing agent should not be such as to have any deleterious effect on the plating

itself or on the products of the plating process. Therefore, it is preferable to use a reducing organic acid, for example formic acid, ascorbic acid or oxalic acid for this purpose. In this case, the pH range of the plating bath can be adjusted with the said acid, or by use of an alkaline additive such, for example, as alkali hydroxide or aqueous ammonia.

It is necessary to choose a suitably related density of gold, temperature, cathode current density and pH. Ordinarily, good results can be obtained by choosing a density of gold between 10 and 25 g/l, a temperature of the bath between 55 and 65°C, a cathode current density between 0.1 and 0.5 A/dm² and pH between 4 and 5. The current efficiency in this case is between 90 and 95%.

When using a plating bath as referred to above but including a nickel salt it is preferable for obtaining good results to employ the nickel salt at a concentration of 0.5 to 10 g/l, calculated as nickel, and to employ a greater cathode current density, such as from 1 to 3 A/dm². In this case, it is desirable to add a large quantity of reducing organic acid to prevent decomposition of the guanidine compound. The current efficiency in this case is approximately 20%.

The electrochemical deposit of the present invention keeps its mirror brightness up to plating thicknesses of 10×10^{-4} cm. and is scarcely affected by hydrogen brittleness up to $30-40 \times 10^{-4}$ cm.

A preferred plating bath, containing nickel, which constitutes a further feature of this invention comprises an aqueous solution comprising a cyano complex salt of gold at a concentration of 5 to 25 g/litre calculated as gold, a nickel salt of an organic or inorganic acid at a concentration of 0.5 to 10 g/litre, calculated as nickel, at least 200 g/litre at a reducing organic acid, and the foregoing general formula, the pH of the solution being between pH 4 and pH 6.

Four specific examples of aqueous solutions for gold plating according to the invention are given below.

EXAMPLE I

	KAu (CN) ₂	30 g/l
	Amino-guanidine carbonate	20 g/l
	Sulphamic acid	to pH 4
5	Cathode current density	0.2 A/dm ²
	Temperature	50°C
	Agitation	none

When plating with this solution, a bright electro-deposit of thickness 10×10^{-4} cm. and good adhesion and free from cracks is obtained. The current efficiency is approximately 90%.

EXAMPLE II

	KAu (CN) ₂	30 g/l
15	Ethylene guanidine	10 g/l
	Formic acid (85%)	250 g/l
	Ammonia water	to pH 4
	Cathode current density	0.2 A/dm ²
	Temperature	50°C
20	Agitation	none

The same result as that of Example 1 is obtained with this solution.

EXAMPLE III

	KAu (CN) ₂	15 g/l
25	Creatine	10 g/l
	Formic acid (85%)	250 g/l
	Ammonia water	to pH 4
	Nickel sulfate	2 g/l
	Cathode current density	2 A/dm ²
30	Temperature	60°C
	Agitation	conventional

Using this plating solution, a mirror-bright electro deposit is obtained up to a plating thickness of nearly 10×10^{-4} cm. It is observed that the hydrogen is generated from the face of the cathode during electrolysis, but the electro-deposit shows no cracks and has a good adhesion. The current efficiency is approximately 20%. The deposit formed contains 2% nickel.

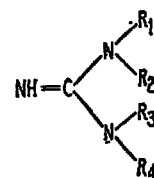
EXAMPLE IV

	KAu (CN) ₂	15 g/l
	L-arginine	10 g/l
	Formic acid	250 g/l
	Ammonia water	to pH 4
	Nickel citrate	2 g/l as nickel
	Cathode current density	2 A/dm ²
	Temperature	60°C
	Agitation	conventional

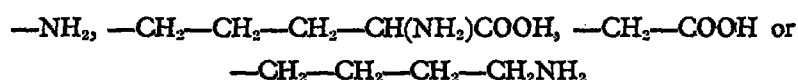
Using this plating solution, a mirror-bright electro-deposit is obtained up to a plating thickness 10×10^{-4} cm. It is observed that the hydrogen is generated from the face of the cathode during electrolysis, but the electro-deposit shows no cracks and has good adhesion. The current efficiency is approximately 20%. The nickel content of the deposit is in this case about 1%.

WHAT WE CLAIM IS:—

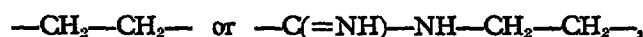
1. A process for the electrodeposition of gold which comprises electrodepositing gold by the passage of an electric current through an aqueous solution of a cyano complex salt of gold comprising between 5 and 25 gram per litre of gold, calculated as metal, the said solution containing guanidine or a derivative thereof of the formula



wherein the groups R₁, R₂, R₃ and R₄ are the same or different and are hydrogen atoms or alkyl groups, or three of them are hydrogen atoms and the fourth is a



group or R₁ and R₃ are hydrogen and R₂ and R₄ together constitute a chain of the structure



the pH of the said solution being controlled to lie between pH 4 and pH 6.

2. A method according to claim 1 wherein the said solution contains 0.5 to 10 g/litre of a nickel salt of an organic or inorganic acid and at least 200 g/litre of a reducing organic acid.

3. A method according to claim 1 wherein the gold concentration is 10 to 25 g/litre, the temperature of the bath is 55—65°C, the pH is between 4 and 5 and the cathode cur-

rent density is between 0.1 and 0.5 A/dm².

4. A method according to claim 2 wherein the gold concentration is 10 to 25 g/litre, the temperature of the bath is 55—65°C, the pH is between 4 and 5 and the cathode current density is between 1 and 3 A/dm².

5. A method according to claim 1 wherein the plating bath used is substantially as set forth in any one of the foregoing specific examples.

6. An aqueous solution for use as a plat-

EXAMPLE I

	KAu (CN) ₂	30 g/l
	Amino-guanidine carbonate	20 g/l
	Sulphamic acid	to pH 4
5	Cathode current density	0.2 A/dm ²
	Temperature	50°C
	Agitation	none

When plating with this solution, a bright electro-deposit of thickness 10×10^{-4} cm. and good adhesion and free from cracks is obtained. The current efficiency is approximately 90%.

EXAMPLE II

	KAu (CN) ₂	30 g/l
15	Ethylene guanidine	10 g/l
	Formic acid (85%)	250 g/l
	Ammonia water	to pH 4
	Cathode current density	0.2 A/dm ²
	Temperature	50°C
20	Agitation	none

The same result as that of Example 1 is obtained with this solution.

EXAMPLE III

	KAu (CN) ₂	15 g/l
25	Creatine	10 g/l
	Formic acid (85%)	250 g/l
	Ammonia water	to pH 4
	Nickel sulfate	2 g/l
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30	Temperature	60°C
	Agitation	conventional

Using this plating solution, a mirror-bright electro deposit is obtained up to a plating thickness of nearly 10×10^{-4} cm. It is observed that the hydrogen is generated from the face of the cathode during electrolysis, but the electro-deposit shows no cracks and has a good adhesion. The current efficiency is approximately 20%. The deposit formed contains 2% nickel.

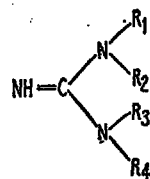
EXAMPLE IV

	KAu (CN) ₂	15 g/l
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	Temperature	60°C
	Agitation	conventional

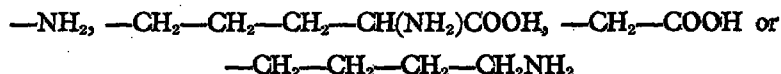
Using this plating solution, a mirror-bright electro-deposit is obtained up to a plating thickness 10×10^{-4} cm. It is observed that the hydrogen is generated from the face of the cathode during electrolysis, but the electro-deposit shows no cracks and has good adhesion. The current efficiency is approximately 20%. The nickel content of the deposit is in this case about 1%.

WHAT WE CLAIM IS:—

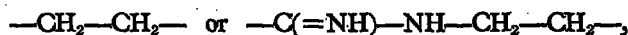
1. A process for the electrodeposition of gold which comprises electrodepositing gold by the passage of an electric current through an aqueous solution of a cyano complex salt of gold comprising between 5 and 25 gram per litre of gold, calculated as metal, the said solution containing guanidine or a derivative thereof of the formula



wherein the groups R₁, R₂, R₃ and R₄ are the same or different and are hydrogen atoms or alkyl groups, or three of them are hydrogen atoms and the fourth is a



75 group or R₁ and R₃ are hydrogen and R₂ and R₄ together constitute a chain of the structure



the pH of the said solution being controlled to lie between pH 4 and pH 6.

2. A method according to claim 1 wherein the said solution contains 0.5 to 10 g/litre of a nickel salt of an organic or inorganic acid and at least 200 g/litre of a reducing organic acid.

3. A method according to claim 1 wherein the gold concentration is 10 to 25 g/litre, the temperature of the bath is 55–65°C, the pH is between 4 and 5 and the cathode cur-

rent density is between 0.1 and 0.5 A/dm².

4. A method according to claim 2 wherein the gold concentration is 10 to 25 g/litre, the temperature of the bath is 55–65°C, the pH is between 4 and 5 and the cathode current density is between 1 and 3 A/dm².

5. A method according to claim 1 wherein the plating bath used is substantially as set forth in any one of the foregoing specific examples.

6. An aqueous solution for use as a plat-



- ing bath in the electrodeposition of gold which comprises a cyano complex salt of gold at a concentration of 5 to 25 g/litre, calculated as gold, a nickel salt of an organic or inorganic acid at a concentration of 0.5 to 10 g/litre, calculated as nickel, at least 200 g/litre of a reducing organic acid, and guanidine or a guanidine derivative of the formula set forth in claim 1, the pH of the solution being
- 5 between pH 4 and pH 6.
- 10
7. An aqueous solution according to claim 6 substantially as hereinbefore set forth in either of the foregoing specific Examples 3 and 4.

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