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3,475,290
**BRIGHT GOLD PLATING SOLUTION
 AND PROCESS**

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No Drawing. Filed Apr. 13, 1966, Ser. No. 546,122

Claims priority, application Japan, May 7, 1965,

40/26,539

Int. Cl. C23b 5/46, 5/42

U.S. Cl. 204-43

6 Claims

ABSTRACT OF THE DISCLOSURE

A process and electrolyte for electroplating bright gold. The electrolyte has a pH of about 4-6 and comprises a cyano complex of gold and, as brightening agent, an organic alkyl or alkylene guanidine compound. The bath may additionally contain a nickel salt and a reducing organic acid.

The present invention relates to a plating solution for obtaining a bright gold plating.

It is natural that bright gold plating is generally needed in great many cases for enhancing values of plated goods, and these gold or alloy platings which are presently used in industrial plan, have almost all thicknesses of no more than $1\sim 2 \times 10^{-4}$ cm.

However, there are some cases where these thicknesses are not sufficient to resist corrosion, climate and friction. While thicknesses of plating films increase, degrees of brightness in the plated surface decrease in general. Moreover internal stresses of the plating films increase, which causes bad adhesion, cracks, etc. This tendency is particularly distinguished in case of the bright plating bath. Therefore, one makes use of the supplementary means such as buffing, annealing, etc., in order to obtain bright platings. But these means are not only expensive but inapplicable to a great many goods such as electronic parts, jewelry, etc.

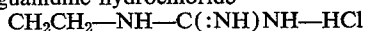
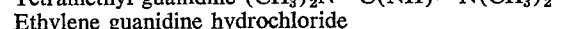
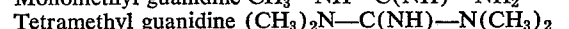
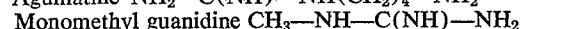
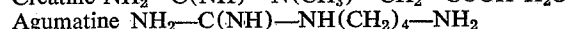
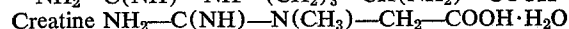
An object of this invention is to provide a plating bath for obtaining a thick and bright plating surface.

It needs no saying that the object of the present invention can be achieved without sacrificing the operational conditions necessary to utilize this bath in industry.

It has been found that when an aqueous gold plating bath containing a cyano complex salt of gold, and an organic alkyl or alkylene guanidine compound maintained at pH of from 4 to 6 is utilized for plating gold, a bright thick gold coating can be obtained.

Among the organic alkyl or alkylene guanidine compounds which can be utilized in the plating bath of this invention, the following are included:

L-arginine



In this case, the thickness of plating film presenting the brightening effect is approx. $10\sim 30 \times 10^{-4}$ cm. counting on the differences of the alkyl and alkylene guanidine compound added. With the plating bath of this invention cracking or poor adhesion, which are frequently seen in the acid plating bath, does not occur.

Furthermore it was found that bright plating can be carried out at high speed by adding organic and inorganic nickel salts to the said bath.

Generally, when the nickel salt is added to the acidic cyanide gold bath, the current efficiency in cathode becomes extremely bad, so that plating is carried out very slowly. While, it is a well-known fact that if one increases current density for supplying the deficiency above-mentioned, a plating film will be obtained that will have a hydrogen brittleness. In this plating film cracks, bad adhesion, etc. will occur.

The bath according to the invention suffers also a certain decrease of the current efficiency. Even if one increases the current density the bath has many obstacles due to the hydrogen brittleness of plating film. Moreover the plating bath can give more brightness at high speed by increasing a current density. In this case, the plating film is an alloy plating comprising 1~3% nickel.

Though it is not clear that the alkyl guanidine and alkylene guanidine compounds and the nickel salts act with that microscopic action in electrolysis, it seems that the principal cause of brightness appearing originates from a group of alkyl guanidine and alkylene guanidine in molecule.

The above two concepts are the essentials of this invention.

Therefore the object of this invention can be achieved by firstly preparing the plating bath which is made by adding proper quantities of the said soluble alkyl guanidine and alkylene guanidine compounds and of the said nickel salt to the aqueous solution of cyano complex salt of gold and secondly controlling the concentration of gold from 5 to 25 g./l., a pH of bath from 4 to 6 of weak acidity, a temperature from 10 to 70° C., a cathode current density from 0.1 to 3.0 A./dm.².

In case of applying this bath to the practical plating, the first problem is that the said alkyl guanidine and alkylene guanidine compounds are weak for oxidation, consequently they decompose rapidly due to suffer electrolytic oxidation of anode during plating and loses its brightening effects at the same time.

This situation is all the more remarkable as the current density in anode increases.

The bath needs a large quantity of reducing agents as depolarizer to supply the deficiency above-mentioned.

Concerning this reducing agent, it should not have any bad influence on plating by itself as well as its decomposition products, and also it must be able to do the quantitative analysis of the said alkyl guanidine and alkylene guanidine compounds which is needed for controlling the plating solution. Therefore, it is recommended to use a reducing organic acid, for example formic-acid, ascorbic acid, oxalic acid, etc., for this purpose.

In this case, pH range of the plating bath can be adjusted with the said acid, alkali hydroxide, ammonia water, etc.

Then it is necessary to choose properly a concentration of gold, temperature, cathode current density and pH, as there is a certain relation among them.

Ordinarily, one could get good results by choosing a concentration 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./dm.² and pH between 4 and 5. The current efficiency: 90~95%.

In the plating bath of high speed comprising a nickel salt, it is preferable for obtaining good results to make a concentration of nickel from 0.5 to 10 g./l. and a cathode current density greater such as from 1 to 3 A./dm.². In this case, it needs to prevent a decomposition of the said alkyl guanidine and alkylene guanidine compounds by adding a large quantity of reducing organic acid. The current efficiency: 20%.

The electrodeposit keeps its mirror brightness till the thickness of the plating deposit reaches from 10 to

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30×10^{-4} cm., moreover it scarcely causes troubles due to a hydrogen brittleness.

EMBODIMENT 1

KAu(CN) ₂	g./l.	30	5
Ethylene guanidine	g./l.	10	
Formic acid (85%)	g./l.	250	
Cathode current density	A./dm. ²	0.2	
Temperature	° C.	50	
Agitation		No	10

Ammonia water till a pH becomes 4.

Utilizing the above conditions a bright electrodeposit was obtained having a thickness of 10×10^{-4} cm., good adhesion and no cracks. The current efficiency was 90%. 15

EMBODIMENT 2

KAu(CN) ₂	g./l.	15	
Creatine	g./l.	10	
Formic acid (85%)	g./l.	250	20
Nickel sulfate	g./l.	2	
Cathode current density	A./dm. ²	2	
Temperature	° C.	60	
Agitation		Properly	25

Ammonia water till a pH becomes 4.

In case of the plating with above conditions, the electrodeposit presents mirror brightness until the plating thickness of nearly 10×10^{-4} cm. It is observed that the hydrogen is generated from the face of cathode during electroanalysis, but the electrodeposit causes no cracks and has a good adhesion. The current efficiency: 20%. The plating deposit comprises 2% nickel. 30

EMBODIMENT 3

KAu(CN) ₂	g./l.	15	35
L-arginine	g./l.	10	
Formic acid (85%)	g./l.	250	
Nickel citrate	g./l. as nickel	2	
Cathode current density	A./dm. ²	2	40
Temperature	° C.	60	
Agitation		Properly	

Ammonia water till a pH becomes 4.

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The same result as that of the Embodiment 2 is also obtained in case of the plating with above conditions. Nickel content: 1%.

What we claim is:

1. A bath for the deposition of a bright thick gold plate comprising an aqueous solution containing cyano complexed gold in an amount to provide from 5 to 25 grams per liter of gold as metal in said solution, and an organic alkyl or alkylene guanidine compound present in an amount sufficient to provide a bright electrodeposit, said bath having a pH of from 4 to 6.

2. The bath of claim 1 wherein said guanidine compound is ethylene guanidine.

3. The bath of claim 1 wherein said bath contains from about 0.5 to 10 grams per liter of an organic or organic salt of nickel.

4. The bath of claim 1 wherein the bath contains at least 200 grams per liter of an organic reducing acid.

5. The bath of claim 4 wherein said bath contains 0.5 gram to 10 grams per liter of an organic or inorganic salt of nickel.

6. A process for the electrolytic deposition of gold which comprises passing an electrolytic current of a density of from about 0.1 to 3 A./dm.² at the cathode through an aqueous solution containing cyano complexed gold in an amount to provide from 5 to 25 grams per liter of gold as metal in said solution, and an organic alkyl or alkylene guanidine compound in an amount sufficient to provide a bright electrodeposit, said bath having a pH of from 4 to 6.

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U.S. Cl. X.R.

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