

1 An Electrolytic Bath for the Deposition of
Gold and Gold Alloy Coatings

5 The invention relates to a gold bath for the
electrolytic deposition of highly lustrous and
ductile gold alloy coatings based on potassiumcyano-
aurate (III) which contains an acid of at least one of
the alloying metals cobalt, nickel, indium, tin, zinc,
10 or cadmium in the form of water-soluble salts and a
complex forming agent at a pH of less than 3.

 In electrical engineering, the majority of gold
coatings are deposited nowadays from weakly acidic
15 electrolytes which operate in the pH range of from
3.5 to 5. They contain the gold in the form of
potassiumdicyanoaurate (I), $\text{KAu}(\text{CN})_2$, and, as buffers,
salts of weak inorganic or organic acids such as
phosphates, citrates or phosphonates. The properties
20 of the deposited layers are greatly influenced by
additions of metal salts, in particular of nickel,
cobalt, or indium. Coatings which are lustrous, have
a Vickers pyramid hardness of from 150 to 180 and
possess good resistance to mechanical wear are obtained
25 from these baths under conditions in which from 0.2 to
0.5% Ni or Co are also deposited. These coatings are
substantially pore-free from about 5 μm . They are
distinguished by good electrical conductivity and low
contact resistance.

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 The coatings from these baths also have consider-
able disadvantages, however. Their ductility is low.
Cracks are formed during light mechanical pre-shaping.
They contain a relatively large amount (about 1%) of
35 non-metallic impurities which probably lead to func-
tional disturbances in electrical weak current
contacts. The

1 contact resistance probably does not remain constant
under thermal stress and impairs operation of elec-
trical devices, probably also on account of these
impurities.

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The content of the alloying metal in the coating
is greatly dependent on the current density and the
pH, so that the operating conditions must be kept
within close limits in order to obtain coatings of
10 uniform quality. The average current density is
restricted to about 1 A/dm², the bath temperature
should not be higher than 40°C and the pH must be
kept between 3.5 and 4 with most baths. At pH 4,
the layers are often only milky-lustrous or even
15 matt. pH values below 3.5 cannot be adopted because
the KAu(CN)₂ disintegrates at pH 3 with separation
of gold cyanide, AuCN. Attempts have nevertheless
been made to utilize such baths at pH values below 3
(for example DE-AS 1262723, US-PS 2978390), but the
20 results were not satisfactory.

Attempts have also been made to use baths in the
acidic range which contain the complex of trivalent
gold with potassiumcyanide, potassiumtetracyanoaurate
25 (III), KAu(CN)₄.

A process for the production of tetracyano gold
(III) acid and a bath on this basis is described in
US-PS 3598706. A hydrochloric acid bath for the
30 preliminary gold plating of refined steel is
described in US-PS 4168214, the tetracyano gold
(III) complex being formed by a reaction of gold (III)
chloride with potassiumcyanide in the bath and a
pH of between 0.1 and 1.5 being adjusted. This bath
35 additionally contains alloying metals such as nickel,
cobalt, tin or indium, and ethylene diamine hydro-
chloride as

1 complex forming agent. A pure alloy bath for the
deposition of gold/tin coatings based on $\text{KAu}(\text{CN})_4$
in a hydrochloric acid medium is claimed in DE-OS
2658003.

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Baths in which the gold is present in trivalent
form have the disadvantage over baths based on mono-
valent gold salts that only one third of the quantity
of gold is deposited owing to the differences in
10 valency with identical current densities and times.
This disadvantage can only be compensated by the
adoption of correspondingly high current densities.
However, this is not possible with the formerly known
baths because the deposited layers are matt and rough
15 so that thicker coatings cannot be produced econo-
mically. A further substantial disadvantage resides
in the high chloride content in these baths which leads
to unpleasant evolution of chlorine at the anode. If
the baths additionally contain hydrochloric acid, then
20 problems of corrosion also occur in the apparatus.

An object of the present invention was therefore
to find a gold bath for the electrolytic deposition of
gold alloy coatings based on potassiumcyanoaurate(III)
25 which contains an acid, at least one of the alloying
metals cobalt, nickel, indium, tin, zinc or cadmium
in the form of water-soluble salts and a complex-
forming agent at a pH of less than 3, which yields
highly lustrous and ductile coatings even at high
30 current densities and in which chlorine evolution does
not occur.

This object has been achieved according to the
invention in that the electrolyte contains, in addition
35 to an amine, an aminocarboxylic acid or a phosphonic
acid as the complex-forming agent, from 20 to 200 g/l

- 1 of sulphuric acid, phosphoric acid, citric acid or mixtures thereof as the acid. (A pH range of from 0.4 to 2.5 is particularly advantageous.
- 5 Baths which contain from 1 to 20 g/l of gold in the form of potassiumcyanoaurate (III), from 10 to 200 g/l of sulphuric acid, phosphoric acid and/or citric acid, from 0.1 to 20 g/l of at least one of the alloying metals cobalt, nickel, indium, zinc, tin or cadmium in
- 10 the form of water-soluble salts and from 1 to 100 g/l of an amine, an aminocarboxylic acid or a phosphonic acid, which are capable of forming a complex with the alloying metal have proven suitable. The addition of salts of the acids used such as, for example, potassium-
- 15 dihydrogenphosphate, potassiumhydrogensulphate or potassiumcitrate is also advantageous. Temperatures of from 40 to 60°C and current densities of from 0.1 to 20 A/dm² are preferably adopted.
- 20 It has surprisingly been found that lustrous gold layers can be deposited over a broad current density range from acidic electrolytes based on the tetracyanoaurate (III) complex if the baths contain alloying metals and, at the same time, suitable complex-
- 25 forming agents and suitable acids. Alloying metals can be Co, Ni, In, Sn, Zn or Ce. Suitable complex-forming agents include amines, aminocarboxylic acids or phosphonic acids. If the alloying metals are only added in the form of simple salts, as in the formerly
- 30 known baths, the distribution of metal in the coating is irregular because the quantity of alloying metal deposited generally depends greatly on the current density. It has now surprisingly been found that, when using the above-mentioned complex-forming agents, the
- 35 deposition of the alloying metal is substantially independent of the current density so that, with

1 optimum selection of gold content, pH and bath temperature, the coatings have a constant alloying metal content. In other known baths, this independence does not generally exist.

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The use of high current densities thus becomes possible and deposition rates of the type occurring that the known weakly acidic gold baths in the pH range of between 3.5 and 5 can thus be achieved.

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The use of the above-mentioned complex-forming agents and the above-mentioned acids in the electrolytic baths is known, but it was not expected that the combination of these substances under the prescribed conditions would control the deposition of the alloying metals so strongly because the stability of the complexes with the above-mentioned metals is normally slight at pH values below 3.

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The properties of the deposited layers from the bath according to the invention have particular advantages over the coatings from the so-called weakly acidic gold baths. The layers are not only hard and wear-resistant but also very ductile. They can be deposited with few pores even in a thin layer. The contact resistance is low and remains constant even when stored in heat. The content of non-metallic impurities is very low.

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Baths according to the invention contain:
from 1 to 20 g/l of gold as $\text{KAu}(\text{CN})_4$
from 10 to 200 g/l of phosphoric acid, sulphuric acid or mixtures thereof, citric acid, phosphates, sulphates
from 0.1 to 20 g/l of an alloying metal, which may be
35 Co, Ni, In, Sn, Zn, Cd
from 1 to 100 g/l of an amine, an aminocarboxylic or

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1 phosphonic acid.

 The $\text{KAu}(\text{CN})_4$ is produced in known manner by
reaction of AuCl_3 with KCN and is crystallized from
5 the mother liquor. A salt containing little chloride
is thus obtained. The quantity of acid contained in
the bath is not critical. Better conductivity is
achieved with higher contents. A proportion of the
phosphoric acid can also be added as KH_2PO_4 if
10 excessively low pH values would be achieved with the
acid alone. A number of compounds for the groups of
suitable complex-forming agents are mentioned by way
of example below:

Amines:

15 Ethylenediamine

Tetraethylenepentamine

Triethylamine

Diethylenetriamine

Triethylenetetramine

20 Aminocarboxylic acids:

Nitrilotriacetic acid

Ethylenediaminetetraacetic acid

1,2-diaminocyclohexanetetraacetic acid

Bis-2-aminoethylethertetraacetic acid

25 Diethylenetriaminepentaacetic acid

Phosphonic acids:

1-hydroxyethane-1,1-diphosphonic acid

Aminotrimethylenephosphonic acid

Ethylenediaminetetramethylphosphonic acid

30 The bath according to the invention is advantageously
used in the pH range of from 0.4 to 2.5.

 Substantially lower as well as substantially higher
pH values lead to disintegration of the gold complex
35 with deposition of the insoluble gold (I) cyanide.

1 The bath is preferably used at pH values of between
0.6 and 2.0. The bath can be used at room temperature,
but higher temperatures of up to 60°C are advan-
tageous for increasing the rate of deposition. The
5 current density range which can be used is extremely
wide. Lustrous layers are achieved, in particular,
at current densities of from 0.2 to at least 10 A/dm².

The invention will be illustrated in more detail
10 below with reference to the following examples.

Example 1

A bath is produced by dissolving the following
constituents:

15 75 g of 85 % phosphoric acid are diluted in 500ml of
distilled water. 50ml of a cobalt complex solution
and 3.5g of KAu(CN)₄, dissolved in water, are then
added. The bath is made up to about 900ml with water,
the pH is adjusted to 1.5 with potassiumhydroxide
20 solution and is finally made up to 1 l with water.
The bath is heated to 25°C. A light yellow lustrous
gold layer having a thickness of 1.2 µm is deposited
on a copper plate cathode at a current density of
2A/dm² in 20 minutes.

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The gold content is now increased to 8 g/l, the
bath heated to 50°C and the deposition repeated at a
current density of 8 A/dm². 3 µm of gold are now
deposited in 10 minutes. The coating is also light
30 yellow and lustrous. About 0.5% of cobalt are
detected in both layers. From the second sample, the
copper substrate is dissolved with 3:1 dilute nitric
acid. A ductile gold foil which does not break even
when bent is obtained. The cobalt complex solution
35 used when making up the bath is produced in the
following manner:

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- 1 47.8 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ corresponding to 10 g of Co are dissolved in about 600ml of water with heating; 222ml of 60% 1-hydroxyethane-1,1-diphosphonic acid are added and made up to 1 l.

5 Example 2

A bath of the following constituents is produced according to example 1:

- 26.3ml 85% H_3PO_4
10 13.6ml of 96% H_2SO_4
50ml of cobalt complex solution (as in example 1)

- The bath is again made up to 1 l. 1.73g of $\text{KAu}(\text{CN})_4$ (1g of Au) are added and the pH is adjusted to
15 0.6 using sulphuric acid.

An adhering gold layer of 0.2 μm is deposited on a cathode composed of 18 Cr 8 Ni-steel in 5 minutes at a current density of $2\text{A}/\text{dm}^2$.

20 Example 3

1 l of bath is produced by dissolving the following constituents in water:

- 25g of KH_2PO_4
25 60 g of 85% H_3PO_4
4.2 g of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
13.8 g of $\text{KAu}(\text{CN})_4$ (8 g/l AU)
10 g of ethylenediamine

- 30 The pH is adjusted to 2.0 and the bath heated to 40°C . A 2.5 μm thick lustrous gold layer is deposited on a copper plate in 10 minutes at a current density of $5\text{A}/\text{dm}^2$. 0.4% of Ni are contained in the gold.

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Example 4

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Depositions are carried out from a bath containing the following constituents:

90 g/l of 85% H_3PO_4

10 g/l of 96% H_2SO_4

6 g/l of $\text{In}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$

8.6 g/l of $\text{KAu}(\text{CN})_4$ (5 g/l Au)

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9 g/l of ethylenediaminetetraacetic acid

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The pH of the bath is adjusted to 1.8. A lustrous light yellow gold layer having a thickness of 2 μm is deposited on a nickel-plated copper plate in 10 minutes at a current density of 9 A/dm^2 and at a bath temperature of 50°C.

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