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Electrolytic bath for electrochemically depositing gold and its alloys.

The present invention relates to an electrolytic bath intended for electrochemically depositing gold or its alloys.

Electrolytic gilding was born in the wake of the invention of the battery by Alisandro Volta. It was in fact Luigi Brugnatelli, Volta's scholar and collaborator, and professor of chemistry at the university of Pavia, who in 1805 discovered means of gilding silver medals with the aid of the battery. The method that he employed is described notably in a letter addressed to Van Mons, of Brussels. Brugnatelli made use of a dissolution of gold chloride in ammonia solution, in which the object to be gilded was immersed, and had the latter connected via a silver or steel wire with the negative pole of a battery. Nothing was heard of the method at that time probably due to the impossibility of obtaining a constant current, and therefore a satisfactory deposit, with Volta's battery, or indeed due to the state of war which carried on until 1815, which meant that this invention was not mentioned by the distinguished scientific persons who were commissioned by Napoleon to communicate the scientific progress after the French Revolution. It was necessary to wait for the result of the pieces of research by Antoine Becquerel on the causes of irregularity of the current and on the general means of avoiding it, and Daniell's invention of the constant current battery. This source of current thus enables homogeneous and ductile metal deposits to be obtained. It was Auguste de la Rive, a physician from Geneva, who was first to really apply the battery to gilding. He obtained, in 1840, an electrolytic gold deposit on brass, copper and silver by using a solution of gold chloride under a very low current. The deposit had, despite everything, an appearance fault. The acidic electrolyte did in fact constantly attack the surface of the substrate. Several people brought their contribution to the improvement of the de la Rive method, such as Elsner, Boettger, Perrot and Smée. It was



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at the end of 1840 that the precursor of modern gold baths appeared with the pieces of work of the English brothers Henry and George Elkington and of the Frenchman Henry de Ruolz, who developed the use of alkaline solutions of gold cyanide in potassium cyanide.

It was these types of electrolytes which were used for nearly eighty years without any modification being made in order to proceed with electrolytic gilding. The applications of these baths were in the jewellery trade, gilding of art bronzes and zincs, which were employed above all for the manufacture of pendula, candelabra, cups, chandeliers, and the fabrication of gilded wires for braids.

It was the development of the electronic industry at the start of the Forties that caused a renewed interest in gold baths. The users of electrolytic gilding were in demand of deposits which were bright, hard, good conductors and with a control of thickness, *inter alia*. The pieces of research led in order to obtain these results led to the development of acid and neutral gold baths, intended for bright deposits in the Fifties. The Sixties saw the development of acidic gold alloy baths which led to deposits having specific physical properties such as ductility, resistance to corrosion, purity of deposit, etc. It was also at that moment that non-cyanide-containing gold electrolytes reappeared, always with the objective to obtain bright and hard gold deposits. In the Seventies, the sophistication always growing in electronics, but above all the strong increase in the price of gold, led the users of gold baths to develop methods of selective plating and to minimise the amount of gold in the deposits, by developing baths of gold alloy rather than pure gold. The increase in the consumption of electronic products was also determining in the research for electrolytes enabling increasing the speed of deposition with a strong levelling power and a good penetration, *i.e.* while at the same time obtaining a good distribution of the deposit. Since the Eighties, and the advent of acidic baths of hard gold alloyed with nickel, cobalt,

iron, indium, or other metals, research was focalised on their improvement by the addition of organic additives enabling the use of these electrolytes under high current densities (brighteners, surfactants), and enabling increasing the resistance to rubbing (teflon, carbon-containing chains) or enabling the cathode yield (formates) to be increased. These growing concerns in relation to ecotoxicological problems enabled seeing the appearance of novel gold baths without cyanide or sulphite, but unfortunately with indeed less efficiency than those obtained with cyanide-containing acidic gold baths.

The most demanding applications in terms of speed of electrodeposition are without any doubt those of connectors. In fact, since the Forties, the connector industry has not ceased to grow, and this implies a more and more massive production of pieces which are coated with precious metals.

In the perspective of an optimisation of production costs, the speed of deposition of metals in surface treatment is the parameter which was and which is still the most sought after to optimise (A.M. Weisberg *in* Gold Plating Technology, F.H. Reid and W.Goldie, Electrochemical Publications Limited, Ayr, 1974).

The most efficient gold baths as regards speed of electrodeposition, which preserve the deposit's excellent properties of brightness, of ductility, of porosity, of hardness, of resistance to corrosion and to rubbing, of low contact resistance, are baths called «Acide Hard Gold », which are intended for depositing gold hardened by alloying with a very small amount of a common metal, most commonly cobalt or nickel, originating from an acidic electrolyte based on the citric acid/citrate system.

The improvement of the speed of electrodeposition is also a demand of the jewellery industry with types of baths ranging from citrate-based electrolytes to phosphate-based electrolytes.

Hitherto, the methods of improvement of the speed of electrodeposition were based either on the addition of a gold reducer, enabling to not affect the cathode yield by the reduction of gold (III) originating from the oxidation of the gold (I) salt constituting the anode bath (US 4,238,300, US 4,670,107, US 4,795,534), or based on the addition of an organic or metallic brightener enabling the use of higher current densities to the detriment of the cathode yield (US 4,767,507, US 4,591,415).

At present, despite the drawbacks set forth above, cyanide-containing electrolytic gold baths remain very much used due to their performances. However, one of the well-known drawbacks of such baths is that the presence of cyanides in the bath is responsible for the formation of polymers during electrolytic deposit. These polymers come to pollute the deposits and consequently harm the quality of the electrolytic deposit.

Furthermore, it is classical to have recourse to the use of secondary metals, in particular cobalt and nickel, as hardener and/or brightener of the electrolytic gold deposits.

It is particularly frequent to prepare gold deposits called « hard gold » from solutions of cyanoaurate (I) buffered with the citric acid-potassium citrate system at a pH of between 4 and 5, and containing cobalt as deposit hardening metal. These deposits are accompanied with a co-deposition of carbon and nitrogen. There is therefore a contaminant formed during the electrodeposition of gold from such baths. The presence of this contaminant seems to be responsible for the relatively high contact resistance of the deposit in two different ways. The polymers increase the contact resistance of the deposit, not only by forming a film at the surface of the deposit, but also by being present within this deposit. The formation of polymers is dependent upon the availability of the free

cyanides in the electrolyte. The amount of polymer included in the deposit is also largely dependent upon the content of cobalt included.

Moreover, the presence of cobalt oxides at the surface of the deposit is also responsible for the contact resistance of the gold-cobalt deposits, in particular by the formation of a complex with the free cyanides.

Hence, the problems linked to the use of cyanide-containing gold baths are still found increased in the case of alloys and more particularly in the case of gold-cobalt alloys which are widely used when hard gold deposits are sought after.

The publication entitled « Notes on the electrodeposition of thick gold deposits », Charles L. Bauer, *Plating* (1952), 39, 1335-6, describes tests carried out with the view to improving the properties of a thick deposit of gold, intended for applications in thermoforming. In the bath used according to this document, vanillin is used at a concentration of 0.3 g/L for a gold concentration of 18 g/L, and it is specified in this document that from 30 auxiliary agents tested, only vanillin and potassium sulphite enabled improving the quality of the deposits and that vanillin enables obtaining grains which are much finer, and this signifies that vanillin is used in this bath as brightener.

Czech patent CS 107 253 1 describes a method intended for depositing two successive coats of bright and hard gold by having recourse to an electrolytic bath containing vanillin as brightening agent at a concentration of 0.5 g/L, for a concentration of potassium gold cyanide of 8 g/L, and this corresponds to a vanillin concentration of the order of 0.1 mole per mole of gold to be deposited.

M. Dettke *et al.* described, in US patent US 3,878,066, a method using a combination of formaldehyde, acetaldehyde or of one of their bisulphite compounds with arsenic and an aliphatic amine-containing

compound for obtaining a very bright gold deposit having an excellent adherence.

The property of aldehydes to be cyanylated in the presence of cyanide is well known. It is in particular made use of in US patent US 5,380,562 which relates to a method of chemically depositing gold using a bath which comprises a cyanoaurate or an alkaline cyanide, a reducing agent, an alkaline hydroxide, and agent controlling the formation of crystals, and a stabilising agent, and in which an aldehyde or a ketone is added at the same time as the gold salt, so as to prevent the accumulation of free cyanides in the bath.

It has now been demonstrated that the use of well-determined aldehydes in baths intended for electrolytically depositing gold or gold alloys enabled considerably increasing the speed of deposit of metal or of alloy, while at the same time reducing the contact resistance and in minimising environmental problems, in particular in the case of the use of cyanide-containing baths.

The present invention in particular enables improving the speed of electrodeposition of gold by enabling the use of gold electrolytes with high current densities, up to 120 A/dm^2 , without affecting the cathode yield.

Thus, according to a first aspect, the invention relates to an electrolytic bath intended for depositing gold or alloys of gold, this bath containing a well-determined auxiliary agent which enables the speed of electrodeposition of gold or of its alloys to be improved considerably, while at the same time reducing the contact resistance and enabling high current densities to be used.

According to a second aspect, the invention relates to a method of electrolytically depositing gold or alloys of gold on a substrate, using the bath of the invention as electrolytic bath.

According to a third aspect, the invention relates to a novel use of a well-determined family of organic compounds which have at least one aldehyde function as auxiliary which is intended to improve the performances of a method of electrolytic deposition of gold or of alloys of gold on a substrate.

The invention applies to any known method which makes use of a step of electrodeposition of gold or of alloys of gold, both in the field of decoration as well as in the field of electronics and connectics.

The invention is of particular importance in cases of methods of electrolytic deposit of gold from a cyanide-containing bath, in particular from an electrolytic bath containing gold in the form of cyanoaurate (I) or cyanoaurate (III) and, more particularly, in cases of deposits of gold hardened by a secondary metal, in particular by cobalt, iron or nickel.

According to one of its essential features, the invention relates to an aqueous electrolytic bath for electrochemically depositing gold or its alloys comprising at least one soluble gold compound intended to be deposited electrolytically and, optionally, at least one secondary metal compound intended to be co-deposited in the form of an alloy with gold, characterised in that it further comprises 0.3 to 3 moles, per mole of gold contained in the electrolytic bath, of an organic compound comprising one or two aldehyde functions, said organic compound being :

- either glyoxal, or
- an organic compound having 3 to 20 carbon atoms and one or two aldehyde functions in the form :
 - of a linear, branched, saturated or unsaturated aliphatic group, or
 - of a group containing at least one saturated, unsaturated or aromatic ring,

it being possible for said organic compound to further comprise at least one heteroelement selected from oxygen, nitrogen, sulphur, and

phosphorus, or to be in the form of a salt, particularly in the form of a sulphonate.

Thus, according to this first aspect, the invention relates to an aqueous electrolytic bath intended for electrolytically depositing gold or its alloys. The person skilled in the art knows perfectly well that a bath intended for electrolytically depositing a metal differs from a bath known as « chemical bath » for depositing the same metal, not only by the implementation conditions (passage of a current and the presence of electrodes in the case of an electrochemical bath), but also by the nature of its constituents.

Thus for example, in the case in which gold is deposited via a soluble salt such as a cyanoaurate (I), a chemical bath will comprise a significant amount of reducing agents and will be characterised by the presence of a high concentration of free cyanides, while in an electrochemical bath, the presence of free cyanides will be sought to be removed as much as possible. Furthermore, the magnitudes of the speeds of deposit from a chemical bath and from an electrochemical bath are not at all the same, and this *a priori* excludes the use of chemical baths for implementing continuous deposits on substrates.

It is the fact that the electrolytic bath can be constituted by any bath which is used classically for electrodepositing gold or gold alloy that essentially characterises the first aspect of the invention, as from the moment at which it further contains an organic compound comprising one or two aldehyde functions as defined above.

The electrolytic baths of the invention advantageously contain 1.5 to 2.5 moles of said organic compound comprising one or two aldehyde functions per mole of gold, preferably of the order of 2 moles of said organic compound per mole of gold.

It will be easily understood that the amount of aldehyde function-containing organic compound will depend upon both the

concentration of soluble gold salts in the bath and upon the molar mass of this aldehyde.

The electrolytic baths of the invention advantageously contain contents of gold which can vary widely but in general are of between 1 and 100 g/L (the soluble salt contents are with respect to the content of metal).

Thus, the content of compounds bearing one or two aldehyde functions can vary over wide ranges. In general, the baths of the invention contain, as a function of the molar basis of the aldehyde, 0.1 to 50 g/L of at least one organic compound comprising one or two aldehyde functions as defined above.

The family of organic compounds which can be used according to the invention as auxiliary agent in a bath for electrochemically depositing gold or alloys of gold is either glyoxal, which has the advantage of containing two aldehyde groups, or an organic compound having 3 to 20 carbon atoms and at least one aldehyde function.

It can be aliphatic compounds, but also compounds which contain one or more rings, these compounds optionally further containing at least one heteroelement such as oxygen, nitrogen, sulphur, and phosphorus.

The family of products which can be used according to the invention also comprises salts of the above products, and in particular sulphonates which have additionally the advantage of having surfactant properties if they are sufficiently long.

In general, from the products above, those will be advantageously selected which are soluble in the medium, or at least those which can be dissolved therein by adding, if need be, a surfactant or any other product which enables the aldehyde function-containing organic compound to be rendered soluble in the bath.

According to a first variant, the organic compound used according to the invention is glyoxal.

According to another variant, the organic compounds used according to the invention will be selected from the aldehydes of formula R-CHO in which R is a linear or branched, saturated or unsaturated aliphatic group having 3 to 12 carbon atoms.

Alkyl chains having 3 to 9 carbon atoms will preferably be selected.

According to another variant, the organic compound has 4 to 20 carbon atoms and comprises at least one saturated, unsaturated or aromatic ring, or is in the form of a salt, particularly in the form of a sulphonate, of one of these compounds.

When recourse is made to organic compounds which contain a ring, in particular when this ring is aromatic, a compound in which the ring, in particular the aromatic ring, bears at the most two substituent groups are preferably selected, for obvious reasons of solubility of this compound.

According to yet another variant, the organic compound has 4 to 20 carbon atoms and contains at least one saturated, unsaturated or aromatic heterocycle, or is in the form of a salt, particularly in the form of a sulphonate, of one of these compounds.

Advantageously, the organic compound used according to the invention will be selected from the group consisting of propionaldehyde, butyraldehyde, valeraldehyde, capronaldehyde, 1-heptaldehyde, caprylic aldehyde, pelargonaldehyde, decanal, undecanal, laurylaldehyde, glyoxal, glyoxalic acid, glyoxal-bis(sodium hydrogen sulphite), glyoxal-1,1-dimethyl acetal, acrolein, crotonal, benzaldehyde, phenylacetaldehyde, cuminic aldehyde, cinnamaldehyde, anisic aldehyde, and phthalic aldehyde.

As set forth above, the electrolytic bath intended for depositing gold or its alloys will furthermore comprise any additives which are commonly used in such baths.

It will therefore be possible for it to comprise, in particular :

- a) Various metals acting as inorganic brighteners or as hardeners,
- b) Metals known as « secondary metals » or « alloy metals » which are generally selected from periods 4, 5 and 6 of Mendeleev's periodic classification of the elements, at a concentration in general of between 0.01 and 60 g/L.

These alloy metals are in general selected from cobalt, nickel, iron, indium, cadmium, arsenic, manganese, tin, lead, and copper.

The preferred metals will be cobalt, nickel, and iron.

However, it is with cobalt that the effect of lowering the contact resistance, due to the presence of the aldehyde function-containing compound, will be the greatest.

In general, the secondary metal is introduced into the bath in the form of sulphate, carbonate, hydroxide, oxide, acetylacetonate, citrate, gluconate, sulphamate, or of a mixture of these compounds.

- c) Brightening agents :

These brightening agents are all those which are classically used in the field of the electrolytic deposit of gold.

3-(3-pyridyl) acrylic acid or 3-(3-quinolyl) acrylic acid, or one of their salts, will be advantageously selected as brightening agent, at contents of between 0.01 and 10 g/L.

- d) Conducting salts :

These salts contribute to the good functioning of the electrolytic system. In general, the bath contains at least 10 g/L of a conducting salt, preferably selected from the group consisting of citrate, phosphate, borate or sulphate salts, and their mixtures.

e) Buffer-type agents which are intended to stabilise the pH, said buffer preferably being of acetic, citric, boric, phosphoric, or phthalic type.

f) Wetting agents :

Tolyltriazole or benzotriazole will preferably be selected as wetting agents.

Finally, even if the invention is not limited to the electrolytic baths in which the gold is in cyanoaurate (I) or cyanoaurate (III) form, the invention more particularly applies to this type of bath, which is well-known in the prior art for having the drawback of leading to a pollution of the electrolytic deposit through the formation of polymers.

Hence, the aldehyde function-containing organic compound according to the invention is found to be introduced in a particularly advantageous way into baths in which the gold is found in cyanoaurate (I) or (III) form, but it can also be used in other baths with the effect of improving the performances of the electrolytic deposit. It will in particular be introduced into the baths in which the gold is in gold sulphite, gold thiosulphate or gold chloride form.

According to a second aspect, the invention relates to a method of electrodepositing gold or an alloy of gold, according to which an electrolysis of an electrolytic bath as defined above is carried out.

As set forth above, the presence of an aldehyde function-containing organic compound as defined above considerably improves the performances of all the electrolytic baths for depositing gold or alloys of gold and in particular cyanide-containing baths which contain gold in cyanoaurate (I) or cyanoaurate (III) form.

The main advantages of the introduction of the aldehyde function-containing organic compound are to improve the speed of electrodeposition, to lower the contact resistance and to enable the use of particularly high current densities.

The improvement of the invention is applicable to all types of methods of electrolytic deposit of gold, and for all types of application, whether it be for decoration, for preparing electronic components or in connectics.

The current densities used in the methods of the invention can vary within wide ranges, generally between 0.5 and 120 A/dm².

Of course, current densities of less than 10 A/dm² will in general be used for applications in the field of decoration, while current densities of the order of 10 to 120 A/dm² will be employed for applications known as « high speed » applications, this type of high speed method is in general reserved for the field of electronics and connectics.

The method of the invention, insofar as it enables the use of particularly high current densities, which can be up to 120 A/dm², finds a particularly advantageous application in electronic applications in which it is sought to work with a maximum deposit speed, and in which the deposits desired must, *inter alia*, be bright, ductile and non-porous. The baths used in this field must, in order to obtain high productivities, function under the highest current densities possible, and this in particular enables the use of the auxiliaries used according to the invention.

However, the baths of the invention can also be used at lower speeds and current densities and in particular in the fields of decoration.

As set forth above, the development of the invention is applicable to all methods which are classically used for depositing gold or alloys of gold.

In particular, all types of soluble or insoluble anodes which are used classically can be used in the method of the invention.

However, insoluble anodes will preferably be used, and preferably of platinum-containing titanium, of iridium oxide-covered platinum or of precious metal such as platinum, and a metallised substrate will be placed as cathode.

Finally, as already set forth and as will emerge from the following examples, the invention relates, according to a third aspect, to the use of an organic compound as defined above in an electrolytic bath intended for electrolytically depositing gold or one of its alloys, as auxiliary agent which improves the speed of electrodeposition of gold or of its alloys and/or which reduces the contact resistance.

The preferred formulations of baths according to the present invention can, in a non-restricting manner, be described by the following general composition in which the concentrations of metal derivatives (of gold and optionally of alloy metals) are with respect to the metal :

- gold.....	1 to 100 g/L
- alloy metal such as Co, Ni, Fe, Cd.....	0 to 50 g/L
- Brightener, preferably 3-(3- pyridyl) acrylic acid.....	0.01 to 10 g/L
- Citric acid and/or potassium citrate.....	10 to 300 g/L
- Aldehyde.....	0.01 to 100 g/L

The operating conditions are advantageously the following :

- pH.....	3.5 to 12 (as a function of the nature of the gold complex)
- Temperature.....	10 to 75°C
- Agitation.....	Moderate to very vigorous
- Current density.....	0.1 to 80 A/dm ²
- Anode.....	All those used classically, particularly platinum-containing titanium, iridium oxide-covered platinum, or precious metals such as platinum

EXAMPLES

In the Examples, concentrations of gold and alloy metals are with respect to the metal.

The Examples which follow illustrate the good performances of the invention.

a) In all these Examples, the substrate to be metallised is prepared by a suitable procedure, according to the nature of the metal. For example, the copper-containing substrates or nickel substrates are electrolytically degreased beforehand, after a rinse with water, the substrate is depassivated in sulphuric acid diluted to 5-20% by volume, the substrate is rinsed with deionised water before being introduced into one of the electrolytes of the invention.

Optionally, certain additives can be added. Thus :

- As conducting salt, sodium sulphate can be used, but also potassium sulphate or ammonium sulphate, or a mixture thereof.
- An acetic, citric, boric, orthophosphoric buffer, or any other buffer system which is efficient in the pH range concerned can be used for stabilising the pH of the bath.
- A wetting agent can be added in order to avoid the adsorption of hydrogen formed at the cathode during electrolysis and, consequently, in order to avoid its inclusion in the deposit. A cationic, anionic or non-ionic wetting agent can be suitable, it will be for example possible to use benzotriazole in low amount.

EXAMPLE 1 : Decorative gold bath (Comparative Example)

- gold (introduced as potassium cyanoaurate (I)).....	2 to 10 g/L	
- Ammonium citrate.....	90 to 130 g/L	
- Trans 3-(3-pyridyl)acrylic acid.....	0.5 to 1.5 g/L	
- pH (Citric acid / Potassium hydroxide).....	3.5 to 5	
- Temperature.....	40 to 60°C	
- Agitation.....	Moderate	to
	vigorous	
- Current density.....	1 to 20 A/dm ²	
- Anode.....	Platinum-containing	
	titanium	

This bath deposits gold at more than 99.9%, the deposit is bright, ductile, with a contact resistance of 12 mOhm, a low porosity and an excellent resistance to corrosion. Its speed of electrodeposition is of 0.05 to 0.5 µm/minute. It is used ideally in methods known as « rack plating » or « dip plating » methods.

EXAMPLE 2 : Decorative gold bath

- gold (introduced as potassium cyanoaurate (I)).....	2 to 10 g/L	
- Ammonium citrate.....	90 to 130 g/L	
- Trans 3-(3-pyridyl)acrylic acid.....	0.5 to 1.5 g/L	
- Pelargonaldehyde.....	0.5 to 4 g/L	
- pH (citric acid / Potassium hydroxide).....	3.5 to 5	
- Temperature.....	40 to 60°C	
- Agitation.....	Moderate to vigorous	
- Current density.....	1 to 20 A/dm ²	
- Anode.....	Platinum-containing	
	titanium	

This bath deposits gold at more than 99.9%, the deposit is bright, ductile, with a contact resistance of 5 mOhm, a low porosity and an excellent resistance to corrosion. Its speed of electrodeposition is of 0.1 to 0.7 µm/minute. It is used ideally in methods known as « rack plating » or « dip plating » methods.

EXAMPLE 3 : Decorative gold bath

- gold (introduced as ammonium gold sulphite).....	2 to 10 g/L
- potassium bisulphite.....	2 to 15 g/L
- Arsenic (as oxide).....	2 to 50 mg/L
- Isovaleraldehyde.....	0.5 to 4 g/L
- pH (boric acid / potassium hydroxide).....	8 to 12
- Temperature.....	40 to 60°C
- Agitation.....	Moderate to vigorous
- Current density.....	1 to 10 A/dm ²
- Anode.....	Platinum- containing titanium

This bath deposits gold at more than 99.9%, the deposit is bright, ductile, has a low porosity and an excellent resistance to corrosion, with a contact resistance of 7 mOhm. It deposits at a speed of 0.1 to 0.7 µm/minute. It is used ideally in methods known as « rack plating » or « dip plating » methods.

EXAMPLE 4 : High speed gold-cobalt bath

- gold (introduced as potassium cyanoaurate (I)).....	5 to 20 g/L
- Cobalt (as sulphate).....	0.5 to 1.5 g/L
- potassium citrate.....	50 to 180 g/L
- Trans 3-(3-pyridyl)acrylic acid.....	0.5 to 1.5 g/L
- Butyraldehyde.....	0.5 to 10 g/L
- pH (citric acid / potassium hydroxide).....	3.5 to 5
- Temperature.....	40 to 60°C
- Agitation.....	Vigorous to very vigorous
- Current density.....	10 to 80 A/dm ²
- Anode.....	Platinum- containing titanium

This bath deposits gold at close to 99.5%, the deposit is bright, ductile, with a low contact resistance, a low porosity and an excellent resistance to corrosion. The cobalt here acts not only as metallic brightener but also as alloy metal hardener. It enables, at the deposit, to give a good resistance to rubbing and to positively pass the test known as the « British Telecom » test. It is used ideally in methods known as « continuous plating », « selective masked plating », or « selective jet plating » methods.

The contact resistance is 5 mOhm after thermal ageing for 1 hour at 250°C. As an indication, it is under the same conditions of 14 mOhm, when the bath does not contain any aldehyde (measurement according to the ASTM B667-97 Standard).

The deposit speed is 0.5 to 11 µm/minute with aldehyde, 0.4 to 8.5 µm/minute without aldehyde, using a rotating cathode turning at a speed of 1.5 m/s, as a means of deposit, or a deposit material by jet plating.

EXAMPLE 5 : High speed gold-nickel bath

- gold (introduced as potassium cyanoaurate (I)).....	5 to 20 g/L
- Nickel (as sulphate).....	0.5 to 1.5 g/L
- potassium citrate.....	50 to 180 g/L
- Trans 3-(3-pyridyl)acrylic acid.....	0.5 to 1.5 g/L
- Butyraldehyde.....	0.5 to 10 g/L
- pH (citric acid / potassium hydroxide).....	3.5 to 5
- Temperature.....	40 to 60°C
- Agitation.....	Vigorous to very vigorous
- Current density.....	10 to 80 A/dm ²
- Anode.....	Platinum- containing titanium

This bath deposits gold at close to 99.5%, the deposit is bright, ductile, with a low contact resistance of 7 mOhm, a low porosity and an excellent resistance to corrosion, and leads to a speed of 0.5 to 11 $\mu\text{m}/\text{minute}$. The nickel acts as metallic brightener and as alloy metal hardener. It enables, at the deposit, to give a good resistance to rubbing and to positively pass the test known as the « British Telecom » test. It is used ideally in methods known as « continuous plating », « selective masked plating », or « selective jet plating » methods.

EXAMPLE 6 : High speed gold-cobalt baths

- gold (introduced as potassium cyanoaurate (I)).....	5 to 20 g/L
- Cobalt (as acetylacetonate).....	0.5 to 1.5 g/L
- potassium citrate.....	50 to 180 g/L
- formic acid.....	30 to 60 g/L
- Trans 3-(3-pyridyl)acrylic acid.....	0.5 to 1.5 g/L
- Heptaldehyde.....	0.5 to 10 g/L
- pH (citric acid / potassium hydroxide).....	4.5 to 6
- Temperature.....	40 to 60°C
- Agitation.....	Vigorous to very vigorous
- Current density.....	10 to 80 A/dm ²
- Anode.....	Platinum-containing titanium

This bath deposits gold at close to 99.5%, the deposit is bright, ductile, with a contact resistance of 7 mOhm, a low porosity and an excellent resistance to corrosion, and leads to a deposit speed of 0.5 to 11 $\mu\text{m}/\text{minute}$. The cobalt acts as metallic brightener and as alloy metal hardener. It enables, at the deposit, to give a good resistance to rubbing and to positively pass the test known as the « British Telecom » test. It is used ideally in methods known as « continuous plating », « selective masked plating », or « selective jet plating » methods.

EXAMPLE 7 : High speed gold-cobalt bath

- gold (introduced as potassium cyanoaurate (I)).....	5 to 20 g/L
- Cobalt (as gluconate).....	0.5 to 1.5 g/L
- potassium citrate.....	10 to 50 g/L
- Trans 3-(3-pyridyl)acrylic acid.....	0.5 to 1.5 g/L
- Hexaldehyde.....	0.5 to 10 g/L
- pH (citric acid / potassium hydroxide).....	4.5 to 6
- Temperature.....	40 to 60°C
- Current density.....	10 to 80 A/dm ²
- Anode.....	Platinum-containing titanium

This bath deposits gold at close to 99.5%, the deposit is bright, ductile, with a contact resistance of 7 mOhm, a low porosity and an excellent resistance to corrosion. It leads to a deposit speed of 0.5 to 11 $\mu\text{m}/\text{minute}$. The cobalt acts as metallic brightener and as alloy metal hardener. It enables, at the deposit, to give a good resistance to rubbing and to positively pass the test known as the « British Telecom » test. It is used ideally in methods known as « continuous plating », « selective masked plating », or « selective jet plating » methods.

CLAIMS

1. An aqueous electrolytic bath for electrochemically depositing gold or its alloys comprising at least one soluble gold compound intended to be deposited electrolytically and, optionally, at least one secondary metal compound intended to be co-deposited in the form of an alloy with gold, characterised in that it further comprises 0.3 to 3 moles, per mole of gold contained in the electrolytic bath, of an organic compound comprising one or two aldehyde functions, said organic compound being :

- either glyoxal, or
- an organic compound having 3 to 20 carbon atoms and one or two aldehyde functions in the form :
 - of a linear, branched, saturated or unsaturated aliphatic group, or
 - of a group containing at least one saturated, unsaturated or aromatic ring,

it being possible for said organic compound to further comprise at least one heteroelement selected from oxygen, nitrogen, sulphur, and phosphorus, or to be in the form of a salt, particularly in the form of a sulphonate.

2. The electrolytic bath according to claim 1, characterised in that it contains 1.5 to 2.5 moles of said organic compound comprising one or two aldehyde functions per mole of gold, preferably of the order of 2 moles of said organic compound per mole of gold.

3. The electrolytic bath according to one of claims 1 or 2, characterised in that said organic compound is glyoxal.

4. The electrolytic bath according to one of claims 1 or 2, characterised in that said organic compound is an aldehyde of formula

R-CHO in which R is a linear or branched, saturated or unsaturated aliphatic group having 3 to 12 carbon atoms.

5. The electrolytic bath according to one of claims 1 or 2, characterised in that said organic compound has 4 to 20 carbon atoms and comprises at least one saturated, unsaturated or aromatic ring, or is in the form of a salt, particularly in the form of a sulphonate, of one of these compounds.

6. The electrolytic bath according to one of claims 1 or 2, characterised in that said organic compound has 4 to 20 carbon atoms and contains at least one saturated, unsaturated or aromatic heterocycle, or is in the form of a salt, particularly in the form of a sulphonate, of one of these compounds.

7. The electrolytic bath according to one of claims 1 to 4, characterised in that said organic compound is selected from the group consisting of propionaldehyde, butyraldehyde, isovaleraldehyde, valeraldehyde, capronaldehyde, hexaldehyde, heptaldehyde, caprylic aldehyde, pelargonaldehyde, decanal, undecanal, laurylaldehyde, glyoxal, glyoxalic acid, glyoxal-bis(sodium hydrogen sulphite), glyoxal-1,1-dimethyl acetal, acrolein, crotonal, benzaldehyde, phenylacetaldehyde, cuminic aldehyde, cinnamaldehyde, anisic aldehyde, phthalic aldehyde.

8. The electrolytic bath according to one of claims 1 to 7, characterised in that it contains 1 to 100 g/L of gold.

9. The electrolytic bath according to one of claims 1 to 8, characterised in that it contains at least one metal acting as inorganic brightener or as hardener.

10. The electrolytic bath according to one of claims 1 to 9, characterised in that it contains at least one secondary metal selected from periods 4, 5 and 6 of Mendeleev's periodic classification of the elements, at a concentration of between 0.01 and 60 g/L.

11. The electrolytic bath according to claim 10, characterised in that said secondary metal is cobalt, nickel or iron, preferably cobalt.

12. The electrolytic bath according to one of claims 10 or 11, characterised in that said secondary metal is introduced into said bath in the form of sulphate, carbonate, hydroxide, oxide, acetylacetonate, citrate, gluconate, sulphamate, or of a mixture of these compounds.

13. The electrolytic bath according to one of claims 1 to 12, characterised in that it contains an organic brightening agent.

14. The electrolytic bath according to claim 13, characterised in that it contains 0.01 to 10 g/L 3-(3-pyridyl)acrylic acid or 3-(3-quinolyl)acrylic acid, or one of their salts.

15. The electrolytic bath according to one of claims 1 to 14, characterised in that it contains at least 10 g/L of a conducting salt, preferably selected from the group consisting of citrate, phosphate, borate or sulphate salts, and their mixtures.

16. The electrolytic bath according to one of claims 1 to 15, characterised in that it contains a buffer intended for stabilising the pH, said buffer preferably being of acetic, citric, boric, phosphoric, or phthalic type.

17. The electrolytic bath according to one of claims 1 to 16, characterised in that it contains at least one wetting agent, preferably tolyltriazole or benzotriazole.

18. The electrolytic bath according to one of claims 1 to 17, characterised in that the gold is introduced in the form of cyanoaurate (I) or cyanoaurate (III).

19. A method of electrodepositing gold or an alloy of gold, characterised in that it comprises electrolysing an electrolytic bath as defined in one of claims 1 to 18 in implementing current densities of between 0.5 and 120 A/dm².

20. The method according to claim 19, characterised in that said electrolysis is carried out using insoluble anodes, preferably of platinum-containing titanium, of iridium oxide-covered platinum or of precious metal such as platinum, and a metallised substrate placed as cathode.

21. Use, in an electrolytic bath intended for electrolytically depositing gold or one of its alloys, of an organic compound as defined in claim 1 or one of claims 3 to 7, as auxiliary agent which improves the speed of electrodeposition of gold or of its alloys and/or which reduces the contact resistance.

22. Use according to claim 21, characterised in that said agent is used at a concentration of 0.3 to 3 mole per mole of gold contained in the bath, preferably at a concentration of 1.5 to 2.5 moles, per mole of gold contained in the bath, more preferably at a concentration of the order of 2 moles per mole of gold contained in the bath.