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⑦① Applicant: **ENGELHARD CORPORATION**  
**Menlo Park, CN 40**  
**Edison New Jersey 08818(US)**

⑦② Inventor: **Green, Rebecca Victoria**  
**Chapel Farm St. Briavels Common**  
**Nr. Lydney Gloucestershire GL15 6SG(GB)**  
Inventor: **Wilkinson, Peter**  
**Mile House Grove Road Berry Hill**  
**Coleford Gloucestershire GL16 8QH(GB)**

⑦④ Representative: **Fisher, Adrian John et al**  
**CARPMAELS & RANSFORD 43 Bloomsbury**  
**Square**  
**London WC1A 2RA(GB)**

⑤④ **Electroless deposition.**

⑤⑦ An aqueous liquor for use as an electroless gold deposition bath, which comprises a source of gold (eg. an alkali metal gold cyanide) and a reducing agent (eg. an alkali metal borohydride), is stabilised by the incorporation of a mixture of an alkali metal or ammonium ferrocyanide and an alkali metal or ammonium ferricyanide or the incorporation of 1-H-tetrazole or another redox mediator. The liquor will in general also contain an alkali metal cyanide and may contain a chelating agent (eg. EDTA) and an accelerator (eg. thallium sulfate).

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## ELECTROLESS DEPOSITION

Field of the invention

The present invention relates to a liquor for use as an electroless gold deposition bath and to a process for depositing gold on a substrate using such a liquor.

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Background to the invention

An electroless (autocatalytic) deposition system has two main advantages over conventional electroplating. It can deposit metal on electrically isolated or non-conducting substrates and it can deposit an even thickness of metal over a component, regardless of geometry. For some time the electronics industry has been searching for a truly autocatalytic gold deposition process. Most of those previously developed have proved unsuitable due to the instability of the solutions. A survey of previously proposed electroless gold deposition systems has been provided by H.O. Ali and I.R.A. Christie, "A review of electroless deposition processes", Gold Bull., 1984, 17(4), pages 118-127 (the teaching in which article is incorporated herein by reference).

The term "autocatalytic deposition" means that the metal already deposited on the workpiece acts as a catalyst for further deposition of the same metal from the solution onto the workpiece. In galvanic deposition, for example copper deposition from an acidic solution onto an iron substrate, the more noble metal (Cu) replaces the less noble metal (Fe) on the surface. However, once the surface is covered with copper the reaction stops. In galvanic (immersion) gold deposition baths, the more noble metal (Au) replaces less noble metal, in particular either copper or nickel, on the surface of the component, until it is covered with gold, whereupon the reaction ceases. The maximum thickness of gold deposited by this method is 0.1-0.2  $\mu\text{m}$ . An autocatalytic bath, however, will deposit more metal on the same metal substrate and, in theory, assuming that all the operating parameters are within their limits, will continue to deposit the desired metal to an unlimited thickness.

In an autocatalytic bath metal ions are reduced to metal atoms by electrons provided by the oxidation of a reducing agent. For electroless gold deposition wherein the reducing agent is potassium borohydride, the oxidation consists of two steps:

- (1)  $\text{BH}_4^- + \text{H}_2\text{O} \rightarrow \text{BH}_3\text{OH}^- + \text{H}_2$   
 (2)  $\text{BH}_3\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{BO}_2^- + \text{H}_2$

At optimum agitation, that is when the reaction is not diffusion controlled, the formation of  $\text{BH}_3\text{OH}^-$  is the rate determining step. The reduction of  $\text{Au}(\text{CN})_2^-$  to gold metal by  $\text{BH}_3\text{OH}^-$  in a bath containing  $\text{KAu}(\text{CN})_2$ , KCN, KOH and  $\text{KBH}_4$  is investigated by Y. Okinaka in "An electrochemical study of electroless gold-deposition reaction", J. Electrochem. Soc., Vol. 120, No. 6 (June 1973), pages 739-744 (the teaching in which article is incorporated herein by reference).

Electroless deposition baths are prone to spontaneous decomposition, which is the sudden precipitation of metal ions from the solution as metal particles (sometimes known as "plating up"). In an attempt to prevent this all commercial electroless baths have hitherto contained stabilisers, in particular alkali metal cyanides such as KCN. Metallic impurities in the bath may also cause this decomposition and so chelating agents are added to complex any dissolved metals. Accelerators are often added to increase deposition rates.

For successful electroless (autocatalytic) deposition it is considered important that all operating parameters should be closely controlled. It is therefore accepted that the tank used to contain the solution must be properly constructed from a suitable material and must be kept clean. The solution should be continuously filtered (up to ten solution turnovers per hour is common for electroless nickel deposition). The temperature must be controlled to within plus or minus 5% of the optimum value, agitation must be sufficient but not too vigorous and bath loading should be maintained at the optimum level. In electroless nickel systems low or high bath loadings can cause spontaneous decomposition, the optimum being 0.5-1  $\text{dm}^2/\text{l}$ . Baths must be analysed frequently and kept at their optimum by small, regular additions of the necessary chemicals. Automatic dosing meters are often used for this purpose. Thus, the operation of an autocatalytic (electroless) deposition system has required a conscientious and skilled person.

Despite such measures, electroless gold deposition systems have hitherto still suffered from the problems of instability, in particular a variable rate of deposition (typically varying from 0 to 3  $\mu\text{m}$  per hour) and a tendency to precipitate gold in bulk suddenly. Furthermore, such systems cannot be replenished and,

therefore, are usually operated to exhaustion or until precipitation occurs. Clearly, then, there is a need in the art for an electroless system which is stable, replenishable and capable of depositing gold of high purity at an acceptable rate. Desirably, such a system should be suitable for wire bonding and should have a robustness approaching that of the electroless copper or nickel systems already available, in order to  
 5 reduce the demand on operator skill.

### Summary of the invention

10 The present invention provides an aqueous liquor for use as an electroless gold deposition bath, comprising a source of gold and a reducing agent, which liquor also contains a reduction-stabilising agent selected from (a) a mixture of an alkali metal or ammonium ferrocyanide and an alkali metal or ammonium ferricyanide, (b) 1-H-tetrazole, (c) redox mediators and (d) mixtures of any of these.

The present invention also provides a method for the electroless deposition of gold, onto a surface of a  
 15 substrate, from an aqueous liquor comprising a source of gold and a reducing agent, wherein the liquor also contains a reduction-stabilising agent selected from (a) a mixture of an alkali metal or ammonium ferrocyanide and an alkali metal or ammonium ferricyanide, (b) 1-H-tetrazole, (c) redox mediators and (d) mixtures of any of these.

The present invention also provides an article having at least one surface onto which gold has been  
 20 deposited by such a method.

### Description of preferred embodiments

25 The aqueous liquor according to the present invention contains a source of gold in solution. In principle, any of the gold compounds, including salts and complexes, that have been used or proposed previously for use in electroless gold deposition (plating) solutions come into consideration, these including such compounds as  $\text{MAu}(\text{CN})_2$ ,  $\text{MAu}(\text{CN})_4$ ,  $\text{MAuO}_2$  and  $\text{MAu}(\text{OH})_4$  wherein M is ammonium or alkali metal, in particular potassium;  $\text{M}_3\text{Au}(\text{SO}_3)_2$  wherein M is ammonium or alkali metal, in particular sodium;  $\text{AuCN}$ ; and  
 30 alkali metal gold imides, in particular potassium gold succinimide or potassium gold phthalimide. However, the alkali metal gold cyanides are particularly preferred, especially potassium gold cyanide, which may be represented by the formula  $\text{KAu}(\text{CN})_2$ .

It will be understood that the gold compound may be formed in situ. Thus, for example, with the addition of a sufficient (at least stoichiometric) amount of cyanide ions, any gold in the solution will, in  
 35 effect, be present as a cyanide complex. Also, due to the presence of the reducing agent,  $\text{Au}^{\text{III}}$  will tend to be converted into  $\text{Au}^{\text{I}}$  in the solution.

Normally, the liquor will have a gold concentration (expressed as elemental gold) of up to 10 g/l and it has been found that the concentration is desirably at least 0.25 g/l in order to achieve an acceptable deposition rate. Although gold concentrations as high as 3.5 g/l have been tested satisfactorily, the gold  
 40 concentration is preferably maintained at a level of between 0.8 and 1 g/l in order to minimise the effects of dragout and to ensure a good distribution of the deposit.

The aqueous liquor according to this invention also contains a reducing agent in solution. Various reducing agents have been proposed in the prior art for use in electroless gold plating solutions, including hypophosphites, formaldehyde, hydrazine and boron-based compounds such as borohydrides and amine  
 45 boranes (eg. isopropyl amine borane, di- or tri-ethylamine borane and di- or tri-methylamine borane), although the amine boranes can be unpleasant to use and are expensive. However, the alkali metal borohydrides, especially potassium borohydride, are preferred, these being particularly effective in conjunction with the alkali metal gold cyanides.

The reducing agent will usually be present in an amount of 1 to 25 g/l, preferably 5 to 15 g/l. Potassium  
 50 borohydride, for example, may be used typically at a level of 5 to 21.6 g/l.

In accordance with the present invention, the aqueous liquor also contains a reduction-stabilising agent, that is to say an agent that is intended to stabilise the reaction(s) whereby the gold is reduced in order to reduce or inhibit the tendency to random deposition varying from the very slow to the very sudden or even to the spontaneous precipitation of the gold. Depending upon its nature, the reduction-stabilising agent is  
 55 generally employed in an amount of from 0.25 to 100 g/l, more usually 1 to 10 g/l.

For this purpose, the aqueous liquor in certain preferred embodiments may contain in solution an alkali metal or ammonium ferricyanide and an alkali metal or ammonium ferrocyanide; the potassium compounds,  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$  and  $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$ , are preferred. Preferably, 0.25 to 3 parts by weight of alkali metal or

ammonium ferricyanide, more preferably 0.4 to 2.5 parts by weight thereof, will be used per part by weight of alkali metal or ammonium ferrocyanide. Subject to such ratios, potassium ferrocyanide and potassium ferricyanide, for example, may be used typically at levels of, respectively, 1 to 50 g/l and 0.5-20 g/l.

In certain other preferred embodiments, the aqueous liquor contains 1-H-tetrazole as a reduction-stabilising agent. Although 1-H-tetrazole - which may be used typically at levels of 1 to 10 g/l - may be used as the sole such agent, useful results have also been obtained using it in the presence of an alkali metal ferricyanide, especially  $K_3Fe^{III}(CN)_6$ .

Other reduction-stabilising agents may be selected from the class of compounds known as redox mediators (oxidation-reduction mediators). Redox mediators are known in biochemistry and cell biology as chemicals that promote transfer of electrons essential to the analysis of enzymes and tissues and have recently been proposed as additives in microbial fuel cells as they couple rich sources of electrons within micro organisms to an electrode (see J. Bennetto, "Microbes come to power", New Scientist, 16 April 1987, pages 36-39). Redox mediators which come into consideration are, for example, thionine (at a level, for example, of 1 to 5 g/l), resorufin (at a level, for example, of 1 to 5 g/l) and 1,10-phenanthroline (at a level, for example, of 0.25 to 1 g/l).

It will, of course, be understood that only those redox mediators that are compatible with the hot alkaline liquor used in the plating process can be used. For example, tetrazolium violet, 2-hydroxy-1,4-naphthoquinone and 2,3-epoxy-2,3-dihydro-1,4-naphthoquinone have been found to cause bulk precipitation of gold from the plating liquor.

It is known that electron transfer between  $[Fe(CN)_6]^{4-}$  and  $[Fe(CN)_6]^{3-}$  is very fast (see A.G. Sharpe, The Chemistry of Cyano Complexes of the Transition Metals, Academic Press (1976), pages 115-120) and, although the Applicants do not wish to be bound by any theory, it is thought that the ferrocyanide/ferricyanide mixtures may act as electron reservoirs thereby reducing or eliminating the tendency to spontaneous decomposition and thus may, like 1-H-tetrazole, act in a similar manner to the redox mediators in stabilising the gold-reduction ( $Au^+ \rightarrow Au^0$ ) process.

The pH of the aqueous liquor may be adjusted, as appropriate, for the deposition to proceed properly. When employing an alkali metal borohydride as the reducing agent, the pH of the liquor has not been found to be a critical parameter: as long as there are sufficient hydroxide ions for the formation of  $BH_3OH^-$  ions, the deposition reaction will proceed. Thus, an alkaline pH, usually at least 11 and conveniently between 11 and 11.5, will in general be maintained when using such a borohydride, and may also be appropriate if a different reducing agent is employed. The liquor may contain alkali metal hydroxide, eg. sodium or potassium hydroxide (which latter, for example, may be used typically at a level of 5 to 22.4 g/l), to achieve the alkaline pH and/or a buffer salt may be used, such a buffer salt being selected, for example, from the alkali metal (especially sodium or potassium) orthophosphates, pyrophosphates, citrates, tartrates, borates and metaborates.

In order to improve the performance of the aqueous liquor of this invention as an electroless gold deposition bath, it is preferred to add an organic chelating agent, which serves to complex or otherwise combine with metal ions present as impurities in the plating solution and thereby prevent their interference with the deposition or plating process. Such chelating agents are generally employed in an amount of from 0.1 to 100 g/l, preferably 1 to 20 g/l, and include ethylenediaminetetraacetic acid (EDTA) and the alkali metal salts thereof, diethylenetriaminepentaacetic acid and the alkali metal salts thereof, nitrilotriacetic acid and the alkali metal salts thereof, ethanolamine and triethanolamine. EDTA has been found to be particularly effective in complexing nickel in solution and may be used typically at a level of 1 to 10 g/l. Ethanolamine and triethanolamine may be used typically at levels of, respectively, 25-75 ml/l and 5-50 ml/l.

Normally, the aqueous liquor according to the present invention will contain an alkali metal cyanide, such as sodium, potassium or lithium cyanide, in order to improve the stability of the source of gold, in particular when a gold cyanide complex is used. In general, such cyanides are employed in an amount of 0.1 to 50 g/l, preferably 1 to 25 g/l. Amongst such auxiliary stabilisers, potassium cyanide is particularly preferred and may be used typically at a level of 5 to 22 g/l.

It is also possible to include one or more other auxiliary, stabilisers. Alpha-hydroxynitriles have been proposed as stabilisers in electroless deposition baths (see US-A-3,589,916) but for the purposes of the present invention, the use of glycine has been found to be beneficial. It is possible that the glycine, which may typically be used at a level of 1 to 10 g/l, acts as a chelating agent within the aqueous liquor.

The aqueous liquor of the present invention may also contain an accelerator in order to improve the rate of deposition. As taught in US-A-4,307,136, water-soluble salts of semi-metals and metals of Groups IIIB, IVB and VB of the Periodic Table (especially those elements in the 4th, 5th and 6th periods), such as thallium, lead or arsenic, may be used for this purpose, although in certain embodiments the presence of such an accelerator has increased the sensitivity of the bath to the presence of nickel contaminants.

The concentration of the accelerator (expressed as elemental metal or semi-metal) will generally be from 0.001 to 500 mg/l, more usually 0.001 to 100 mg/l. Preferred accelerators are thallium (eg. as thallium sulfate), which can be used typically at a level of 0.001 to 7 mg/l (calculated on the elemental thallium), and lead (eg. as lead sulfate), which can be used typically at a level of 2 to 50 mg/l (calculated on the elemental lead).

It will be understood, of course, that any of the specified components (gold source, reducing agent, reduction-stabilising agent, chelating agent, auxiliary stabiliser, and accelerator) may be constituted by a mixture of two or more compounds of the appropriate description. When alkali metal compounds have been mentioned above as possible components, the corresponding ammonium compounds may also come into consideration; however, the potassium compounds are usually the least expensive and the most readily available in high purity.

The aqueous liquor of the present invention may be employed in conventional manner as an electroless gold deposition bath. Thus, the substrate to be plated will be immersed in the bath for a period of time sufficient to achieve a deposit of gold of the desired thickness.

Since the electroless deposition of the gold is an autocatalytic process, the substrate should present a catalytically active surface, especially a surface of a metal such as nickel, cobalt, iron, steel, palladium, platinum, copper, brass, manganese, chromium, molybdenum, tungsten, titanium, tin, silver, kovar and permalloy. However, and especially in cases where contamination of the bath by dissolution of the substrate or base metal will adversely affect the purity of the gold deposit and the stability of the plating bath, it would be possible to carry out a pre-plating step in order to provide a thin deposit of gold on the substrate surface, for example using a galvanic gold deposition process, for instance the "Atomex" process (as described in US-A-3,230,098).

If a nickel undercoat is deemed necessary, it is recommended that nickel-boron type (ENi-B) electroless nickel deposits be used as the undercoat in preference to nickel-phosphorus type (ENi-P) electroless nickel deposits (since the present formulation will not deposit gold on the latter). If an ENi-P undercoat has to be used, it should be flashed with ENi-B prior to the electroless plating with gold.

A pre-dip containing potassium borohydride and potassium hydroxide (typically 5 g/l of each) has proven useful in accelerating the initiation of the gold deposition, protecting the gold bath from contamination and reducing the heat-sink effect of large components. Immersion of the substrate in the pre-dip for 1 minute at 80 °C has been found to be suitable.

Non-metallic substrates may be prepared for gold-plating in accordance with this invention by first rendering the surfaces thereof catalytically active, for example by the method described in US-A-3,589,916.

Where the substrate is provided by an article that also comprises surfaces which do not require to be plated, it is possible to mask such surfaces in known manner, the masking material being removed after the plating step.

Articles which may be gold-plated or gold-metallised in accordance with this invention include electronics components, especially those which have electrically isolated islands, pads and tracks, for example microwave components, chip carriers, printed circuit boards, integrated circuits and transistor headers.

The gold deposition bath will normally be operated at a temperature of 80 °C  $\pm$  5 °C. If the temperature exceeds 85 °C, there may be a significant risk of spontaneous decomposition whereas below 75 °C there is a significant reduction in the rate of gold deposition. During operation, the bath should be agitated, for example by magnetic stirring. Preferably, the rate of stirring is from 200 to 600 rpm; higher rates of stirring may cause spontaneous decomposition, while lower rates of stirring will reduce the rate of gold deposition on the substrate.

Surface loadings as low as 0.5 dm<sup>2</sup>/l and as high as 10 dm<sup>2</sup>/l have been tested satisfactorily; the tolerance to loadings as high as 10 dm<sup>2</sup>/l is surprising, since prior-art autocatalytic systems would be expected to undergo spontaneous decomposition at loadings as high as this. However, the recommended surface loading for practical applications is from 1 to 3 dm<sup>2</sup>/l, depending upon the bath volume.

As the deposition or plating reaction proceeds, the components in the bath liquor may be replenished as appropriate. Thus, the source of gold will need to be replenished so as to maintain the concentration of gold at the required level. In principle, the gold compound added by way of replenishment need not be the same as the gold compound used in making up the initial liquor.

Potassium borohydride decomposes rapidly at 80 °C. Accordingly, when this reducing agent is used, it is desirable to analyse the bath every thirty minutes during operation and to replenish the potassium borohydride (the concentration of which typically decreases by 30% for each thirty minutes that the bath is at the working temperature), as appropriate. The accelerator, if used, normally also requires to be replenished frequently. The ferrocyanide and ferricyanide if used, have also been found to require frequent replenishment.

Examples

The present invention is illustrated in and by the following examples.

The aqueous solutions were made up in a new, or at least scratch-free, beaker with carbon-treated demineralised water (the carbon treatment being effected in order to remove any colloidal polymer from the ion-exchange resin). Distilled water could have been used instead. A solution of the accelerator (if used), the reducing agent and a solution of the gold source were added, in that order and with stirring, to an aqueous liquor already containing the reduction-stabilising agent, chelating agent and auxiliary stabiliser(s). The solution was heated to 80 °C and filtered if any particulate matter was visible therein.

The exemplary formulations were investigated as electroless gold deposition baths using life tests on substrates provided (unless otherwise stated) as copper panels electroplated with pure gold to 2.5 µm and at a surface loading of 0.5 dm<sup>2</sup>/l, since at such a low loading any weaknesses in a system under test tend to be quickly revealed. In these tests, the baths were operated at a temperature of 80 °C ± 4 °C, with magnetic stirring with a PTFE coated stirrer at 400 rpm.

The concentration of the reducing agent was analysed every 30 minutes and replenishment was effected with the required amount dissolved in the minimum quantity of carbon-treated demineralised water. The gold and other constituents were replenished after each 0.25 g of gold had been removed from solution. Filtration, through two glass-fibre filter papers under vacuum, was effected if particles of gold appeared on the bottom of the beaker or if the solution (initially an orange/yellow colour, turning to very pale yellow upon heating) turned light brown.

Example 1

An aqueous liquor was prepared with the following formulation:

gold (present as KAu(CN) <sub>2</sub> )	1 g/l
potassium orthophosphate, K <sub>3</sub> PO <sub>4</sub>	12 g/l
potassium cyanide, KCN	11 g/l
potassium borohydride, KBH <sub>4</sub>	10.8 g/l
monoethanolamine	50 ml/l
potassium ferrocyanide	5 g/l
potassium ferricyanide	2 g/l
thallium (present as the sulfate)	2 mg/l

The liquor was tested as an electroless gold-deposition bath and it was found that an acceptable rate of deposition (2.5-3.0 µm/h) could be achieved without precipitation (plating up) of gold into the liquor.

Example 2

An aqueous liquor was prepared with the following formulation:

gold (present as KAu(CN) <sub>2</sub> )	1 g/l
potassium cyanide	11.0 g/l
potassium hydroxide	11.2 g/l
EDTA	5.0 g/l
potassium borohydride	10.8 g/l
potassium ferrocyanide	5.0 g/l
potassium ferricyanide	2.0 g/l
monoethanolamine	50 ml/l

When tested, this liquor was found to provide a robust bath, which was resistant to nickel contamination. The deposition rates were, in general, about 1 µm/h. Initiation of deposition on nickel was found to take, in general, from 5 to 15 minutes; the contact with the nickel surface in this test did not cause spontaneous decomposition of the liquor.

Example 3

An aqueous liquor was prepared with the following formulation:

5	gold (present as $\text{KAu}(\text{CN})_2$ )	1 g/l
	potassium cyanide	11.0 g/l
	potassium hydroxide	11.2 g/l
	EDTA	5.0 g/l
10	potassium borohydride	10.8 g/l
	potassium ferrocyanide	5.0 g/l
	potassium ferricyanide	2.0 g/l
	triethanolamine	10.0 ml/l
	glycine	4.5 g/l

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When tested, this liquor provided a robust bath, resistant to nickel contamination. The gold turnover was between 150 and 200%, with a mean deposition rate of 2.5  $\mu\text{m/h}$ . Initiation of the deposition on nickel was immediate; the contact with the nickel surface in this test did not cause spontaneous decomposition of the liquor.

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Example 4

An aqueous liquor was prepared with the following formulation:

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	gold (present as $\text{KAu}(\text{CN})_2$ )	1 g/l
	potassium cyanide	11 g/l
	potassium hydroxide	11.2 g/l
30	potassium borohydride	10.8 g/l
	monoethanolamine	50.0 ml/l
	EDTA	5.0 g/l
	potassium ferrocyanide	5.0 g/l
	potassium ferricyanide	2.0 g/l
35	thallium (present as the sulfate)	2.0 mg/l

When tested, this aqueous liquor provided a robust, general purpose bath which proved particularly suitable for depositing gold on copper and copper alloys. The bath could normally be operated to 200-250% gold turnover, with a mean deposition rate of 2-2.5  $\mu\text{m/h}$ , at a low loading of 0.5  $\text{dm}^2/\text{l}$ , the gold being replenished with further  $\text{KAu}(\text{CN})_2$ . Such replenishment was found to have no adverse effect on the free cyanide concentration.

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The potassium ferrocyanide, potassium ferricyanide, thallium and monoethanolamine were replenished as the bath was used, at rates of 1.25 g, 0.5 g, 0.5 mg and 2.5 ml respectively, per 0.25 g gold removed by deposition.

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The bath liquor (unlike certain prior-art formulations) did not spontaneously decompose when presented with a nickel surface. Initiation of the deposition on nickel was immediate. The bath liquor was, however, sensitive to soluble nickel contamination, it being found that a concentration of nickel of 10 mg/l could cause spontaneous decomposition. This sensitivity could be overcome by omitting the thallium from the solution.

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The deposits obtained from the baths of Examples 2, 3 and 4 were 99.9% pure gold (with 0.1% K) having a density of 19.3  $\text{g/cm}^3$  and a hardness of between 90 and 95 HV. The deposits which were up to 30  $\mu\text{m}$  in thickness were matt and lemon yellow (Examples 2 and 4) or orange-yellow (Example 3) in colour.

55 Example 5

An aqueous liquor was prepared with the following formulation:

gold (present as $\text{KAu}(\text{CN})_2$ )	1.0 g/l
potassium cyanide	11.0 g/l
potassium hydroxide	11.2 g/l
EDTA	5.0 g/l
potassium borohydride	10.8 g/l
monoethanolamine	50.0 ml/l
thallium (present as the sulfate)	2.0 mg/l
1-H-tetrazole	1.0 g/l

When tested as a gold plating bath, the liquor reached 188% gold turnover, with a mean deposition rate of  $2.07 \mu\text{m/h}$ . The gold deposit was comparable in properties to those of the preceding Examples.

#### Example 6

An aqueous liquor was prepared with the following formulation:

gold (present as $\text{KAu}(\text{CN})_2$ )	1.0 g/l
potassium cyanide	11.0 g/l
potassium hydroxide	11.2 g/l
EDTA	5.0 g/l
potassium borohydride	10.8 g/l
monoethanolamine	50.0 ml/l
potassium ferricyanide	2.0 g/l
thallium (present as the sulfate)	2.0 mg/l
1-H-tetrazole	1.0 g/l

When tested as a gold plating bath, the liquor reached 225% gold turnover, with a mean deposition rate of  $2.05 \mu\text{m/h}$ . The gold deposit was comparable in properties to those of the preceding Examples.

#### Comparison Example A

An aqueous liquor was prepared with the following formulation:

gold (present as $\text{KAu}(\text{CN})_2$ )	1.0 g/l
potassium cyanide	11.0 g/l
potassium hydroxide	11.2 g/l
potassium borohydride	10.8 g/l

When tested, the above solution gave deposition rates of about  $1 \mu\text{m/h}$  and proved to be prone to spontaneous decomposition, especially when in contact with nickel.

It will be seen from the foregoing description that in accordance with the present invention it is possible to formulate aqueous liquors for electroless gold deposition baths that are replenishable, that are stable (in particular resistant to precipitation) and that give acceptable and reasonably constant rates of gold deposition with good distribution.

It will of course be understood that the present invention has been described above purely by way of example, and modifications of detail can be made within the scope of the invention.



## Claims

1. An aqueous liquor for use as an electroless gold deposition bath, comprising a source of gold and a reducing agent, characterised in that it also contains a reduction-stabilising agent selected from (a) a mixture of an alkali metal or ammonium ferrocyanide and an alkali metal or ammonium ferricyanide, (b) 1-H-tetrazole, (c) redox mediators and (d) mixtures of any of these.
2. A liquor according to claim 1, characterised in that it contains potassium ferrocyanide and potassium ferricyanide.
3. A liquor according to claim 1 or 2, characterised in that the source of gold is an alkali metal gold cyanide.
4. A liquor according to claim 1, 2 or 3, characterised in that the reducing agent is an alkali metal borohydride.
5. A liquor according to any of claims 1 to 4, characterised in that it also contains a chelating agent.
6. A liquor according to claim 5, characterised in that the chelating agent is EDTA or a salt thereof, monoethanolamine, triethanolamine or a mixture of any of these.
7. A liquor according to any of claims 1 to 6, characterised in that it also contains, as an auxiliary stabilizer, glycine, an alkali metal cyanide or a mixture thereof.
8. A liquor according to claim 7, characterised in that it contains, as an auxiliary stabilizer, potassium cyanide.
9. A liquor according to any of claim 1 to 8, characterised in that it contains thallium and/or lead.
10. A liquor according to any of claims 1 to 9, characterised in that it contains an alkali metal hydroxide and/or a buffering agent to maintain the liquor at a pH at which oxidation of the reducing agent takes place.
11. A method for the electroless deposition of gold, onto a surface of a substrate, from an aqueous liquor comprising a source of gold and a reducing agent, characterised in that the said liquor also contains a reduction-stabilising agent selected from (a) a mixture of an alkali metal or ammonium ferrocyanide and an alkali metal or ammonium ferricyanide, (b) 1-H-tetrazole, (c) redox mediators and (d) mixtures of any of these.
12. A method according to claim 11, characterised in that the aqueous liquor is according to any one of claims 2 to 10.



DOCUMENTS CONSIDERED TO BE RELEVANT																	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)														
A	METAL FINISHING ABSTRACTS, vol. 16, no. 1, January/February 1974, page 24, right-hand column, abstract A; & SU-A-397 562 (INST. INORGAN. CHEM., ACAD. SCI.) 24-05-1971 ---		C 23 C 18/44														
A	US-A-3 485 643 (ZEBLISKY) -----																
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)														
			C 23 C														
The present search report has been drawn up for all claims																	
Place of search THE HAGUE		Date of completion of the search 28-07-1989	Examiner NGUYEN THE NGHIEP														
<table border="0"><tr><td><b>CATEGORY OF CITED DOCUMENTS</b></td><td></td></tr><tr><td>X : particularly relevant if taken alone</td><td>T : theory or principle underlying the invention</td></tr><tr><td>Y : particularly relevant if combined with another document of the same category</td><td>E : earlier patent document, but published on, or after the filing date</td></tr><tr><td>A : technological background</td><td>D : document cited in the application</td></tr><tr><td>O : non-written disclosure</td><td>L : document cited for other reasons</td></tr><tr><td>P : intermediate document</td><td>.....</td></tr><tr><td></td><td>&amp; : member of the same patent family, corresponding document</td></tr></table>				<b>CATEGORY OF CITED DOCUMENTS</b>		X : particularly relevant if taken alone	T : theory or principle underlying the invention	Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date	A : technological background	D : document cited in the application	O : non-written disclosure	L : document cited for other reasons	P : intermediate document	.....		& : member of the same patent family, corresponding document
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