DEPOSITION OF GOLD WITHOUT EXTERNAL CURRENT SOURCE

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The relative merits of different plating methods are discussed and a new type of electrolyte for autocatalytic gold plating is described. The chemical system of this bath has an ideal combination of properties such as stability and high deposition speed, combined with long bath life and high metal turnover.
The bath's composition, maintenance and sensitivity to contaminants are discussed, and its operating characteristics and the properties of the gold coatings formed from it are presented. Areas suitable for its application are suggested.

INTRODUCTION

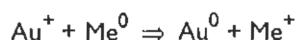
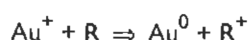
For the deposition of metals from solutions containing metal salts, negative electrical charges are required which convert the positively charged metal ion by so-called 'reduction' into the zero-valent state, i.e. into the metallic form.

In the usual case of electrolytic metal deposition an external source of current provides the necessary charges for reduction at the cathode.

In this article two deposition methods are discussed (*cf.* [1]) which do not depend on such an external source of current. The charges required for the deposition in these processes are supplied either by charge exchange reactions or are derived from chemical reducing agents (**Table 1**). In charge exchange processes, a relatively less noble metal, usually the basis material, dissolves and the more noble metal ion in the solution is reduced and deposited on the substrate. Such processes are referred to as immersion or displacement plating processes.

Table 1

Gold deposition without external current source

Charge exchange:	**Chemical reduction:**
 $Au^{+} + Me^{0} \Rightarrow Au^{0} + Me^{+}$	 $Au^{+} + R \Rightarrow Au^{0} + R^{+}$
Me^{0} is less noble than Au, is substrate or auxiliary anode e.g. Cu, Ni, electroless Ni	R is organic or inorganic non-metallic reducing agent, e.g. $NaBH_4$, DMAB, N_2H_4, NH_2OH etc.

In the case of chemical reduction processes on the other hand, a suitable chemical compound – a reducing agent – supplies the necessary negative charges. The reducing agent is oxidized at the same time. Such processes are usually referred to as autocatalytic or electroless plating process. The basic mechanisms of the two types of gold deposition without the application of externally generated electric current are summarized in (Table 1).

Reasons for Using Gold-Plating Processes without External Current Source and Fields of Application

These processes are used wherever electrically insulated areas on parts or surfaces that cannot be contacted are to be gold-plated. Sometimes the aim is just simply to deposit very thin (e.g. 0.1 μm) layers uniformly on bulk articles or to reach an optimally uniform thickness distribution which is independent of the coating thickness. Characteristic of all electroless processes is the possibility of achieving uniform coating thicknesses all over the articles to be plated if the electrolyte is stirred and/or the articles are moved appropriately. They can be used for the uniform internal and external coating of hollow articles into which the electric field in an electrolytic process would not spread so that electrolytic internal deposition on internal surfaces would be difficult or impossible.

As will be described below, gold-plating without an external current source is used only where electrolytic processes – processes with an external source of current – cannot be used (Table 2). Chemical processes, particularly for thick layers, are more complicated to operate, considerably slower and thus also more expensive than electrolytic processes. This is mainly caused by their low deposition speeds and also by the costs of the reducing agents. Electrolytic processes work faster and are easier to handle and thus cheaper.

The metal turnover possible is also very much higher for electrolytic processes than for chemical processes.

Typical fields of application of electroless reductive gold-plating are in the electronics industry, e.g. on printed circuit boards, and in semiconductor electronics. Such applications include contact areas, bonding surfaces on chip carriers, particularly ceramics, parts with glass-insulated bushings, transistor parts, cases, and many others.

Table 2

Disadvantages of gold deposition without external current source in comparison with electrolytic processes

Immersion gold plating

- Very slow (0.1 – 0.3 μm/h)
- Decreasing deposition speed
- Limited thickness (0.1 – 0.3 μm)
- Pitting corrosion possible

Electroless gold plating

- Slow (2.0 μm/h and more; electrolytically: > 60 μm/h rack)
- Very alkaline (pH 13 – 14)
- Very sensitive to contamination (self-decomposition)
- Limited life-time

GOLD PLATING WITHOUT EXTERNAL CURRENT SOURCE BY CHARGE EXCHANGE

As mentioned above, in gold plating of this type the relatively less noble basis material dissolves, the corresponding metal ions go into solution, the more noble gold, which still is in solution in the form of ions, acquires the electrons and is deposited on the basis material. This process can also be called a form of corrosion.

An important feature of this process is the fact that the charge exchange comes to a standstill as soon as a sufficiently thick and dense gold layer has been deposited (**Figure 1**, left), so that the basis material cannot be dissolved any longer. The coating thickness which can usually be achieved is about 0.1 to 0.3 μm, depending on the kind of substrate material and its surface quality, and the composition or the kind of gold electrolyte used.

If the substrate is very rough, if there are inhomogeneities and defects in the substrate, or if the gold electrolyte contains halogenide ions as activators and complexing agents, the process may continue with pitting corrosion in the basic material until coating thicknesses of several micrometres of gold are reached (**Figure 2**, page 19). Needless to say, however, a part can be seriously damaged by pitting corrosion so that this process must be avoided (loss of material, adhesion problems).

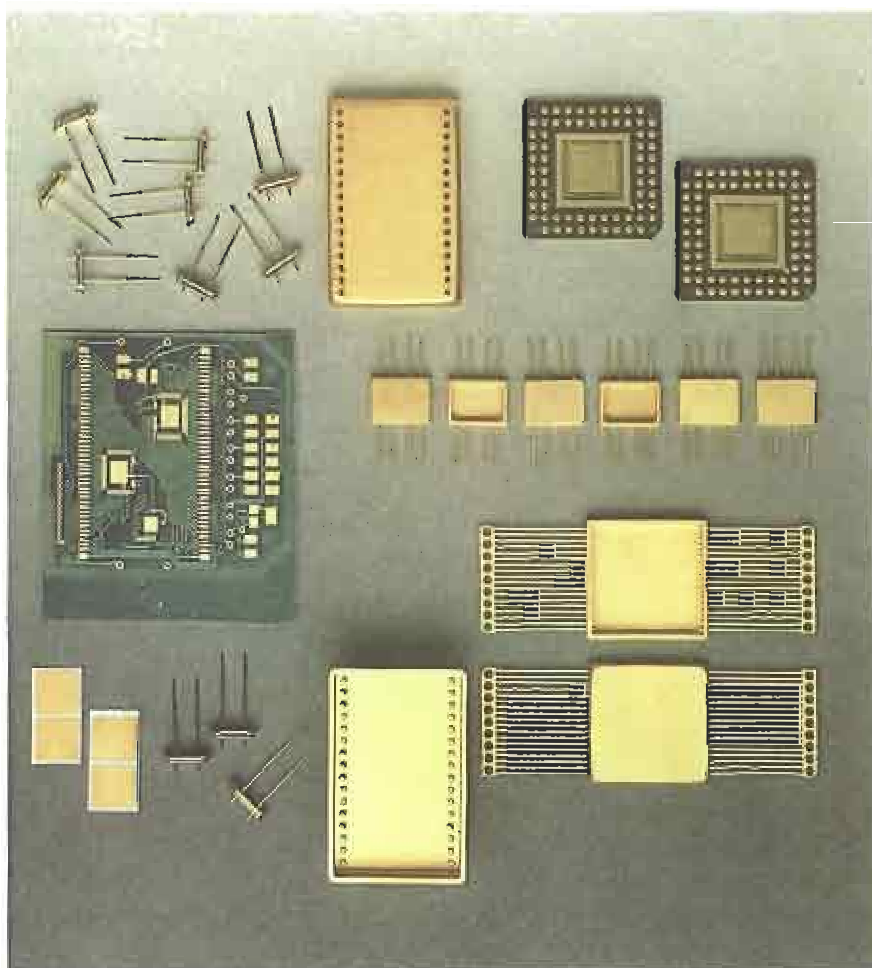
The main characteristics (**Table 3**, left) of the charge exchange process are the low deposition speed, the decrease of deposition speed with time, the limited coating thickness, and the fundamental risk of pitting corrosion in the basis material.

Advantages are the easy bath maintenance and the good activation effect, i.e. good adhesion on nickel and copper. Furthermore, overplating is excluded.

Typical bath compositions and operating parameters for immersion gold plating as reported in the literature are as follows:

Au:	1 – 5 g/l
NH_3:	1 – 20 g/l
Citric acid:	10 – 100 g/l
Complexing agent:	0.5 – 20 g/l
pH ranges:	3 – 6, 7 – 8
Temperature:	70 – 95 °C

Data in respect of two commercially available baths can be found in **Table 4** (page 18). There are different bath modifications for different basis materials. They are among other things distinguished by the fact that they do not contain halogenide ions.



Examples of electronic components plated with electroless processes

Gold Plating without External Current Source by Chemical Reduction

General Remarks and a Short Survey of the Literature

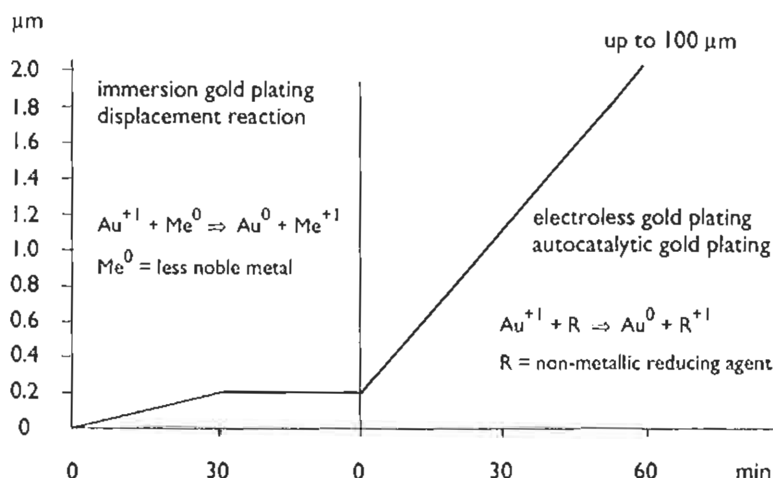


Figure 1
Comparison of plating speed of immersion (left) and electroless (right) plating processes

The deposition of gold on a gold substrate is the main distiguishing mark of electroless gold-plating by chemical reduction in a process working autocatalytically. The gold substrate or an already present gold layer (electrodeposited or electrolessly deposited) must have an autocatalytic effect on the further deposition. Only if it is guaranteed that this is the case and that the base substrate (basis material of Cu, Ni, etc.) does not participate in the deposition process, may the process be called chemical gold-plating.

The difference between the charge exchange process and chemical gold-plating is impressively shown in **Figure 1**. The gold is reduced at a constant rate if the other parameters are kept constant or controlled correctly. Theoretically, unlimited coating rhicknesses are possible.

Sometimes substrates, e.g. metallized ceramics, must be previously activated in a suitable way by seeding or they must be intermediately coated. During the chemical gold-plating a short charge exchange reaction always takes place first, until a catalytically working gold layer has been formed. Thus, ions from the basis material get into the gold electrolyte, and may adversely affect its lifetime.

Table 3
Gold deposition without external current source: typical properties

Charge exchange (immersion):	**Chemical reduction (electroless):**
$Au^+ + Me^0 \Rightarrow Au^0 + Me^+$	$Au^+ + R \Rightarrow Au^0 + R^+$
– very low deposition speed	– relatively high deposition speed
– decreasing deposition speed	– constant deposition speed during bath life
– limited layer thickness	– limited layer thickness
– pitting corrosion on the basis material possible	– no pitting corrosion

A variety of bath formulations for chemical gold-plating can be found in the literature (Table 5, page 18). Not only different gold compounds like $KAu(CN)_2$, AuCN, $KAu(CN)_4$ and $HAuCl_4$ are used for this purpose, but also various reducing agents such as sodium hypophosphite, hydrazine, hydroxylamine, N,N-diethylglycine, formaldehyde, thiourea, $NaBH_4$, and dimethylamine botane (DMAB). The pH ranges from

Table 4

Comparison of some parameters of immersion and electroless gold plating processes

	AURUNA® 511	AURUNA® 512	AURUNA® 515
Mechanism:	immersion	immersion	electroless (reduction)
Base material:	Cu, (Ni)	Ni, Ni/Fe	Au, Cu
Gold concentration:	4 g/l	3 g/l	2.5 g/l
Temperature:	90 – 98 °C	90 – 98 °C	75 °C
pH value:	Cu: 5.8 (Ni: 5.1)	4.5	13.8
Agitation:	vigorous	vigorous	moderate
Deposition speed:	0.1 – 0.3 µm/h	0.1 – 0.3 µm/h	2 µm/h
Max. deposit thickness:	0.2 – 0.3 µm	0.2 – 0.3 µm	unlimited
Halogen ions:	–	–	–

very alkaline (pH 13.7) in some baths to very acidic (pH less than l) in other formulations.

There is some doubt as to whether some of these formulations really are genuine chemical processes. Indeed, in practical trials it can be observed that some processes partly work according to the exchange principle.

Table 5

Types of electroless gold baths (after [3])

Au components	pH	t, °C	Reducing agents	Authors
$KAu(CN)_2$	7 – 7.5	93	Na-hypophosphite	Swan, Gostin
AuCN + KCN	7.5 – 13.5	96	Na-hypophosphite	Brookshire
AuCN + KCN	3 – 4	70 – 80	Na-hypophosphite	Ezawa, Ito
$KAu(CN)_2$	7 – 7.5	95	hydrazine	Swan, Gostin
$HAuCl_4$	> 10	85	hydrazine + sulfite + hydroxylamine	Luce
$KAu(CN)_2$	5 – 5.5	90	N,N-diethylglycine	Walton
$KAu(CN)_2$	alk.	70 – 80	hypophosphite + formaldehyde	McCormach/ Zeblinski
$KAu(CN)_2$	6.5 – 7	83 – 90	thiourea	Oda/Hayashi
$KAu(CN)_2$	alk.	75	$NaBH_4$	Okinaka
$KAu(CN)_2$	alk.	85	dimethylaminoborane (= DMAB)	Okinaka
$HAuCl_4$	13		DMAB	McCormack
$HAuCl_4$	10		DMAB + formaldehyde	Rick
$KAu(CN)_4$	> 1		?	Heraeus
$KAu(CN)_2$	alk.	90	DMAB	ACR
$KAu(CN)_2$	alk.	75	DMAB	Uyemura
$KAu(CN)_2$	13.7	75	DMB	Degussa

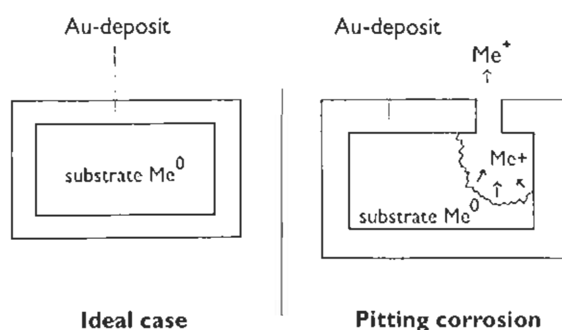


Figure 2

Pitting corrosion when gold plating with an immersion process (charge exchange)

Systems based on the use of $KAu(CN)_2$ and the reducing agents $NaBH_4$ or DMAB (dimethylamino-borane) have been examined most extensively and probably have been the most successful in practice. Our knowledge of these types of bath is essentially based on the work of Okinaka [2] and his colleagues. Okinaka showed in his work that the reducing agents $NaBH_4$ and DMAB react according to different mechanisms and that baths and their behaviour therefore depend among other things on the hydroxide concentration.

He showed that in both cases the BH_3OH^- ion is the actual reducing agent which itself is formed in a preliminary reaction appropriate to the reducing agent involved (**Figure 3**).

Thus, $NaBH_4$ first must partially hydrolyze and this is favoured in the acidic or less alkaline pH range (**Figure 3 a**).

In the case of DMAB, the amine (dimethylamine) attached to the BH_3 molecule must be displaced by an OH^- ion in order to generate BH_3H^- ions (**Figure 3 b**). It is clear that this displacement reaction is favoured in the very alkaline pH range, where many OH^- ions are present.

In addition, Okinaka confirmed that $NaBH_4$, even during rest periods at room temperature, decomposes more easily by hydrolysis than DMAB, which is more stable. Okinaka preferred $NaBH_4$ because, according to his findings, higher deposition speeds could be reached with it than with DMAB. Okina- ka has also identified fundamental problems with regard to the lifetimes of such baths, namely their sensitivity to metallic contaminants, the need to regenerate and replenish them and the maintaining of a constant deposition speed during the lifetime of a bath.

The fundamental weakness of a chemical gold bath is inherent in the system itself: it is a thermodynamically unstable system, a redox system, which would like to react only in one direction, namely in the direction of gold deposition. The main task now is to keep the system sufficiently *stable* on the one hand and, on the other hand, to *destabilize* it sufficiently in order to reach acceptable deposition speeds. This is a difficult compromise which in the end leads to an optimization of the system.

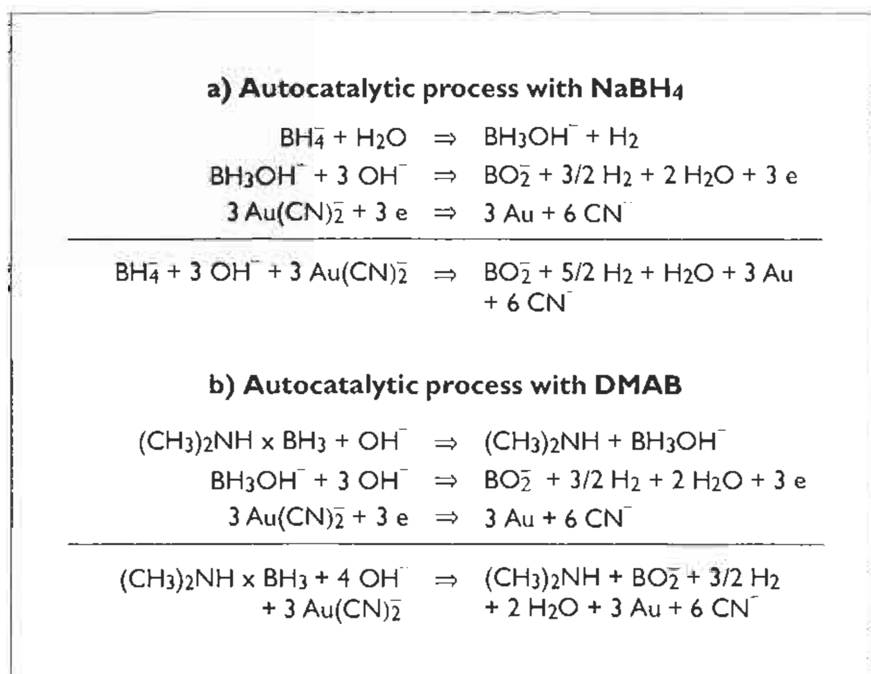


Figure 3

Electroless gold deposition using borohydrides

Table 6
AURUNA 515 – Bath characteristics

Type:	electroless (reductive) alkaline, cyanidic	
pH value:	13.7 – 14	(20 °C)
Au content:	2.5 g/l	(2.0 – 2.5)
Temperature:	75 °C	(73 – 77)
Density:	1.030	(20 °C)
Deposition speed:	2 μm/h	(up to 6 μm/h)
Loading:	1 – 1.5 dm^2/l	
Bath agitation:	low	
Rack movement:	none	
Barrel movement:	slow	
Filtration:	not required	
Exhaust:	required	
Max. thickness:	unlimited	(50 – 100 μm)
MTO:	14 x (rack) 7 x (barrel)	

Table 7
AURUNA 515 – Deposit characteristics

Au content :	99.9 %
Hardness:	60 – 70 HV 0.015
Classification:	III A, acc. to MIL-G-45204 B
Density:	appr. 19 g/cm^3
Appearance:	fine-grained smooth, matte
Bondability:	excellent
Solderability:	excellent

Objectives of the Development of a New Bath for Chemical Gold Deposition

The following were the aims in the development of a new bath:

- high bath stability
- relatively low self-decomposition of the reducing agent, therefore use of DMAB rather than $NaBH_4$
- deposition speed as high as possible and constantly maintainable
- low tendency to random deposition
- long life (metal turnover)
- simple bath maintenance
- low sensitivity to metallic contaminants

These aims have been achieved with the exception of low sensitivity to metallic contaminants, particularly Ni and Sn ions. This can be overcome, however, by inserting a charge exchange process as a preliminary to the actual chemical gold-plating.

This preliminary process reduces the formation of nickel ions from the substrate and thus makes a long lifetime of the chemical gold bath possible.

Bath Composition

The basic components of the new AURUNA 515 bath are $KAu(CN)_2$, KCN, alkali hydroxide, accelerator, depolarizer, and DMAB or dimethylaminoborane as reducing agent. The bath characteristics are presented in Table 6. The low gold content of 2.5 g/l has to be emphasized as well as the relatively low bath temperature of 75 °C and the maximum possible metal turnover, which is considerably better than for comparable state-of-the-art processes.

The deposition speed was purposely limited to 2 μm/h, because the development was aiming at an optimal compromise. A higher deposition speed would have increased the risk of random deposition of gold and could have limited the life of the bath.

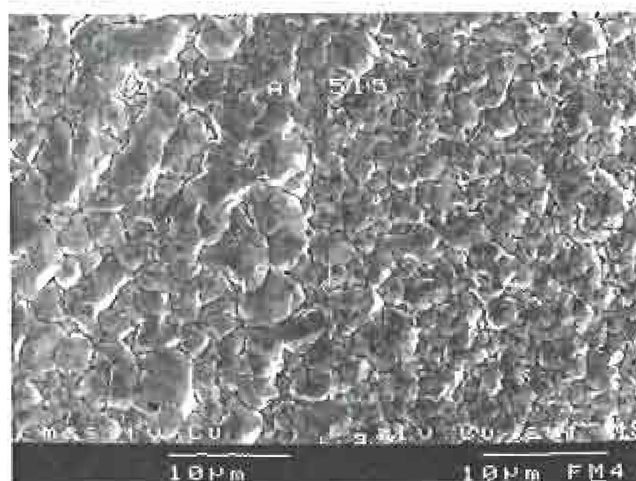


Figure 4
Surface structure of electroless gold (AURUNA 515) SEM-photo, x 3000

Coating Properties

The properties of the gold deposits from AURUNA 515 baths are summarized in **Table 7**. These gold layers are soft fine gold coatings of high purity, suitable for bonding and soldering purposes. The surface structures of two coatings are shown in a micrograph obtained by scanning electron microscopy (**Figure 4**).

Bath Maintenance

In general, the bath maintenance is influenced by the following factors during the operation of the bath:

- decreasing gold content (caused by deposition)
- decreasing content of reducing agent (caused by Au deposition *and* by self-decomposition)
- rising CN^- concentration (resulting from decomposing $KAu(CN)_2$)
- decreasing OH^- content (caused by attachment of OH^- ions to BH_3)

Other factors, like temperature and stirring speed, can be easily kept constant.

The effect of changing bath and operating characteristics on the deposition speed can be seen in **Table 8** (page 22).

Gold content, content of the reducing agent, and OH^- content can be corrected by replenishing the corresponding components. With regard to the consumption of the reducing agent, two causes should be distinguished: the consumption which is caused by the reduction reaction and that caused by spontaneous decomposition.

An example of an empirically found replenishment schedule to be used in actual practice is shown in **Figure 5**. The reducing agent is replenished in two steps – gold-dependent and time-dependent. The decisive time is the time during which the bath is at operating temperature.

Cyanide has a stabilizing effect in chemical gold baths which leads to a decrease in the deposition speed. On the one hand a minimum content of cyanide of several g/l is necessary because otherwise the bath would decompose spontaneously. On the other hand, a rising cyanide content during the lifetime of the bath may bring the deposition to a standstill.

By adding an accelerator, this problem can be elegantly solved without having to remove the cyanide from the system or having to bind it (**Figure 6**). Binding the cyanide with the aid of AuCN (simultane-

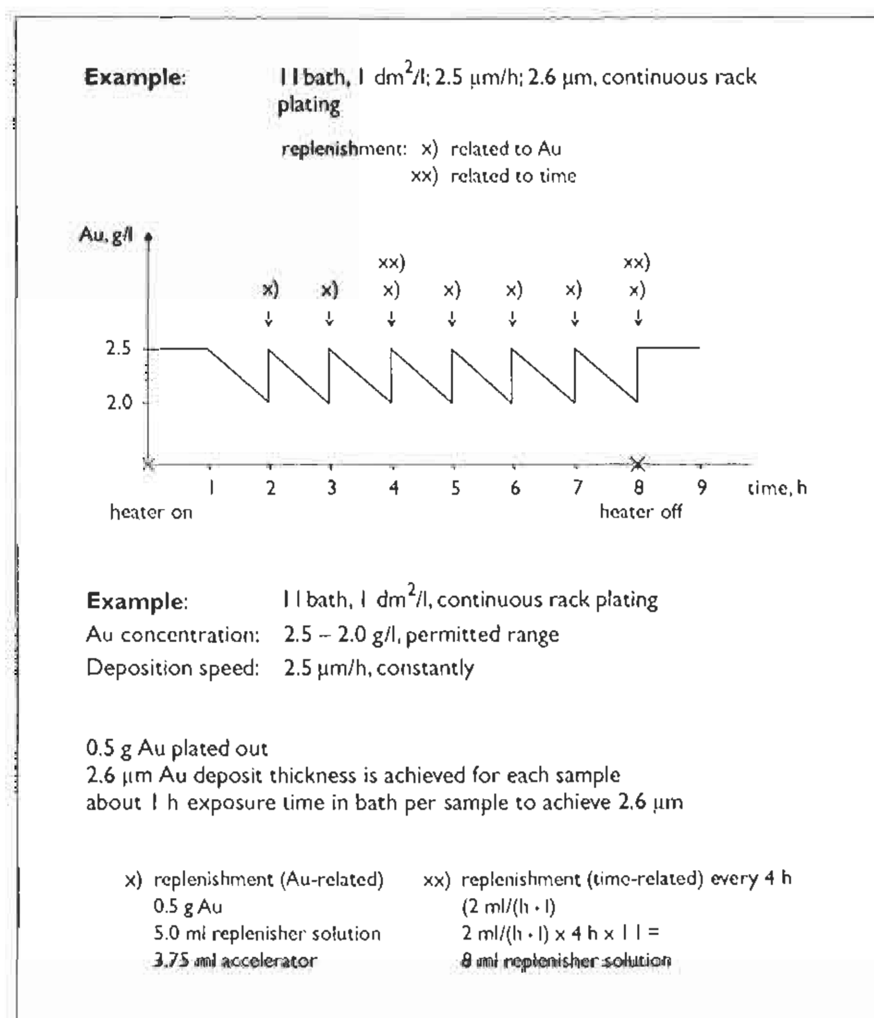
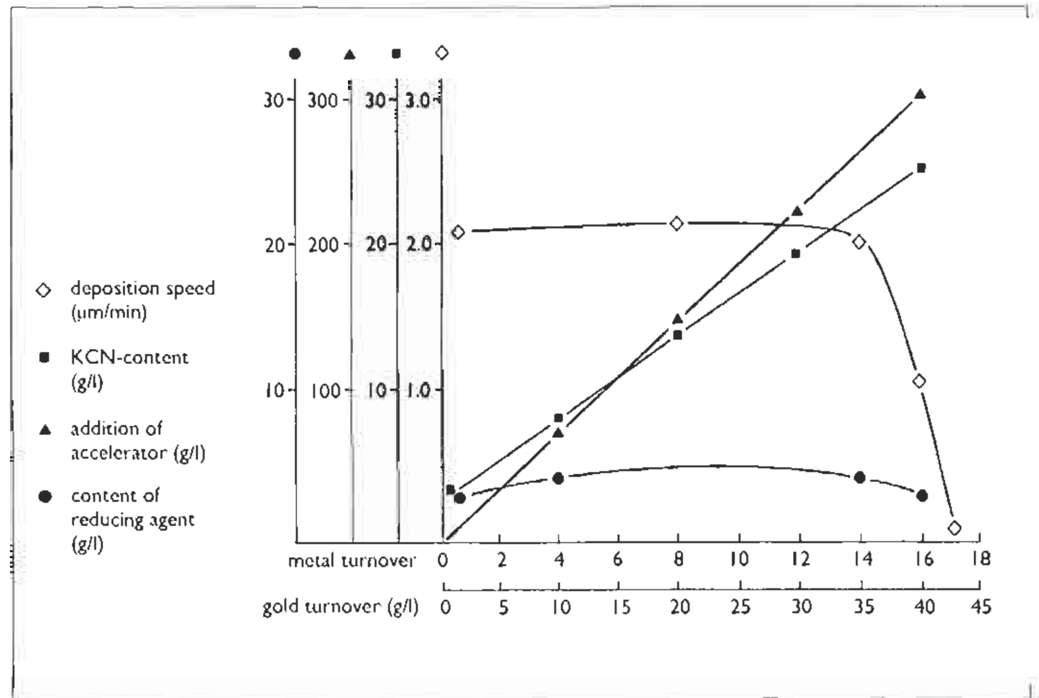


Figure 5
AURUNA 515 – Replenishment

Figure 6
AURUNA 515 – Rack plating long-time test



ously with gold replenishment) was given up because such a step would require a great deal of equipment to guarantee that on the one hand AuCN is dissolved fast enough as cyanide is consumed and, on the other hand, not too much cyanide is captured and the gold content does not rise inadmissibly. Furthermore, no solid particles of AuCN must get into the bath because these would act as nuclei for random deposition.

Table 8
AURUNA 515 – Effects of components/parameters on plating speed (V)

Gold	↓	⇒	V↓
Reducing agent	↓	⇒	V↓
Temperature	↓	⇒	V↓
pH value	↓	⇒	V↓
KCN	↑	⇒	V↓
Accelerator	↑	⇒	V↑

Accelerator empirically compensates the inevitable increase of KCN associated with metal turnover

With regard to the deposition speed, the accelerator neutralizes, so to speak, the effect of surplus cyanide or cyanide formed during the reduction in the bath (**Figure 6**).

Coating Sequences of Different Substrate Materials

Copper basis materials (and of course gold coatings themselves) can be directly chemically gold-plated without an intermediate layer, after the obligatory cleaning of the parts by soak cleaning or acidic cleaners.

Nickel coatings should be pre-gilded in an immersion plating bath. AURUNA 512 is suggested for the purpose. Zinc and iron alloys must also be pre-gilded and the use of the immersion plating bath AURUNA 511 is recommended in order to avoid contamination of the chemically active electrolyte.

Barrel-ware of copper or relatively thickly pre-gilded articles can also be chemically gold-plated without an intermediate layer. Copper ions in the bath do not affect the plating operation.

Barrel-ware (bulk articles) made of other basis materials must first be chemically nickel-plated and then pre-gilded in a charge exchange process before

Table 9

AURUNA 515 – Limits for metallic contaminants

Ion	Concentration		Effect
Ni^{2+}	<< 10 ppm		at 10 ppm self-decomposition
Sn^{2+}	<< 10 ppm		
Sn^{4+}	<< 10 ppm		
Cu^{+}	2.5 g/l Cu as $Na_2Cu(CN)_3$	⇒	stable
Cu^{2+}	500 ppm Cu as $CuSO_4$	⇒	self-decomposition (nuclei)
Fe^{2+}	1 g/l Fe as $Fe(CN)_6^{4-}$	⇒	stable
Fe^{3+}	1 g/l Fe as citrate	⇒	stable
Al^{3+}	1 g/l Al as sulfate	⇒	stable

they can subsequently be chemically gold-plated. The use of the AURUNA 512 bath is suggested.

The sensitivity of the chemical gold electrolyte to some metallic contaminants is shown in Table 9.

Table 10

AURUNA 515 – Advantages and positive properties in comparison with the state of the art

- Good combination of high stability and relatively high deposition speed
- Long life, i.e. high metal turnover (MTO) possible
  Barrel: 7 MTO
  Rack: 14 MTO
- Easy maintenance
- Reproducibility of results (bath and deposit properties)
- During bath lifetime no significant changes of bath deposition properties

Summary and Advantages of the Newly Developed Process

With the new gold electrolyte a system has been created which is an ideal combination of opposite properties such as stability on the one hand and relatively high deposition speed on the other, combined with a long bath life (Table 10). Per litre of bath, in rack operation metal turnover of up to 14 times is possible if the bath is suitably maintained, i.e. 14 x 2.5 g/l = 35 g of Au per litre of bath can be deposited. The speed of gold deposition can be kept constant during the lifetime of the bath by adding an accelerator.

Random deposition and bath decomposition do not occur during the whole lifetime of the bath if the drag-in of nickel and tin ions is avoided. This is possible by simply inserting a preliminary charge exchange (immersion) bath. A clean way of working must be observed.

Bath maintenance may be qualified as easy. During the lifetime of the electrolyte no significant changes occur with regard to the deposition characteristics of the bath and the coating properties.

References

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2. Y. Okinaka, 'Electroless Gold Deposition using Borohydride or Dimethylamine Borane as Reducing Agent', *Plat. Surf. Finish.*, 1970, 57, 914-920
3. Y. Okinaka, in 'Gold Plating Technology', edited by F.H. Reid and W. Goldie, *Electrochemical Publications*, Ayr, Scotland, 1974