New Non-Cyanide and Non-Sulphite Gold Plating Process

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Abstract:

The substitution of cyanide has been a target of development work in industry and research institutes around the globe for many years. Nevertheless, no process has reached technical importance with the inclusion of the relatively unstable gold sulphite complex as a cyanide-free system. A short review will be given of the work published on non-cyanide electrolytes. The suitability of different gold compounds in electroplating is discussed. Proceeding from the idea of an ideal complexing agent for gold, new compounds were postulated and tested. The synthesized new gold compounds based on mercapto-alkylsulphonic acid are non-toxic, non-odorous, stable without any self-reduction and useful for electroplating. Preliminary tests in plating in weakly alkaline solutions showed promising possibilities for pure gold as well as for gold alloy plating with copper and tin as alloying partner, for example.

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1. Environmentally Friendly Plating as a Goal

Avoiding problematic toxic substances as far as possible has been a long-cherished wish in plating. Above all the cyanides belong to this group, but also heavy metals such as Ni, Cd, Pb, or non-metals such as As and Se, or carcinogenic substances such as hydrazine, or the hard complexing agents. These substances are used as complexing agents and conducting salts, or as alloying partners, grain refiners, brighteners, or *for influencing the current efficiency*. Long-term research work has already yielded interesting, unproblematic alternatives in this field (Transparency 1).

Nowadays replacing toxic heavy metals such as cadmium and lead should be a goal. As to replacing Cd, electroforming on the basis of AuAg instead of AuCuCd and the development of AuCuAg as an alternative to AuCuCd baths have been first steps in the right direction. Replacing allergenic Ni as alloying partner and intermediate layer is a consumer demand today. With MIRALLOY® as intermediate layer, a CuSn alloy, and colour gold baths containing Fe and In as alloying partners instead of Ni, *suitable alternatives have been developed*. Last but not least the needs of the moment require that we avoid any hard complexing agents harmful to waste water and use biodegradable substances instead. Environmentally friendly metal finishing must be an issue for all committed plating supply companies, plating departments, and contract platers in our time of high environmental sensitivity.

Due to their extremely high toxicity the cyanides are the first item on the wish list of substances to be replaced, they are a permanent danger for both the operators of plating baths and the environment. Nonetheless, cyanides can be relatively safely *handled provided adequate safety precau*tions are taken. Cyanides are used in a wide variety of bath types. Above all gold itself is used in the form of its cyano complexes as a stable and inexpensive compound throughout a wide pH range.

The following presentation wants to give an overview of the efforts to replace cyanides as complexing agents and conducting salts in gold baths by non-toxic substances.

2. Properties and Advantages of Cyanides as Complexing Agents for Gold

It is well known that the cyanide complexes of gold, namely $KAu(CN)_2$ and $KAu(CN)_4$, are the main basis for the deposition of gold and its alloys. There are good reasons for that (Transparency 2).

The complexes are very stable (pK 37 and 56). They are stable in solution, partly with or without traces of cyanide; they are excellently soluble in water; the complete pH range can be covered. The strong lowering of the gold potential permits the deposition of a large number of alloys. A wide spectrum of possible alloy metal complexes is available.

A very essential aspect is the fact that the cyanide liberated during cathodic gold deposition degrades by means of hydrolysis and oxidation and thus does not accumulate in the bath to a critical extent, i.e. a state of equilibrium can be reached in the bath. Last but not least: Cyanide is cheap and the salts can be easily manufactured.

These advantages of the cyanides are in contrast to their high wastewater toxicity, which can be controlled by simple detoxification, however. When hypochlorite is used there still is the problem of the AOX compounds, however.

3. Overview of Non-Cyanide Gold Baths

Although the efforts to formulate non-cyanide baths go back very far, up to now only the relatively unstable gold sulphite system could gain any economic importance.

As early as more than 150 years ago, Elsner and Wollrich described an electrolyte on the basis of gold sulphite (Transparency 3). Patents for baths on the basis of gold compounds with thiomalate, mercaptoethanol, iodide, hydroxide, thiosulphate, tetrammine nitrate, succinimide, phosphonic acid, and cyanuric acid followed very much later, just to mention the most important ones. In our own house previous work on thiourea, sulphamate, and diphosphate has been documented.

During reconstruction tests, all these systems have more or less shown drawbacks. The thiomalate bath can be briefly operated in a fairly stable way. At higher current loads it has a tendency to decompose and it is not odourless.

The conditions in the mercaptoethanol bath are even more unfavourable, it is toxic and causes clear odour nuisance.

The iodide bath is sensitive to water; it will precipitate when diluted. The gold hydroxide bath can be actually operated, it is stable exclusively at pH-values > 13, however. Sulphite baths are commercially available in different variants and hold their ground in a specific field of application, particularly in fine gold deposition in the semiconductor industry and in alloy deposition with palladium, which is not possible from cyanide systems.

Thiosulphate electrolytes are quite interesting actually, they have a tendency to decompose liberating sulphur, however. EP 611840 shows a way to stabilize the electrolyte with sulphinic acids. Further applications for patents, Japanese ones in particular, deal with the use of goldthiosulphate for electroless deposition.

All other mentioned electrolytes are unstable. Their components partly are poorly soluble or they contain toxic or carcinogenic chemicals such as thiourea. All these approaches are no suitable basis for the target "Development of environmentally friendly baths".

4. The Search for Suitable Gold Compounds

In a study we have succeeded in getting a general idea of the chemistry and stability of water-soluble gold compounds in order to be able to decide which gold compound could justify any development work.

Gold with the atomic number 79 has the electronic structure 4f145d10 6s1 (Transparency 4). Equivalent to a d10 or d8 configuration, gold thus occurs in the valence states I and III. With a value of 2.4, the highest electronegativity of all metals, gold practically occurs in a covalently bonded form only. Large, polarizable ligands are preferred which allow an interaction of the d-electrons and form complex structures with Au. With Au(I), they usually occur in linear form, with Au (III) in square-planar form.

Au(I) compounds which are not complex stabilized disintegrate with disproportionation according to equation 1.

$$3\ Au^{+} \rightarrow 2\ Au + Au^{3+} \quad (1)$$

From the above it seems likely that Au ions in aqueous solution do not form any or only highly unstable aquo complexes. This is an essential reason for the high positive normal potential of Au ions in aqueous media.

As a logical consequence, the potential can be considerably lowered by complexing. The degree of potential lowering depends on the stability of the complex and thus as a first approximation is a good standard for the usability of a compound in an electrolyte.

The following table (Transparency 5) shows the normal potentials of different water-soluble systems of complexes versus gold according to the references. The complex stability increasing from top to bottom is clearly visible. For the mercapto compounds, no concrete values were available, according to the references they are close to the cyanides.

As expected, the most stable gold compounds are the cyanides, immediately followed by the mercapto compounds. The sulphite and thiosulphate complexes are less stable already. The thiourea complex was not further examined because of its carcinogenic effect. All other complexing agents are hardly able to sufficiently stabilize Au in its monovalent form. The Au(III) hydroxo complex is stable only in the strongly alkaline range. The tetrammine complex is sparingly soluble and forms explosive precipitates with different anions and in the acidic and alkaline ranges. In the Au and iodide system, the AuI_2^- complex can only be stabilized in the presence of a very high excess of free iodide. It decomposes already when diluted. This similarly applies to the thiocyanate complexes. Only if there is a thirty-fold excess, Au(I) can be still stabilized, decomposition with disproportionation and hydrolysis will additionally occur. The well-known $AuCl_4^-$ is quite stable in the strongly acidic range. It is strongly oxidizing and highly aggressive. It is well suited to gold refining utilizing the so-called Wohlwill electrolysis. The system is little suited as a basis for coating purposes.

Summarizing these facts we can conclude that apart from the cyanide systems any stable gold baths can be almost exclusively expected from mercapto compounds.

5. New Gold-Mercapto Complexes

As already mentioned before, there were efforts in the past pointing in this direction, e.g. the thiomalate bath. However, the known mercapto compounds have considerable drawbacks, for instance their intensive smell.

To find better and more stable systems, we first of all defined the demands on an ideal complexing agent: (Transparency 6) a mercaptan compound which forms stable Au(I) complexes, which has a high water solubility, and which should be non-odorous, if possible - it should have a low vapour pressure due to salt formation. It should be as resistant as possible to hydrolysis and oxidation, as far as this is possible with an SH compound, and last but not least it should not be a hazardous substance!

Two compounds crystallized out of a number of synthesis tests which meet these demands to a large extent: (Transparency 7) mercaptoethanesulphonic acid (MES) and mercaptopropanesulphonic acid (MPS). They not only form fairly stable Au(I) compounds throughout a wide pH range but they are also very well soluble in water, remarkably, they are practically non-odorous in pure form, and they are no hazardous substances. Their synthesis is simple, for instance by dissolution of gold hydroxide precipitated from tetrachloroauric acid with NH_3 solution, the so-called gold fulminate, in a solution of MES or MPS, where a spontaneous conversion into Au(I) takes place (Transparency 8).

5.1 Electrolytes on MES or MPS Basis

Electrolytes containing 5 g/l Au in the form of the MPS complex have confirmed the expected stability (Transparency 9). There was no spontaneous reduction, not even after a lifetime of months. Even under a load of 2 A/dm^2 and a loading per litre of > 1 A/l, the electrolytes were stable. Relatively high current efficiencies of 30 to 40 % of theory are obtained in the weakly alkaline range at 50 °C and 1 A/dm^2. The layers are ductile and milky to matt.

The pH-value of the bath can be stabilized with the usual buffer systems such as phosphate and borate.

Alloy deposition is possible, e.g. with silver, copper, indium, or tin, it is not possible with iron metals or palladium, however, as first tests have shown (Transparencies 10, 11, and 12). Individual brighteners known from the cyanide systems have been effective in this system as well. A patent on the system has been applied for.

6. Conclusions

The presented system is an essential further development on the way to a non-toxic gold electrolyte. It offers possibilities which seem to merit any further development work.

Replacing the cyanide system completely will not be possible even on this electrolyte basis, however, this will remain an unattainable dream. The possible operating ranges as regards pH-value and current efficiency are too limited for this purpose.

Non-Cyanide Gold Baths

- **Environmentally Friendly Plating:**
  - Replacement of toxic chemicals such as cyanide, hydrazine
  - Replacement of toxic heavy metals, e.g. Cd, Pb, As
  - Replacement of allergenic substances such as Ni, Co
  - Avoidance of hard complexing agents, use of biodegradable substances

Non-Cyanide Gold Baths

- **Advantages of Cyanides**
  - High stability of the complexes: Au(I) pk 37, Au(III) pk 56
  - High water solubility of alkali cyanides and their complexes
  - The complete pH range can be covered (pH 0.5- 14) since the complexes are stable even without free cyanide
  - The strong lowering of the Au potential permits a large number of alloys
  - A wide spectrum of alloy metal complexes is available
  - Cyanide liberated during deposition degrades by hydrolysis and oxidation
  - Cyanide is cheap, the products can be easily manufactured

Non-Cyanide Gold Baths

Literature Review of Non-Cyanide Electroplating Baths

Complexing Agent	Literature	Remark
Sulphite	**Several patents (approx. 1850)**	**In practical use**
Iodide	US-P 1 857 664 (1929)	Sensitive to water
Mercaptoethanol	US-P 3 238 112 (1962)	Smelling, harmful
Thiomalate	**DE-OS 1 621 172 (1967)**	**Stable bath**
Sulphamate	Degussa internal report 5952/M (1967)	Not stable, less soluble
Diphosphate	Degussa internal report 5952/M (1967)	Not stable
Thiourea	Degussa internal report 6/72 (1972)	Carcinogenic
Tetrammine nitrate (Au III)	DD-P 96 514 (1972)	Not stable
Phosphonic acid	DOS 2 324 764 (1973)	
Cyanuric acid	US-P 3 879 270 (1974)	Less soluble
Hydroxide (Au III)	**DE-OS 2 508 130 (1975)**	**Strongly alkaline useful**
Succinimide	US-P 3 917 885 (1975)	
Thiosulphate	EP 611 840 A1 (1994)	Stabilized with sulphinic acid

Non-Cyanide Gold Baths

- Gold: Au

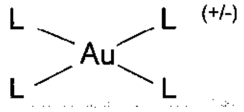
  Atomic number 79

  Electronic structure 4f14 5d10 6s1

  Electronegativity 2.4

  Au (I): L-Au-L $^{(+/-)}$

  Au(III):



Non-Cyanide Gold Baths

Normal potentials of gold complexes vs. gold

Ligand	**Complex**	**Potential E° AuL_n/Au (V)**
H_2O	$Au(H_2O)_2^+$	1.66
	$Au(H_2O)_4^{+++}$	1.50
Cl^-	$AuCl_2^-$	1.15
	$AuCl_4^-$	0.92
SCN^-	$Au(SCN)_2^-$	0.67
	$Au(SCN)_4^-$	0.64
I^-	AuI_2^-	0.58
	AuI_4^-	0.57
NH_3	$Au(NH_3)_4^{3+}$	0.56
OH^-	$Au(OH)_4^-$	0.48
Thiourea	$Au(Thu.)_2^+$	0.38
$S_2O_3^{2-}$	$Au(S_2O_3)_2^{3-}$	0.15
SO_3^{2-}	$Au(SO_3)_2^{3-}$	0.06
R-SH	$Au(R\text{-}S)^{2-}$	?
CN^-	$Au(CN)_2^-$	- 0.65

Non-Cyanide Gold Baths

- **Demands on New Complexing Agents for Gold Baths:**
  - Mercapto compounds with good complex formation with Au(I) ions
  - *High water solubility*
  - Minimal odour nuisance
    - Minimal vapour pressure
    - Formation of stable salts
  - High resistance to hydrolysis and oxidation
  - No hazardous substance

Non-Cyanide Gold Baths

- **MES and MPS**

$HS\text{-} CH_2\text{-} CH_2\text{-} SO_3Na$ **MES**

$HS\text{-} CH_2\text{-} CH_2\text{-} CH_2\text{-} SO_3Na$ **MPS**

- **Stable Au(I) complexes**
  - Stable from the weakly acidic up to the alkaline medium
- **Good water solubility**
- **Non-odorous in pure form**
- **No hazardous substances**

Non-Cyanide Gold Baths

Postulated Reaction Equation

$HS - (CH_2)_n - SO_3Na \quad \triangleq \quad$ MES, MPS $\quad n = 2, 3$

$HS - R \quad R = -(CH_2)n - SO_3Na \quad n = 2, 3$

$$Au^{III}(OH)_3 + 4\ HS - R \xrightarrow{RT} [Au^{III}(S - R)_4]^- + 3\ H_2O + H^+$$

brown-red complex

$$[Au^{III}(S - R)_4]^- \xrightarrow[\text{or time}]{\text{slight heat}} [Au^{I}(S - R)_2]^- + R - S - S - R$$

colourless complex

Non-Cyanide Gold Baths

- Electrolytes on MPS Basis :

5 g/l Au as Au(I) MPS complex
10 g/l MPS
pH 7 - 12
25 - 70 °C
0.5 - 2 A/dm²
Current efficiency 20 - 50 % of theory
Yellow, ductile, matt layers

- Possible alloy metals silver, copper, indium, tin
- Possible buffers phosphate, borate etc.

Non-Cyanide Gold Baths

Gold alloys deposited from the MES/MPS system

Alloy	Complexing agent	Properties of the Layers	With Brightener
Gold-Silver	MES/MPS	Yellow-greenish	Yellow-greenish brilliant
Gold-Copper	MES/MPS	Reddish, dark	Reddish brilliant
Gold-Indium	EDTE/Gluconate	Greyish matt	No brightener found yet
Gold-Tin	Gluconate	Grey, matt	No brightener found yet
Gold-Copper-Tin	Gluconate	Hamilton colour	Brilliant
Gold-Bismuth	Citrate	Black, dull	
Gold-Palladium	MES/MPS	No alloying	
Gold-Nickel	MES/MPS	No alloying	
Gold-Cobalt	MES/MPS	No alloying	

(Conditions: 50 °C, 1 A/dm2, 300 rpm agitation, 2.5 cm/sec rod movement)

Non-Cyanide Gold Baths

Bath composition		Layer composition	
Au g/l	Alloy metal g/l	% Au	% Alloy metal
3	1 Ag	76	24 Ag
3	3 - 6 In	89	11 In
2.5	0.6 Cu	92	8 Cu
2	2 Sn / 1 Cu	84	3.5 Sn / 12.5 Cu