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COMPARATIVE STUDIES REGARDING CYANIDE AND SULPHITE ELECTROLYTES FOR BRUSH ELECTROPLATING OF GOLD THIN FILMS

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Comparative studies regarding gold electroplating accomplished on carbon steel electrical contacts using a toxic electrolyte that contains sodium dicyanoaurate (I), as well as a non-cyanide electrolyte were presented in this paper. In order to determine if the substitute electrolyte can be considered equally suitable to replace the cyanide toxic electrolytes, several comparative analyses of gold thin deposits and a series of characterization methods such as: Scanning Electron Microscopy (SEM) for morphological structure investigation, Energy-Dispersive X-ray Spectroscopy (EDS) for quantitative analyses of the deposits, and Elemental Mapping for the element distribution, were performed. It has been found that gold thin films on a nickel intermediate layer from sulphite electrolyte baths present superior properties being accomplished in a shorter processing time with no effects on operators' health and on the environment.

Keywords: gold, non-cyanide electrolytes, brush electroplating, electrical contacts, selective deposition.

1. Introduction

The history of gold electroplating began in the mid nineteenth century when an electrolysis bath composition containing a potassium gold cyanide double salt was patented. From that moment on, many researchers had developed different electrolyte formulations based on cyanide salts, in order to satisfy a wider range of requirements, such as excellent electrical conductivity, high

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corrosion and photochemical resistance, long term sustainability, process compatibility [1, 2]. However, from the mid twentieth century when the electronics industry had begun its development and till now, it is mandatory that the gold deposits have special physical properties, such as: high conductivity, corrosion and contact resistance, electrical and physical wear resistance. Hence, in the electronics age, the purposes of gold deposition are not just limited to the decorative aspect, because of the elaborate usage of the products that are developed and its rapid growth [1, 2].

By using electrodeposition the parameters can be chosen to obtain coatings with various characteristics and properties such as appearance, corrosion resistance, different special properties of the surface (conductive layer, electrical contacts) and mechanical properties. Coatings do not have usually only one purpose; for example the long-term protection coatings need to be also decorative sometimes [3-7].

Baths for gold deposition can be classified into different categories depending on the plating bath formulation, on the parameters used in the deposition process, the deposition mechanism, the pH of the bath and the properties of the obtained deposit (Figure 1).

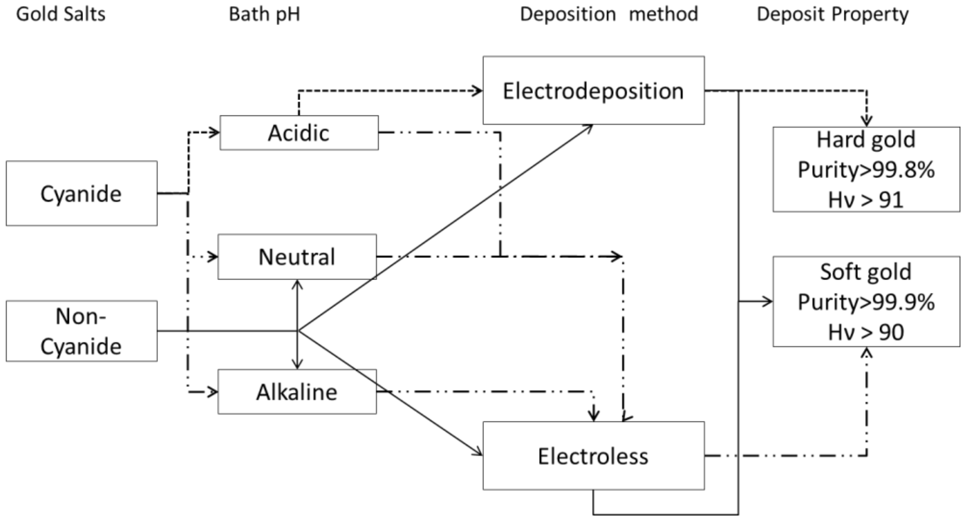

Fig.1. Classification of electrodeposition baths for gold layers

Cyanide-based electrolytic baths include baths that operate at acidic, neutral or alkaline pH, and may result in the deposition of either “hard” or “soft” gold, these names depending on the degree of crystallinity and the hardness of the deposit (Hv – Vickers hardness, [kgf / mm^2]). Cyanide-free baths can only operate at neutral or alkaline pH, either through electroplating or electroless method, but available non-cyanide baths can only lead to obtaining “soft” gold. The “hard” gold deposits can now only be obtained from a cyanide bath and only through the electrodeposition method [1, 7-9].

Gold electrolytic deposits currently have a broad industrial application, especially in the electronics and electrical industry, also in other special areas, such as - watchmaking, control precision devices for measurements and jewellery.

The multiple uses of gold layers correspond to the many properties which, alone or in combined, are of particular importance. These are obtained from a wide variety of golden electrolytes in the presence of many alloying elements. Requirements that apply to gold coatings according to the use areas are grouped together as illustrated in Table 1 [2].

Table 1

Requirements for gold deposits [2]

Types of gold use	**Gold for fixing**	**Contacts**	**Decorative-functional**	**Pure decorative**
General properties				
Deposit thickness, μm	0.1 ... 2	0.5 ... 3	0.5 ... 5(20)	0.5
Colour	-	-	+	+
Gloss level	-	+	+	+
Economization	selective deposition	selective deposition	low caratage alloy	low thickness
Chemical properties				
Anticorrosive protection	(+)	+	+	adding varnish
Porosity	(+)	+	+	-
Oxidation behaviour	+	+	+	+
Electrical properties				
Specific resistance	(+)	(+)	-	-
Mechanical and metallurgical properties				
Ductility	-	+	+	-
Hardness	+ (low)	+	+	(+)
Wear (abrasion)	-	+	+	(+)
Structure	+	-	+ (homogeneous)	-
Fixing capacity	+	-	-	-
Soldering capacity	(+)	+	(+)	-
Legend:	+ = important, (+) = less important, - = non important			

Gold is the most noble of metals; its stability is only reduced in the presence of certain ligands, such as cyanide ions, halide, thiourea and thiocyanate, by formation of stable complex ions.

Gold compounds are formed in the Au (I) and Au (III) oxidation states. These compounds are usually found in the form of complex ions formed by the covalent bonding between a central cation of Au^+ or Au^{3+} and a number of ligands or molecules.

The stability constant for both Au^+ and Au^{3+} complexes is an important parameter because it influences the distribution of free metal ions and complex ions. There are also the factors that determine whether gold ions can be reduced from their complex form, which make them become useful in the electrodeposition process. It should be noted that Au (I) ion is not stable in aqueous solution and is prone to disproportionation, thus forming metallic gold or gold (I) hydroxide when subjected to hydrolysis. Thus, all gold deposition processes from Au (I) complexes take place by direct electroreduction of complex species.

The main reaction for gold electrodeposition from a bath containing the complex ions of Au (I) with the cyanide, sulphite or thiosulphate ions is:

$$\left[Au^{+}L\right]_{complex} + e^{-} \leftrightarrow Au + L \tag{1}$$

To determine the stability of the electrochemical bath is essential to know the stability constant (β) of the complex ions of Au (I), because the disproportionality of the gold in the solution is controlled by the concentration of the complex.

$$\frac{\left[Au^{+}L\right]_{complex}}{\left[Au^{+}\right]\cdot\left[L\right]} = \beta \tag{2}$$

Gold has been deposited from cyanide-based electrolytes, but for safety reasons concerning the disposal of process waste, there is increasing concern about replacing the use of cyanide-based methods.

For applications in microelectronics and optoelectronics field, electrolytic baths based on gold sulphites have a significant number of advantages over cyanide-based ones. After the electrodeposition process, the deposits from non-cyanide baths achieved a uniform thickness across the surface of the substrate, and the gold particles deposited from these baths have an excellent shape, uniform height, and low surface roughness.

The most important reason for using these sulphite baths is that they are not toxic, and the requirements for handling, storage and waste disposal are much more permissive than cyanide baths. In the sulphite electrolytic bath, gold is in the form of $[Au\,(SO_3)_2]^{3-}$. The stability constant of $[Au(SO_3)_2]^{3-}$ is 10^{11} times lower than that of the corresponding cyanide complex; however, these non-cyanide baths have a relatively high stability, especially under alkaline conditions [2, 8].

In steady state, the excess of $[Au\,(SO_3)_2]^{3-}$ tend to decompose, forming gold and sulphite ions:

$$Au(SO_3)_2^{3-} \leftrightarrow Au^{+} + 2SO_2^{3-} \tag{3}$$

A metallic gold precipitate is formed by the following disproportionation reaction:

$$3Au^{+} \rightarrow 2Au^{0} + Au^{3+} \tag{4}$$

The sulphite ion can be decomposed according to the following reaction, with the formation of hydroxyl ions. This equilibrium is pH dependent:

$$SO_2^{3-} + H_2O \leftrightarrow SO_2 + 2OH^{-} \tag{5}$$

At pH value of 7.0, the equilibrium will shift to the right, releasing SO_2.

A second reaction is the cathodic reduction of sulphite to $S_2O_4^{2-}$, which can lead to a chemical reduction of gold ions to metallic gold.

In order to suppress the bath instability resulting from this reaction, all commercially available sulphite baths contain stabilizers. The stabilizers can modify the pH value of the electrochemical bath. In this case, amines (ethylene-diamine used to modify the deposit properties), and arsenic (used as gloss agent) have a negative influence on the hardness and microstructure of the deposit [8].

Due to health and safety concerns of chemical operators, in laboratories where gold electrodeposition operations are carried out using cyanide toxic electrolytes, it has been proposed to replace those electrolytes with gold sulphites-based electrolytes.

Compared to cyanuric electrolyte, the lethal dose for the sulphite base electrolyte is 5 g/kg body weight, therefore the negative effect on the human body is considerably reduced.

In this paper, in order to deposit gold from a non-cyanide bath, it was used a sulphite-based electrolyte. Furthermore, the experimental methods used for gold electrodeposition on the DC motor’s commutators were performed by electrobrushing.

The methods were chosen to make a comparison between the gold deposits from cyanuric and sulphite electrolytes. Electrobrushing is a selective deposition technique that allows to locally depositing the desired metals without immersing the parts in the electrolyte. A particular advantage of this technique is that the parts to be coated do not need to be dismantled.

2. Materials and methods

The electrodeposition methods were used in the field of electrical engineering for special electric machines - DC torque motors with commutators. The brush electroplating process aims to improve brush electrical contact and also to prevent the commutator surface against corrosion. Special electric machines are electric motors with certain features in their operation and construction in relation to conventional electric motors [10-12].

In order to achieve standardized thicknesses of the gold deposits on the commutators surfaces and also to perform the brush electrodeposition utilizing the two types of electrolyte baths, there were used four commutators from scrap DC torque motors with the following serial numbers: the cyanuric electrolyte (samples 092 and 220) and the sulphite electrolyte (samples 244 and 260). After performing some tests, qualitative and quantitative analyses were performed. More details regarding the experimental electrodeposition of gold process are given in Table 2:

Table 2

Details on the experimental electrodeposition of gold process

Used method	***Brush electrodeposition***	
	Sulphite electrolyte	***Cyanuric electrolyte***
Cathode	Electrolytic copper commutator	Electrolytic copper commutator
Anode	graphite	graphite / platinum
Electrolyte	sodium gold (I) sulphite	sodium dicyanoaurate (I)
pH	7.5 – 8.5	6 – 6.5
Temperature, °C	25	25
Time, s	240	240
Layer thickness, μm	min 4	min 4

In order to physical characterize gold layers (thickness and appearance), various characterization methods were used (Table 3). The goal is to compare the uniformity, microstructure and porosity of the layers deposited from the two types of electrolytes.

Table 3

Characterization methods used for metallic layers obtained by electrodeposition

Characterization method	***Obtained results***
SEM (Scanning electron microscopy)	Morphology and topography of the deposited layer
EDS (X-ray spectroscopy with energy dispersion)	Quantitative analysis of deposition
EDS Mapping	Identification of the elements and their distribution in the deposited layer
Coordinate measuring machine (CMM)	The thickness of the deposited layer

3. Results and discussions

Prior to gold electrodeposition, a superficial layer of nickel was deposited on the commutator surface, knowing that it provides better adhesion to the copper substrate and helps to stop the diffusion of copper atoms in the gold layer; also due to its higher hardness in Mohs scale (4 MPa) compared to gold (2.5 MPa) and copper (3 MPa), nickel is used as a hardening agent.

Using the one-dimensional equivalent K_1 from the equation (6), the needed current intensity for the process can be calculated:

$$h = K_1 \cdot i \cdot \tau \qquad (6)$$

where: equivalent K_1 – [$\mu m \cdot A^{-1} \cdot h^{-1} \cdot dm^2$]; current density, i – [$A \cdot dm^{-2}$]; time, τ – [h]; layer thickness, h – [μm].

For the $Na_3Au(SO_3)_2$ sulphite electrolyte, used in gold electrodeposition process, the value of the one-dimensional equivalent K_1 is equal to 38 $\mu m \cdot A^{-1} \cdot h^{-1} \cdot dm^2$ and for $NaAu(CN)_2$ cyanide electrolyte the value of K_1 is also 38 $\mu m \cdot A^{-1} \cdot h^{-1} \cdot dm^2$. Therefore, the value of the needed current intensity will be the same for both solutions.

Determination of the substrate area refers to the total surface area of the commutator which is in direct contact with the anode. The commutator consists of 57 lamellas, each one of square shape with the dimensions of l = 5 mm, from which it results that the cathodic active surface for electrodeposition is equal to 0.14 dm^2.

3.1. Sample preparation and characterisation

In order to achieve the desired standard thickness of 4 μm for deposited layer, in 240 s (0.067 hours) time of exposure (about 1 μm/min) and to facilitate serial production, using equation (6), the optimum value of the required current intensity to use in this process was calculated for I = 220 mA ($i = 1.574\ A \cdot dm^{-2}$).

The operational parameters for gold electrodeposition process are shown in Table 4 and the obtained samples are illustrated in Figures 2 and 3.

Table 4

The operational parameters used in electrodeposition processes

Sample	***Deposition***			***I_{Ni}, [mA]***	***I_{Au}, [mA]***	***τ,[s]***
	Nickel electrolyte	***Cyanuric electrolyte***	***Sulphite electrolyte***			
092	✓	✓	x	345	300	240
220	✓	✓	x	345	200	
244	✓	x	✓	345	300	
260	✓	x	✓	345	200	

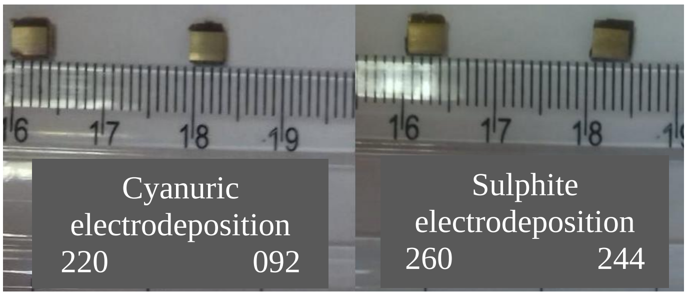

Fig. 2. Samples with gold layers electrodeposited from cyanuric (samples 220 and 092) and sulphite (samples 260 and 244) baths

Fig. 3. Encapsulated samples

After gold electrodeposition the samples were prepared for testing.

Two lamellas from each commutator of some scrap DC torque motors were extracted, from the motors with the following serial numbers: 092; 220; 244; 260. Each lamella was encapsulated in resin, then it was cut into a section view to identify the thickness of the gold deposit layers by means of scanning electron microscopy SEM. Also, for the non-encapsulated lamellas, the morphology and topography of the surface deposition were determined. The quantitative analysis for the gold deposits was carried out using the X-ray spectroscopy with energy dispersion to identify the presence of gold and of other species in the samples.

The comparison between the SEM images of the samples, on which the electrodeposition was performed from both cyanide and sulphite electrolytes, in the same conditions can be observed in the Figures 4 and 5.

The surface of the commutator must have a low roughness to ensure a perfect contact with the torque motor brushes that is why after the electrodeposition process the samples must be polished.

In Figures 4 and 5 are presented the samples 092 and 244, in both cases the electrodeposition was performed at a current intensity of 300 mA. It can be observed that the surface of the specimen 244 is homogenous at 500X magnifications (left), but at greater magnification (50,000X), quasi-spherical formations with diameters of 0.1–1 µm and interconnected porosity can be identified in the microstructure. For the specimen 092 the intergranular grain boundaries cannot be distinguished, this sample has a lower porosity than 244 one; grains of approximatively 80 nm were identified.

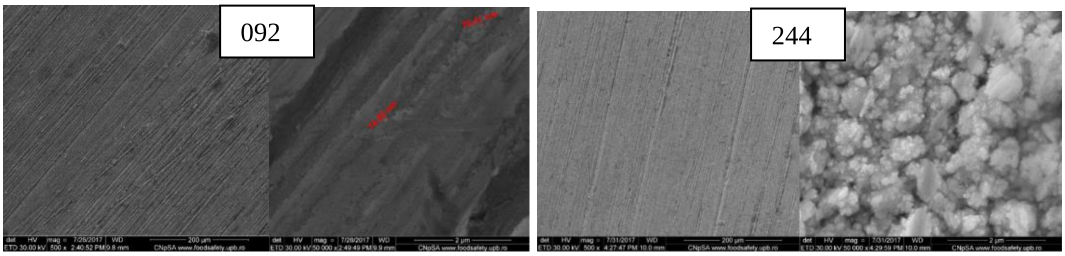

Fig. 4. SEM images for samples 092 and 244 (magnification 500X and 50,000X, respectively)

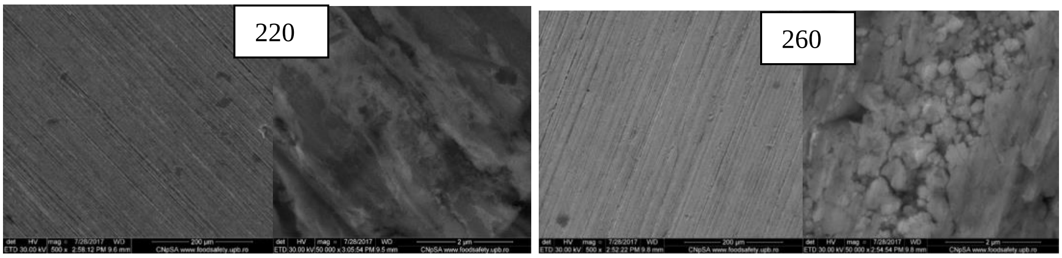

Fig. 5. SEM images for samples 220 and 260 (magnification 500X and 50,000X, respectively)

For the sample obtained from a non-cyanuric electrolyte, it can be observed that at a magnification of 500X this sample is more homogenous than the other sample. The gold layers for these samples (220 and 260) were obtained at a current intensity of 200 mA. At higher magnifications (50,000X), for the specimen 260, smooth areas can be observed in the grain microstructure.

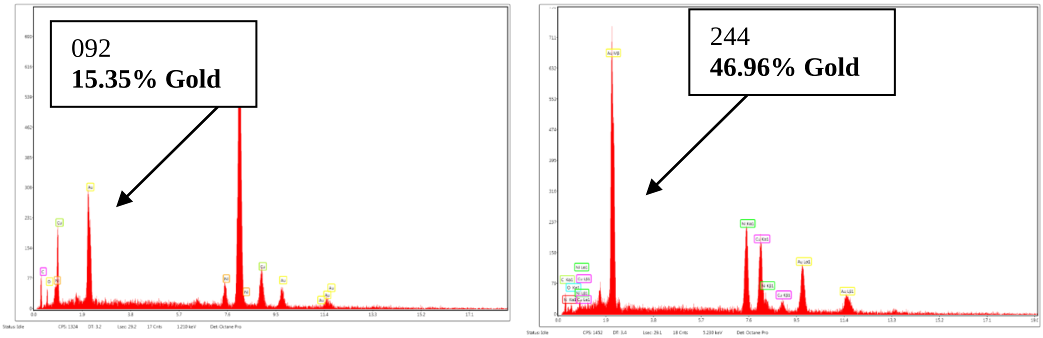

Fig. 6. X-ray spectroscopy spectra for samples 092 and 244

Using EDS–X-ray spectroscopy with energy dispersion analysis, emission lines for all the elements present in the samples were generated at different intensities according to the thickness of the deposits. Regarding the EDS analysis, the emission lines for the following specific elements were identified: copper (base layer), nickel (intermediate layer), gold (final layer), and also the presence of carbon and oxygen due to adsorption.

From EDS spectra (Figure 6), it can be observed that, in the case of cyanuric electrodeposition, the presence of copper at the surface of the samples prevails, the gold is present only in a percent of 9 to 16%. The results for the sulphite electrodeposition show that the presence of gold is higher - 45% and 70%, this demonstrated that the thickness of the deposit obtained using this method is higher.

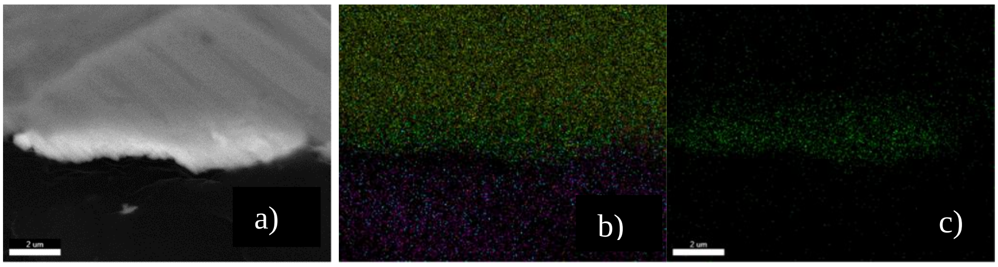

Fig. 7. EDS Mapping for sample 244 (nickel – orange, gold – light green, copper – green)

EDS Mapping is an automated qualitative analysis 2D, which shows the presence of elements and their distribution in the sample. The elements emit characteristic X- rays and can be identified through a specific colour.

In Fig. 7b are shown all the elements present in the sample, the electrodeposited layers (nickel – orange, gold – light green) and the copper substrate (green) can be identified. In Fig. 7c only the distribution of the metallic gold atoms can be observed.

Table 5

CMM measurements results

Sample	Electrolyte	Current intensity, [mA]	Layer thickness, [μm]
092	cyanuric	300	3
244	sulphite	300	7
220	cyanuric	200	1
260	sulphite	200	8

In order to determine the thickness of the deposited layers, the coordinate measuring machine (CMM) was used. Measurements were made directly on the commutator, before and after the electrochemical deposition. By calculating the differences between the initial diameter and the final diameter of the commutators, the following layer thickness values of the gold deposits presented in Table 5 were obtained.

In addition, the efficiency of the sulphite electrolytes in the brush electrodeposition as compared to the cyanuric electrolytes has been proven.

4. Conclusions

Due to its unique property, gold has been indispensable in various industries. Brush electrodeposition of gold is an effective method of selective deposition, but the procedure is performed directly by the chemist operator, so it is important to keep in mind the impact that compounds have on personnel health and also on the environment. Regarding the toxicity of cyanide compounds, more favourable alternatives are used, of which the sulphite compounds have been appreciated.

In this paper, gold electrodeposition on a nickel intermediate layer was performed using a cyanuric - sodium dicyanoaurate electrolytic bath as well as a sodium - gold sulphite electrolyte to perform a comparative analysis of the quality of deposits.

Based on the analysed layers, it has been found that by means of both electrolytes the layers have good characteristics, even though the main advantage of non-cyanide electrolytes is the low impact on the environment and one health of personnel. In addition to this major advantage, others can be included: in obtaining the same layer thickness the required working time is lower; the quality of the deposit was being proven to be superior.

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