

# Silver Electrodeposition from Low and High Concentrated Cyanide Electrolytes Containing Potassium Antimony Tartrate

Kubra Akben\*, Emine Bakan, Servet Timur  
Metallurgical & Materials Eng. Dept.  
Istanbul Technical University  
Istanbul-Turkey

**Abstract** - This study researches the effect of potassium antimony tartrate (PAT) on brightening power of silver electroplating solutions containing low or high concentration of free cyanide. In this study, low free cyanide concentration is below the value of 1 g/L and the results are compared with that of conventional alkaline high concentrated cyanide solutions. The effects of PAT and cyanide concentration on surface visual appearance, morphology and reflectance were reported. PAT added high concentrated cyanide electrolyte formed bright film whereas low concentrated one formed semibright, compact film. Morphological investigations showed that PAT acts as grain refining agent for silver electroplating.

**Keywords:** Silver, electrodeposition, cyanide, potassium antimony tartrate, additive

## I. INTRODUCTION

Pure silver coatings are of practical, technological and industrial importance due to their high electrical and thermal conductivity and high reflectivity properties. It is important to develop smooth and shiny surface for decorative applications, compact and uniform surface for electronic industry [1]. Electrodeposition of silver from cyanide baths is a well-established industrial process. In spite of cyanide toxicity and various environmental problems, the majority of silver electroplating baths in use currently are conspicuously similar to those used in the original process patented by Elkington brothers [2]. But the use of high concentrated alkaline free cyanide electrolytes damages to photoresists and polymers used in electronic industry. Owing to these reasons, alternative electrolytes were formulated using other complex forming compounds. However, some challenges such as synthesizing difficulties, high costs, and complex instability restricted their practical applications.

It is well known that the addition of small quantities of some organic or inorganic compounds to electrolyte modifies the metallic deposit. Appropriate amounts of additives are necessary for obtaining fine-grained, smooth and compact deposits. Potassium antimony tartrate (PAT) was used as an additive in many patents in which silver was electrodeposited from cyanide baths. In the all cases [3-6], high cyanide content or high speed plating process were studied.

The cyanide - pyrophosphate electrolyte was investigated as a mixture of these compounds with no free cyanide addition for electrodeposition of silver-cobalt alloy [7]. However, surface morphological changes of pure silver coating electrodeposited from low and high concentrated cyanide electrolyte with the addition of PAT have not been explicitly revealed in literature.

The purpose of this study is to represent the effect of PAT on silver electrodeposition from low and high concentrated cyanide solutions by the morphological and visual inspection methods. Hull cell tests were applied for determining the optimum current density and amount of PAT. A comparison between PAT added high and low concentrated cyanide electrolytes was revealed. The compositions of bright and semibright silver electroplating solutions and their operating conditions were offered for industrial applications.

## II. EXPERIMENTAL

The compositions of additive free electrolytes are presented in table 1. All chemicals were of analytical grade. Distilled water was used for the preparation of solutions. Hull cell studies were carried out using a 267 ml standard cell at a constant current of 1A for high concentrated cyanide electrolyte (HC electrolyte) and 2A for low concentrated cyanide electrolyte (LC electrolyte). Electrodeposition time was 5 minutes for HC electrolyte and 2 minutes for LC electrolyte. All experiments were studied at room temperature, 25°C. pH of HC electrolytes was 14 but at LC content pH was 7. Experiments were done in triplicate. The copper plates of standard Hull cell size were used as the cathode. The surfaces of copper plates were mechanically polished, degreased by ethyl alcohol and then immersed 1 minute in 5% H<sub>2</sub>SO<sub>4</sub> for activation. The copper plate was then washed in distilled water and dried with compressed air. The pure silver plate (99.9%) was used for HC electrolyte, while platinized titanium mesh electrode was used for LC electrolyte as the anode.

Galvanostatic electrodeposition of samples were studied in a different electroplating cell for characterization. Electrolyte temperature was kept constant at room temperature in a thermostatic bath, and electrolyte was circulated with a rate of 20 liters per hour by a diaphragm

booster pump (Aquafil Water Treatment Systems) during electrodeposition.

Morphology of the electrodeposits formed in the presence and absence of the additive was analyzed by field emission scanning electron microscope (SEM) (Jeol JSM 7000F). The reflection was determined using a reflectance spectrophotometer (Scinco S3100-SA13), and the reflected beam was collected by means of an integrating sphere. This type of reflectance spectrophotometer gives the dependences of total reflection and diffuse reflection as a function of the wavelength of visible light. The arithmetic mean roughness values (Ra) of the coatings and 3D surface roughness profiles were determined by an optical profilometer (Wyko NT1100).

### III. RESULTS AND DISCUSSION

#### A. Hull Cell Test Results

The Hull cell tests were performed at a constant current of 1 A for high cyanide concentrated (HC) electrolyte and 2 A for low concentrated (LC) one. These tests were conducted to determine the operating current density range to obtain bright silver deposits. A Hull cell is a standard cell in a special trapezoidal plate form from a nonconductive material. The cathode side is laid against the anode side with a slope of 38° angle. When the current is passed through the plating solution, the current density along the Hull cathode varies from high to low value which corresponds to shortest and longest distance of cathode to anode, respectively. In this way, the electrolyte composition can be tested by single experiment characterizing the electrolytes over a wide range of current density [8].

Fig. 1 shows the Hull cell patterns obtained in the absence and presence of PAT in different types of electrolytes (HC and LC electrolytes). 0.5, 1, 2 and 3 g/L PAT additions to the HC electrolyte were investigated. Electroplating with 2 g/L PAT added electrolyte formed brightest surface. As seen in fig. 1a bright deposit can be obtained between 1.2 and 3.2 A/dm<sup>2</sup> by this electrolyte. After this investigation, several current densities were studied galvanostatically in a different electroplating cell as previously described in experimental section. According to the test results optimum current density was 2.5 A/dm<sup>2</sup>, therefore characterization samples were electroplated at that current density.

However, mirror bright silver deposit cannot be produced with any concentration level of PAT addition to LC baths. As shown in Fig. 1b, semi-bright silver electrodeposit was achieved with 0.5 g/L PAT addition over a wide range of current density, 0.2-8 A/dm<sup>2</sup>. Other concentrations (0.2, 1, 2 g/L) limited the current density range. According to the experiments optimum current density was 2 A/dm<sup>2</sup> and the characterization samples were electroplated at that current density accordingly.

The original images of the Hull cathodes are demonstrated in Fig. 2. A model plane was used for a better visualization of the surface reflection property. Bright silver coating electrodeposited by 2 g/L PAT added HC electrolyte can be seen in Fig. 2a at current density range of 1.2-3.2 A/dm<sup>2</sup>. Semibright coating electrodeposited by 0.5 g/L PAT added

LC electrolyte can be seen in Fig. 2b at current density range of 0.2-8 A/dm<sup>2</sup>.

#### B. The Effect of Potassium Antimony Tartrate on Coating Morphology

The morphology of silver electrodeposits obtained with HC electrolyte at 2.5 A/dm<sup>2</sup> c.d. in the absence and presence of PAT were investigated by SEM as seen in Fig. 3. Typical rough and dendritic grown morphology of silver film electrodeposited from HC electrolyte with no additive were seen in Fig. 3a. PAT addition to this electrolyte formed nanocrystalline silver film as can be seen from Fig. 3b-d. In the presence of 1 g/L PAT, grain size was considerably smaller (Fig. 3b) and the size decreased with increasing additive concentration up to 2 g/l (Fig. 3c). Exceeding this concentration formed coarser grain size again (Fig. 3d).

The morphology of electrodeposits of LC electrolytes at 2 A/dm<sup>2</sup> is presented in Fig. 4. Nodular growth was observed without addition of PAT at Fig 4a. The SEM images of the sample coated by 0.5 g/L PAT added LC electrolyte, Fig. 4b, showed the grain refinement effect of PAT. Grain size decreased and nodular growth was considerably inhibited with the addition of PAT. Still, smooth surface wasn't achieved (Fig 4b). This cathode had semi-bright appearance, visually.

PAT acts as a brightener performing grain refinement but the leveling effect of cyanide/PAT system is not enough at low concentration of cyanide. Pyrophosphate that is used for increasing conductivity instead of free cyanide salt does not form the same levelling effect of high concentrated cyanide solution. These phenomena form a semibright appearance.

#### C. Effect of PAT on Deposit Roughness

Roughness measurement by optical profilometer can inform about roughness differences between mechanically polished copper substrate and silver electrodeposits. The arithmetic mean roughness value (Ra) of the silver electrodeposits were shown in Fig.5, and it was clearly demonstrated that the surface roughness of the electrodeposits obtained from the solutions containing additive (1-2-3-0.5 g/L PAT) decreased compared to the electrodeposit obtained from additive free blank solution. Ra value obtained for the coating produced from additive free HC bath was 1.18 μm, whereas Ra value for polished copper substrate was 0,50 μm. Further, surface roughness of coatings decreased with increasing additive concentration up to 2 g/L PAT at HC bath (0,18 μm) and thereafter roughness started to become rougher with increasing additive concentration. On the other hand, the roughness of the film coated by 0.5 g/L PAT added LC electrolyte is slightly lower than mechanically polished substrate but also higher than that of surfaces electrodeposited in PAT added HC electrolytes. The obtained minimum roughness value at LC bath was 0,45 μm with the addition of 0.5 g/L PAT. The notable point is that the arithmetic mean roughness value (Ra) of the silver electrodeposits obtained in the presence of PAT is smaller than mechanically polished substrate and electrodeposit generated by HC electrolyte and LC electrolyte without PAT addition. It means that PAT addition to the silver electrolyte formed the lower rough surfaces. This result indicates the

leveling power of antimony added HC and LC silver electrolyte.

*D. Effect of PAT on Deposit Reflectance*

Brightness, the reflecting power, has needed some physical magnitudes for a clear definition. Reflection of a metal surface is a combination of both diffuse and specular reflection constituents. Specular reflection is the mirror like reflection at the air-surface interface, and it occurs when whole of the light falling on a smooth surface will be reflected back at an angle equal to the angle of incidence. Rough surfaces reflect the light back in all directions irrespective of incidence angle and this type reflection is known as diffuse reflection. Therefore, reflection type straightly related to the surface roughness [9]. Since brightness of a surface is defined as the ratio between specular and diffuse reflection, brightness is directly related to the surface roughness.

The specular and diffuse reflection degrees of the ideal silver mirror [10] and silver electrodeposits in the visible wavelength range of the light are compared in Fig. 6. It can be seen from the figure that the type of light reflected from a silver mirror is mostly specular reflection where the degree of diffuse reflection is very small. The electrodeposit obtained in the presence of 2 g/L PAT from HC bath also had high degrees of specular reflection, which approaches close to the ideal reflectance of silver for the wavelength range above 550 nm. Also, it had very low diffuse reflection degree. Consequently, the sample electrodeposited from high cyanide bath with PAT addition had high reflection degree closed to silver mirror.

In the case of 0.5 g/L PAT addition to LC bath, specular reflection values moved away from the ideal reflectance of silver. Also, diffuse reflection values of this sample increased according to the low diffuse reflection degree of silver mirror. This sample had hazy appearance called as semibright in previous sections.

**TABLE 1. ELECTROLYTE COMPOSITIONS FOR ADDITIVE FREE SILVER PLATING BATH**

Component	LC Electrolyte Concentration (g/L)	HC Electrolyte Concentration (g/L)
KAg(CN) <sub>2</sub>	80	80
KCN	0.5	60
KOH	-	7.5
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	80	-

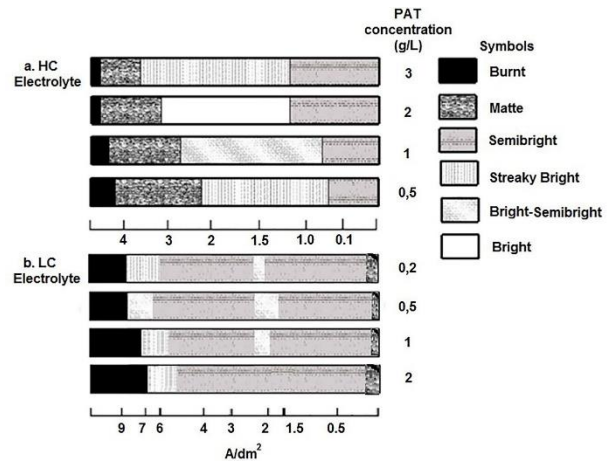


Fig. 1. Hull cell patterns obtained from a) HC, b) LC electrolyte containing various concentrations of PAT.

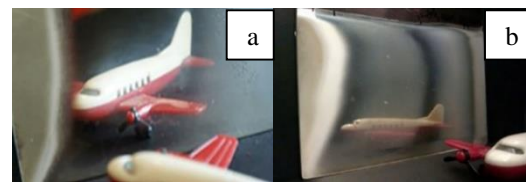


Fig. 2. Mirror-effect images of Hull cathodes electrodeposited from (a) 2 g/L PAT added HC, b) 0.5 g/L PAT added LC electrolytes.

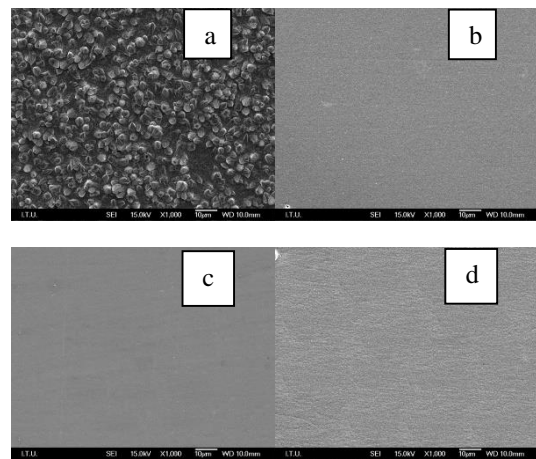


Fig. 3. Scanning electron micrographs of silver films electrodeposited from HC electrolytes with (a) no PAT, (b) 1 g/L PAT (c) 2 g/L PAT, (d) 3 g/L PAT, addition.

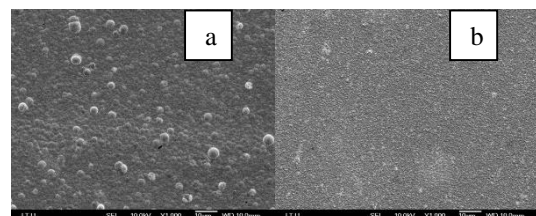


Fig. 4. Scanning electron micrographs of silver coatings electrodeposited from LC electrolytes with (a) no PAT, (b) 0.5 g/L PAT.



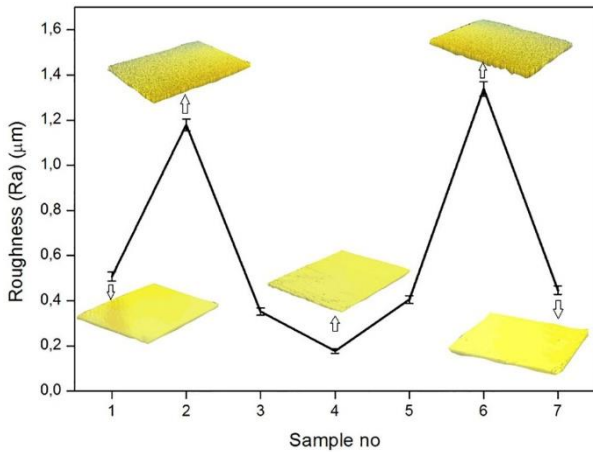


Fig. 5. Average roughness values for (1) mechanically polished copper substrate and silver electrodeposited by (2) HC blank, (3) 1 g/L PAT+HC, (4) 2 g/L PAT+HC, (5) 3 g/L PAT+HC, (6) LC blank, (7) 0.5 g/L PAT+HC electrolytes.

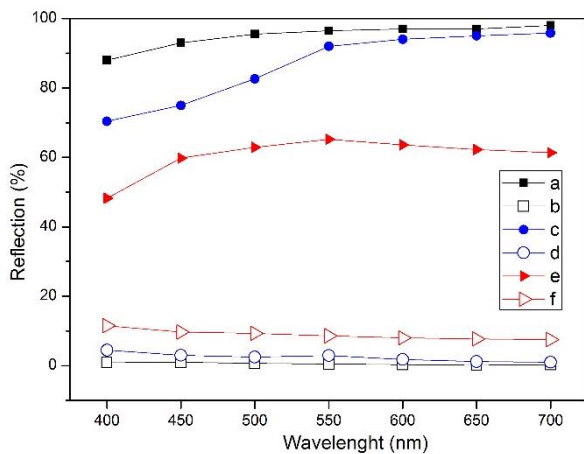


Fig. 6. Specular reflection values of a) ideal silver mirror, c) HC+2 g/L PAT, e) LC+0.5 g/L PAT and diffuse reflection values of b) ideal silver mirror, d) HC+2 g/L PAT, f) LC+0.5 g/L PAT.

#### IV. CONCLUSION

In this study, optimum PAT concentrations were investigated to determine electrolyte compositions for obtaining mirror bright silver coating from HC and semibright silver coating from LC electrolytes. The morphological effect of PAT was also investigated.

It was found that bright silver coating was electrodeposited from 2 g/L PAT added high concentrated silver electroplating bath over a current density range of 1.2–3.2 A/dm<sup>2</sup> at 25 °C. It was observed that the optimum current density in circulated electroplating system was 2.5 A/dm<sup>2</sup>. This sample was described as bright silver coating in visual check. Other characterization results confirmed the visual check. Comparison of morphology of electrodeposits demonstrated the inhibition of dendritic growth and formation of finer grains with the addition of PAT to HC electrolyte. Nanocrystalline, smoothest coating was produced with the addition of 2 g/L PAT. Furthermore, this sample had lowest roughened surface. Also, specular reflection degree of the sample was very close to specular reflectance of silver mirror and diffuse reflection degree of the sample was very low as the silver mirror.

Besides, it was revealed that semibright, compact coating was produced from PAT added low concentrated cyanide electrolyte in a wide current density range of 0.2–8 A/dm<sup>2</sup> at 25 °C. The nodular growth observed in LC bath electrodeposition was prevented considerably with the addition of PAT. But chemical leveling effects were not sufficient to prevent nodular growth completely in this electrolyte. The roughness value of the deposit was higher than that of mirror bright deposit and closed to the mechanically polished copper surface. The reflection values of this deposit was far from the ideal silver mirror. The specular reflection of the sample was lower than that of silver mirror and the diffuse reflection was higher than that of silver mirror. As expected from reflection analysis this sample had semibright appearance, visually.

In view of the above, it is readily obvious that PAT acts as a strong grain refining agent for silver electrodeposition. However, low cyanide concentration smaller than 1 g/L has not sufficient leveling effect to prevent nodular growth completely. The findings of the present study well demonstrated the basic database for producing industrially acceptable bright silver coatings from HC electrolyte and semibright, compact silver coatings from low cyanide electrolytes. Furthermore, it should be noted that, for a better throwing power it must be further researched to use other agents in addition to PAT.

#### ACKNOWLEDGMENT

K. Akben is grateful for PhD scholarship funding from TUBITAK (The Scientific and Technological Research Council of Turkey).

#### REFERENCES

- [1] M. Schlesinger, *Electroless and Electrodeposition of Silver*. Mod. Electroplat. Fifth Ed. 2011.
- [2] Blair, A., *Silver Plating*. *Met. Finish.* 93, 290–297 (1995).
- [3] L. Greenspan, "Mirror Bright Silver Electroplating" U.S. Patent 2 735 808, Feb. 21, 1956.
- [4] D. G. Foulke, "Bright Silver Plating Bath and Process" U.S. Patent 3 219 558, Nov. 23, 1965.
- [5] B. D. Ostrow, "Bath For Electroplating Silver" U.S. Patent 2 777 810, Jan. 15, 1957.
- [6] Y. Rymwid, "High Speed Bright Silver Electroplating Bath and Process" U.S. Patent 4 428 804, Jan. 31, 1984.
- [7] S. L. Nineva, T. V. Dobrovolska, and I. N. Krastev, "Electrodeposition of silver-cobalt coatings. The cyanidepyrophosphate electrolyte," vol. 43, no. 1, pp. 96–104, 2011.
- [8] J.W. Dini, *Electrodeposition: The Materials Science of Coatings and Substrates*, Noyes Publications, New York, USA, 1993.
- [9] K. E. Peiponen, R. Myllylä, A. V. Priezhev, *Optical measurement techniques: innovations for industry and the life sciences*, Springer, 2009, ISBN: 9783540719267.
- [10] A. D. Rakic, A. B. Djuricic, J. M. Elazar, and M. L. Majewski, "Optical properties of metallic films for vertical-cavity optoelectronic devices.," *Appl. Opt.*, vol. 37, no. 22, pp. 5271–5283, 1998.