

## ELECTROPOLISHING OF ELECTROPLATED SILVER

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Electropolishing of silver from cyanide based electrolytes is investigated and reported in this paper. Effect of varying bath ingredients, addition of certain additives, influence of applied voltage resulting current-time behaviour, dissolution rate of silver, surface appearance and brightness after treatment etc. are studied in detail to arrive at the optimum composition and operating parameters.

Keywords : Electropolishing, silver, cyanide based electrolytes

### INTRODUCTION

Electropolishing is an anodic treatment method of metals by which the submicroscopic, microscopic and macroscopic irregularities on the surface are removed thereby imparting a bright and smooth surface finish. Electropolishing can produce surfaces comparable to those resulting from buffing at much lower cost [1,2].

Silver is a precious metal which is electroplated for a wide variety of applications, both decorative and functional. The decorative applications of silver are to produce articles of aesthetic appeal like jewellery, medals, cups etc and to coat on food handling hollowware, flatware, forks, spoons etc. The functional applications of silver are to provide surfaces with good bearing properties, high electrical conductivity and unreactive to many common reagents. When silver is plated for a decorative application it is necessary to get a bright lustrous finish. This may be accomplished either by introducing brighteners in the plating bath or by polishing the surface after electroplating. For polishing the plated surface, use of electropolishing is preferred to mechanical polishing as the latter results in higher loss of costly metal as compared to the controlled removal in the former case.

Electropolishing of silver from thiocyanate, thiosulphate, ammoniacal nitrate and cyanide solutions are mentioned in literature [2-5]. Results of investigation on cyanide based electrolytes are discussed in this paper.

### EXPERIMENTAL

Brass panels of 2.5 x 7.5 x 0.03 cm were mechanically polished and electroplated with silver (10 mm) using a strike and plating schedule as given below:

### Strike

Silver cyanide: 3 g/l; Potassium cyanide: 80 g/l; c.d: 1 A/dm<sup>2</sup>; Anode: Stainless steel; Duration: 30 sec

### Plating

Silver cyanide: 35 g/l; Potassium cyanide: 40 g/l; Potassium carbonate: 60 g/l; c.d: 0.5 A/dm<sup>2</sup>; Anode: Silver; Duration: 30 mts.

Anodic treatment was carried out by keeping the plated specimen as anode in a cell containing the electrolyte under investigation and a ss cathode. The treated surface was observed for brightness visually. Brightness of selected samples was measured in a reflectivity meter. By weighing the panels before and after treatment the thickness of silver dissolved was calculated.

The anodic treatment was carried out under varying conditions of applied voltage and concentration of solution constituents and the conditions favouring bright polishing determined. The current passing through the circuit at varying applied voltages was observed and the stable values of current noted. Under the conditions where wide current fluctuations were observed, current-time behaviour was recorded using a x-t recorder.

### RESULTS AND DISCUSSION

#### Effect of varying KCN concentration

It is seen that potassium cyanide is an essential constituent in producing a bright electropolished silver surface. When anode treatment is done in the absence of KCN or at 25 gpl, surface appearance is either unaffected or brownish film is formed (Table I). This may be due to the formation of silver cyanide or oxide on the surface which will not dissolve in

**TABLE I: Effect of varying KCN concentration**

Conc of KCN g/l	Applied voltage V	Curr-ent mA	Surface appearance	Dissolu-tion rate $\mu\text{m}/\text{mt}$
0	1.0	10	Brownish yellow film	0.05
	2.0	20	Brown film	0.09
	2.5	25	Brown & black film	0.19
	3.0	30	Brown & black film	0.31
	4.0	40	Brown & black film	0.45
25	1.0	50	White	0.56
	2.0	75	White	0.86
	2.5	80	White	0.90
	3.0	80	Brownish white	1.00
	4.0	90	Brown & black film	1.10
50	1.0	65	White	0.74
	2.0	120	Semibright	1.50
	2.5	130	Bright	1.60
	3.0	130	Bright	1.60
	4.0	144	Brown film	1.66
75	1.0	80	White	0.94
	2.0	140	White	2.00
	2.5	160	Bright	2.12
	3.0	170	Bright	2.20
	4.0	190	Brown film	2.25

the absence of sufficient free cyanide. At concentrations of 50 g/l and above, bright surface is obtained at applied voltage of 2.5-3.0 V. From this it is clear that enough free cyanide is essential in bringing about dissolution of surface films thereby bringing about polishing. The current passing through the circuit,  $i_s$  (Fig. 1) and the dissolution rate of silver (Fig. 2) are found to increase with increase in KCN concentration. This may be attributed to the increased conductivity of the solution and the ability of KCN. Increase in applied cell voltage also produces increase in current and dissolution rate.

#### Effect of varying potassium carbonate concentration

Though electropolishing occurs in the absence and at 25 g/l  $\text{K}_2\text{CO}_3$ , only semi bright surfaces are obtained (Table II). At 50 g/l concentration and above bright polished surfaces are obtained at applied voltages of 2.5-3.0 V. This shows that  $\text{K}_2\text{CO}_3$  controls the dissolution of the film formed on silver surface and improves the surface smoothing effect. However,  $\text{K}_2\text{CO}_3$  does not contribute substantially towards the dissolution rate (Fig. 3) or the current passing through the circuit (Fig. 4).

#### Effect of varying silver concentration

Electropolishing phenomenon to obtain bright surface appearance occurs even in the absence of silver (Table III), but the voltage required is slightly higher (3 V). Bright surfaces are obtained at 3.0-3.5 V at 12.5 g/l  $\text{AgNO}_3$  concentration. At 25 and 50 g/l electropolishing occurs at 2.5- 3.0 V. Reflectivity measurements with the bright surface obtained show values of 85- 90%. Current passing through the circuit and dissolution rate (Figs. 5-6) are found to be

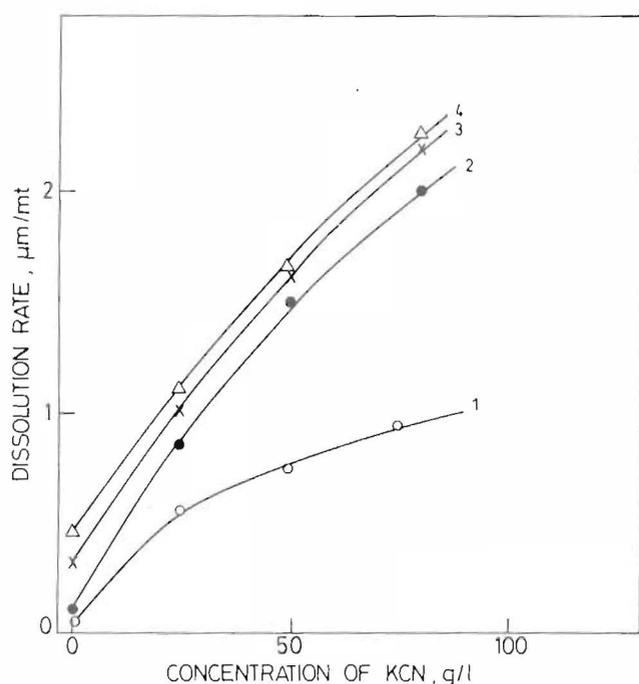


Fig. 1: Influence of KCN concentration on cell current at different applied voltages (1) 1V (2) 2V (3) 3V (4) 4V

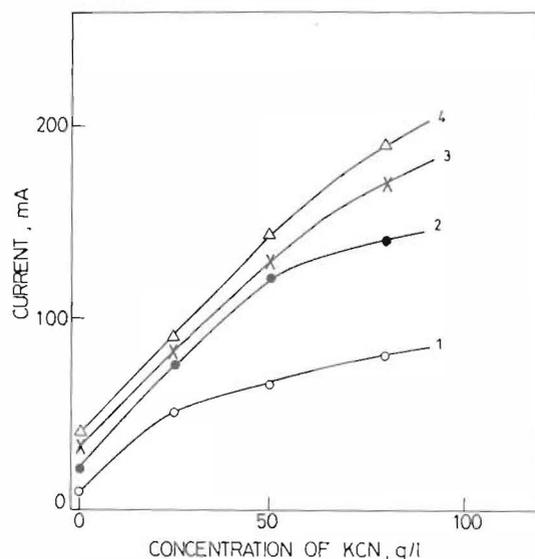


Fig. 2: Influence of KCN concentration on dissolution rate at different applied voltages (1) 1V (2) 2V (3) 3V (4) 4V

TABLE II: Effect of varying  $K_2CO_3$  concentration

Concn of $K_2CO_3$ g/l	Applied voltage V	Current mA	Surface appearance	Dissolution rate $\mu\text{m}/\text{mt}$
0	1.0	50	White	0.40
	2.0	100	White	1.00
	2.5	110	White	1.30
	3.0	120	Semibright	1.40
	4.0	130	Dull	1.46
25	1.0	60	White	0.60
	2.0	110	White	1.40
	2.5	120	Bright	1.45
	3.0	125	Semibright	1.50
50	4.0	140	Brown film	1.56
	1.0	65	White	0.74
	2.0	120	Semibright	1.50
	2.5	130	Bright	1.60
	3.0	130	Bright	1.60
75	4.0	144	Brown film	1.66
	1.0	70	White	0.80
	2.0	130	White	1.54
	2.5	135	Bright	1.66
	3.0	140	Bright	1.66
4.0	150	Brown film	1.68	

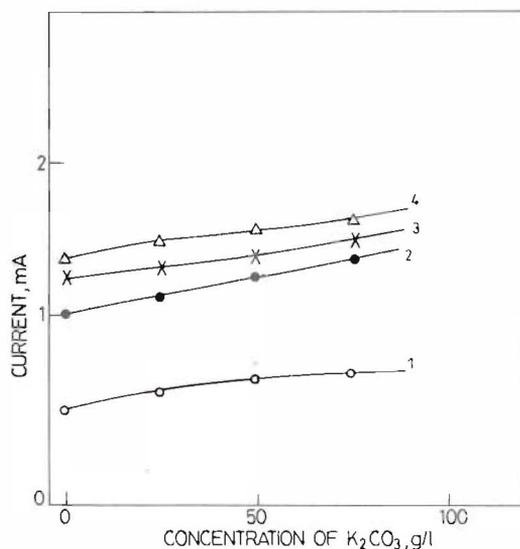


Fig. 4: Influence of  $K_2CO_3$  concentration on cell current at different applied voltages (1) 1V (2) 2V (3) 3V (4) 4V

**Influence of applied voltage on electropolishing**

Table IV shows the relationship between applied voltage and surface appearance. At very low voltages, surface appearance is almost unaffected. Brightening effect is seen above 2.0 V

TABLE III: Effect of varying silver concentration

Concn of $AgNO_3$ g/l	Applied voltage V	Current mA	Surface appearance	Dissolution rate $\mu\text{m}/\text{mt}$
0	1.0	75	White	0.80
	2.0	130	White	1.60
	2.5	145	White	1.70
	3.0	160	Bright	1.84
	4.0	180	Dull white	2.00
12.5	1.0	70	White	0.80
	2.0	125	White	1.50
	2.5	130	White	1.60
	3.0	140	Bright	1.70
25	4.0	160	Dull white	1.80
	1.0	65	White	0.74
	2.0	120	Semibright	1.50
	2.5	130	Bright	1.60
50	3.0	130	Bright	1.60
	4.0	144	Brown film	1.66
	1.0	65	White	0.70
	2.0	120	White	1.44
	2.5	125	Bright	1.50
3.0	130	Bright	1.60	
4.0	140	Brown film	1.60	

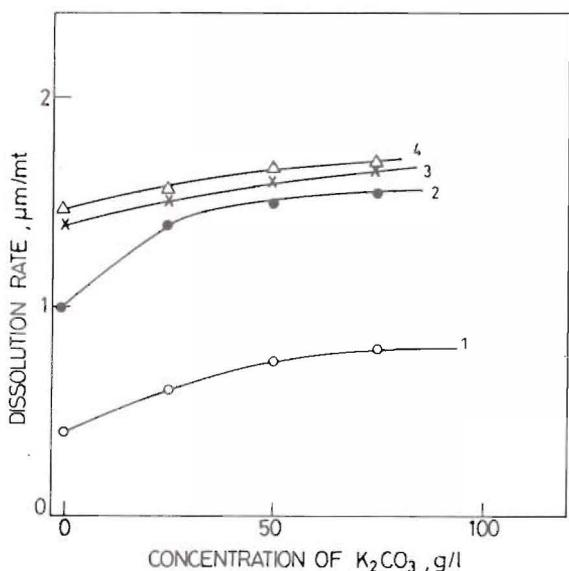


Fig. 3: Influence of  $K_2CO_3$  concentration on dissolution rate at different applied voltages (1) 1V (2) 2V (3) 3V (4) 4V

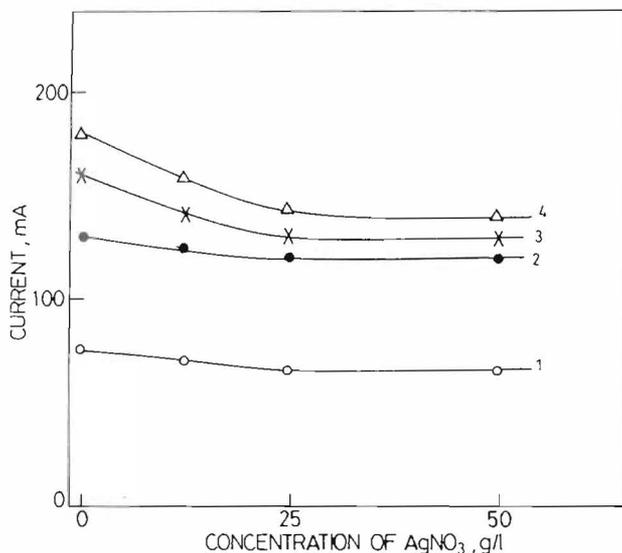


Fig. 5: Influence of AgNO<sub>3</sub> concentration on cell current at different applied voltages (1) 1V (2) 2V (3) 3V (4) 4V

upto 3.25 V. At still higher cell voltages, brown passive films are observed on the surface.

When current passing through the circuit was noted at a particular value of applied cell voltage, it is observed that the current reaches a high value ( $i_m$ ) and quickly reduces and attains a stable value ( $i_s$ ). The fall in value from  $i_m$  to  $i_s$  is generally higher at higher voltages. But at the voltages where electropolishing occurs, there is a continuous fluctuation in current value, the average value is taken as  $i_s$ .

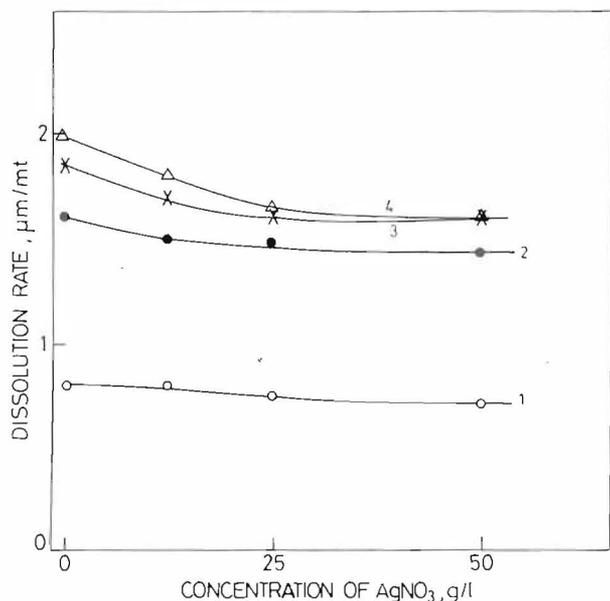


Fig. 6: Influence of AgNO<sub>3</sub> concentration on dissolution rate at different applied voltages (1) 1V (2) 2V (3) 3V (4) 4V

TABLE IV: Influence of applied voltage. Solution composition: AgNO<sub>3</sub> 25, KCN 50, K<sub>2</sub>CO<sub>3</sub> 50 g/l

Applied voltage V	Current mA	Surface appearance	Dissolution rate μm/mt
0.25	20	White	0.30
0.50	35	White	0.47
1.00	65	White	0.74
1.50	95	White	1.10
2.00	120	Semibright	1.50
2.25	130	Semibright	1.59
2.50	130	Bright	1.60
2.75	130	Bright	1.60
3.00	130	Bright	1.60
3.25	130	Bright	1.60
3.50	138	Dull white	1.60
3.75	140	Brown film	1.62
4.00	144	Brown film	1.66
4.50	156	Brown film	1.70
5.00	166	Black film	1.76

Current-voltage and dissolution rate-voltage graphs are shown in Fig. 7. It is seen that the current flowing through the circuit (Curve 1) and the dissolution rate remain almost constant in the electropolishing region. This type of a current-voltage curve is typical of electropolishing systems [6,7] wherein the first rising portion corresponds to metal dissolution, the horizontal portion to polishing phenomenon and the next rising portion to pitting with gas evolution.

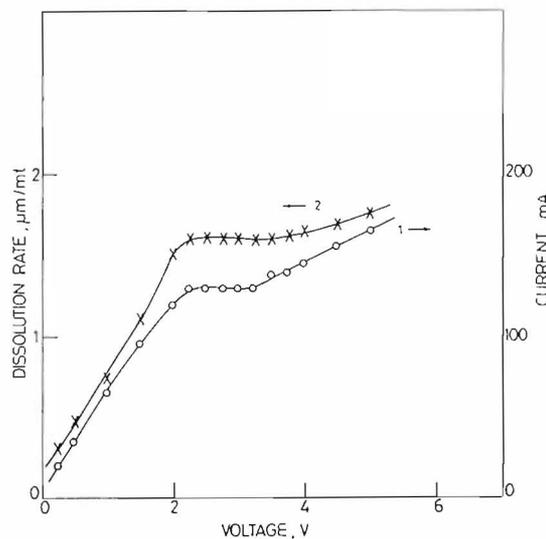


Fig. 7: Influence of applied voltage on cell current (curve 1) and dissolution rate (curve 2) Solution concentration: AgNO<sub>3</sub> 25, KCN 50, K<sub>2</sub>CO<sub>3</sub> 50 g/l

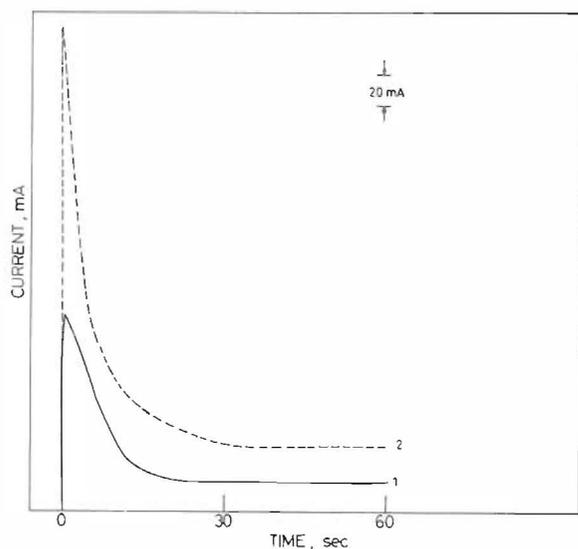


Fig. 8: Current vs time graph during anodic treatment at 2V (curve 1) and 4V (curve 2)

#### Influence of applied voltage on current-time curves

These experiments were aimed at observing the variation of current with time during the anodic treatment so as to get a further insight into the polishing phenomenon. The resulting graphs are shown in Figs. 8-9. When the anodic treatment was done at 2.0 or 4.0 V (Fig. 8) the resultant current decreases from a maximum value and reaches a stable value. But when the voltage was 2.5 or 3.0 V, the resulting i-t graph has the form shown in Fig. 9. This type of current fluctuation is indicative of a cyclic phenomenon [8] involving the formation of a passive film and its dissolution. From this i-t behaviour we can conclude that the polishing action occurs due to a controlled passivation- dissolution mechanism. The passive film formed being thicker in recessed areas leads to preferential dissolution of projecting areas whereby the surface irregularities are removed.

#### CONCLUSION

\* A solution suitable for electropolishing of electroplated silver has the following composition and operating parameters.

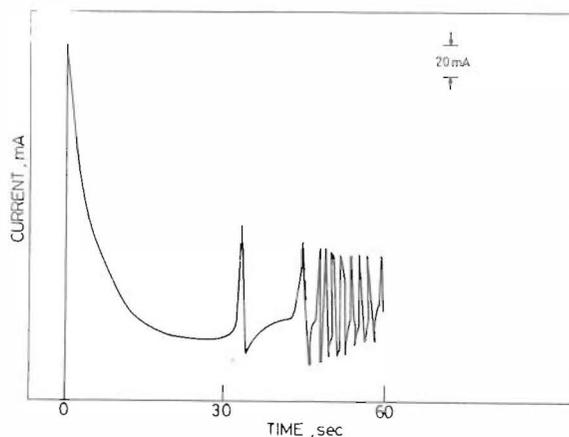


Fig. 9: Current vs time graph during electropolishing at 2.5 V

- \* Silver nitrate: 25 g/l; Potassium cyanide: 50 g/l; Potassium carbonate: 50 g/l; Applied voltage: 2.5-3.0 V; Cathode: ss
- \* The mechanism of electropolishing through the cyclic phenomena of passivation-dissolution-passivation is verified based on the current-time behaviour during electropolishing experiments.

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