Cathodic Adsorption Mechanisms of Typical Leveling and Brightening Agents: A Re-visit

O.A. Ashiru, SABIC Technology Center, Jubail, Saudi Arabia

The cathodic potential and differential capacitance changes associated with leveling and brightening processes were evaluated and compared. The mechanistic factors that are associated with adsorption and desorption processes of leveling and brightening agents on the cathode were isolated and rationalized. Based on the results of the electrochemical test, it was proposed that leveling agents were weakly adsorbed on the cathode surface and will therefore likely retard discharge processes. Brightening agents were strongly adsorbed on the cathode surface, which explains the latter's interaction with the crystallization process and codeposition with the plated metal.

For more information, contact:

Dr. Oluwatoyin A. Ashiru Saudi Basic Industries Corporation (SABIC) SABIC Technology Center P.O. Box 10040 Jubail 31961 Saudi Arabia

Tel: + 966 3 346 877I Fax: + 966 3 347 2064 E-Mail: ashiruoa@sabic.com

Introduction

With the discovery by Schloetter¹, in 1933, that the addition of aromatic sulfonates to a nickel sulfate bath could produce bright deposits. There began a systematic program on the part of many investigators to develop other organic addition agents to accomplish this result. Accompanying this development was an attempt to explain how these organic addition agents modified the characteristics of the deposit to produce level and bright mirror-like surfaces²⁻⁴. These efforts played major role in the industrialization of electroplating processes. Numerous surface-active additives were formulated to control the properties of the finished deposit produced by industrial electroplating²⁻⁴. Although these organic additives are of great practical importance, few fundamental studies have been undertaken to determine the mechanism of their leveling or brightening action. This paper describes a study that was conducted on the adsorption of selected organic additives at silver electrode to establish the role of organic additives used in electroplating. Findings on the kinetics of metal deposition mechanisms and the morphology of the deposits obtained with organic additives have been discussed in earlier publications²⁻⁹. It is essential to obtain information on the adsorption of organic agents at solid electrode surfaces in order to have an understanding of their smoothing and leveling effects. In the present study, adsorption characteristics of the additives on solid electrode surfaces were determined using electrochemical techniques, these data were then used to establish the probable influence of adsorption process on leveling and brightening characteristics of the additives.

In the present study, both cathodic polarization and adsorption studies were carried out. Differential capacity measurement of the solid-solution interface was used to obtain data on the adsorption of organic additives in a supporting electrolyte with no metal deposition process. The adsorption behavior of the organic additives can be accurately determined by electrochemical methods. The significance of these results toward the understanding of the brightening and leveling action of organic additives in electroplating solutions will be discussed.

The main objective of the study is to elucidate the mechanism of adsorption of leveling and brightening agents. The cathodic polarization tests were conducted in a cyanide silver plating bath. In addition, the experimental program isolates and measures the adsorption behavior of the bath-additives on the silver cathode rotating disk without the interference and complication from the conventional plating baths. For this reason, a non-plating and indifferent electrolyte, Na₂SO₄ was used for the adsorption study.

Experimental Work

Cathodic Polarization

The cathodic polarization experiments were conducted on a silver rotating disk electrode (RDE) rotated at a constant speed of 1500 RPM, the disk area is 0.60 cm², and polarized by a potentiostat as explained elsewhere^{10,11}. The disk electrode was made from a 99.9% purity silver electrodes cleaned by using a flaming and quenching technique. The potentiostat was operated in the galvanostatic mode at a fixed plating current - 5 mA/cm². The reference and counter electrodes are a piece of silver wire (3 cm long) and silver panel (6 cm² area) respectively. The differences between the cathodic potentials of the silver RDE in the conventional silver cyanide plating solutions were determined in the presence and absence of a variety of addition agents. Details of the silver plating baths and the operating conditions can be found in earlier studies^{10,12}, the addition agents that were tested are listed and classified in Table 1. The grouping of the addition agents was made according to the numerically largest change in cathodic potential during silver electrodeposition, at 5 mA/cm², when the concentration of the addition agent was raised from 0 to 0.001M, from 0.001M to 0.002M, and from 0.002M to 0.003M.

Adsorption Studies

The differential capacitance versus voltage measurement plots were used to study the kinetics of adsorption of some bath-additives (mainly leveling agents and brighteners) on the silver RDE cathode, rotated at 1500 RPM, in an indifferent 0.5M Na₂SO₄ purified electrolyte. Argon was used to degas the solution. The saturated calomel reference electrode was used while the counter electrode is a piece of platinum plate. The experimental system consists of a potentiostat interfaced with the Solartron 1250 Frequency Response Analyzer (FRA) which is essentially a programmable generator set and fixed at 1 kHz frequency and 5 mV perturbing sinusoidal signal¹² for all the experimental studies. The Faradaic impedance data generated from the test systems were analysed to obtain the corresponding values of the differential capacitance, ((C/(E),over a potential range sweep from 0 to 1600 mV vs. SCE. All experiments were carried out at $25\pm1^{\circ}$ C. The measurements are performed in pure Na₂SO₄ supporting electrolyte, and for a series of about 40 solutions, with appropriate variable concentrations of the additives.

Results and Discussion

Cathodic Polarization

Table 1 presents the grouping of the addition agents according to their effect on silver deposits and the cathodic potential changes ((E) during silver electrodeposition, at 5 mA/ cm^2 . The values in the table are the numerically largest values of (E when the concentration of the addition agent was raised in steps as outlined above; from the data, the following facts emerged with clarity:

(a) All authentic leveling agents, Group 1, increased the cathodic polarization to an extent which is relatively much smaller than the brightening agents (Groups 5 and 6), i.e. the cathode potential rose 10-22 mV in the presence of leveling agents, while it was raised 50-110 mV by the brighteners.

(b) An increase in the cathodic potential in the ranges indicated above did not necessarily guarantee a brightened or leveled silver deposit. Compounds like coumarin and monopropargylamine raised the cathodic potential to the same value as brighteners, but were ineffective in developing a bright silver deposit.

(c) Further experimental work on Group 6 compounds at dilution lower than 10^{-5} M, showed that cathodic potential increases between 30 and 40 mV. These were much less than reported for the same group of compounds at higher concentrations (~ 10^{-3} M) in Table 1. At concentrations around 10^{-5} M, the Group 6 compounds were capable of exhibiting leveling properties on grooves less than 3 (m.

(d) Hydroxyl-compounds such as ethanediol, and 1-2 propanediol (Group 7) increased the cathodic potential by 15 and 11 mV respectively; and yet they have no leveling effects on the cathode. They however have brightening effects on the anode.

(e) Polyethylene glycol and lead chloride have no effect on the cathodic polarization.

The extent of potential increases relates directly to the electrochemical adsorption of the respective adsorption agents on the cathode surface. The fact that leveling agents increase cathodic polarization to a lesser extent compared with the brighteners indicates that leveling agents are weakly adsorbed while brighteners are strongly adsorbed. The brighteners are mostly sulfur containing compounds and are thus capable of strong, specific electrochernical adsorption (chemisorption) because of the affinity of silver for sulfur. The compounds cause a large increase in cathodic polarization therefore, they decrease substantially the current density obtained at a given electrode potential. This explains why a much higher current density is required to attain brightening compared with leveling. The brightening action of hexamine is comparable to the sulfur compounds. The fact that hexamine:



is non-sulfur containing is a complicating factor in its discussion. However, a correlation can be attained by the concept of "available pairs of electrons". This can be explained as follows: nitrogen's available pair of electrons is capable of being shared with other atoms through association or chemical reaction (chemisorption) i.e. to form a coordinated bond. The significance to be drawn from this factor is that the attachment of this organic compound to the silver surface during plating is dependent, in part, on the presence of pairs of electrons available for interaction with the surface atoms of the cathode.

Table 1

Change in cathodic potential accompanying the addition of compounds into the standard cyanide silver plating bath; at 5 A/cm² and 1500 RPM.

Classification of addition agents according to their effects	Addition Agent	Potential Change (mV)
Group 1 (leveling agents)	2-Butyne-1, 4-diol	11
	Hexyl alcohol	20
	Thionine	22
	Ethylenediamine	10
	Pyridine	15
	Hexamine	20
Group 2 (leveling/brightening agents)	Propargyl alcohol	80
	2,5-Dimethyl – 2,5-Hexanediol	40
Group 3 (inconsistent leveling)	Mono-propargylamine	50
	Coumarin	90
Group 4 (leveled patches)	Cetyl-trimethyl ammonium bromide	8
	Cetyl pyridinium chloride monohydrate	4
	Thallium sulfate	2
	Lead chloride	0
Group 5 (brightening agents)	Diethyl-dithio-carbamate sodium salt	110
	Thiosemicarbazide	95
Group 6 (brightening agents with limited leveling power)	Diethyl ammonium diethyl thiocarbamate	100
	Thioacetamide	98
	Thiourea	60
	4:4 Tetramethyl diaminothio- benzophenone	70
	Sodium dithionite	50
	Sodium thiosulfate	70
Group 7	Ethanediol	15
(anode smoothing and	1-2 Propanediol	11
brightening)	Polyethylene glycol	0

The Group 7 compounds i.e. ethanediol and 1,2propanediol were observed in Table 1 to have effects on cathodic polarization which are comparable to that of Group 1 (levelers) and yet not capable of inducing leveling. It is likely, therefore, that these compounds may affect the electrochemistry of charge transfer without being adsorbed on the growth surface. Alternatively, they could be equally well adsorbed in the hollows as on the peaks, because of their greater diffusivity than active leveling agents; or they may be adsorbed like hexyl alcohol but unable to inhibit cathodic reaction.

Compounds like propargyl alcohol which are capable of leveling and brightening simultaneously are not easy to explain. But they have the unique features of exhibiting cathodic polarization increase which is intermediate between leveling and brightening. They probably are strongly adsorbed brighteners but with preferential coverage on the peaks.

Adsorption and Desorption Process

Typical differential capacitance - voltage curves illustrating the effect of leveling agents on the cathodic double layer capacitance in $0.5M \operatorname{Na}_2 \operatorname{SO}_4$ solution containing different leveling agents: 2-butyne-1, 4-diol, hexyl alcohol, and ethylenediamine, are shown in Figs. 1, 2, and 3 respectively. The capacitance-voltage curves for $0.5M \operatorname{Na}_2 \operatorname{SO}_4$ solution are also shown in the Figures.

The nature and extent of adsorption is of considerable importance in view of the fact that during electrodeposition of metals there is a continuous renewal of the surface of the electrode. The double layer capacitance-voltage method depends on the fact that organic molecules adsorbed between the metal electrode and the ions forming the double layer, bringing about a reduction in capacitance of the electric double layer. This is because the intermediate layer of the organic material has a lower dielectric constant than water and furthermore it increases the distance between the surfaces forming the double layer¹³. Consequently, these molecules will bring about a reduction in the electrode capacitance, since the electrode capacitance, C = (A/d (where (= dielectric constant, A = area, and d = distance between the two chargedlayers).

Upon adsorption of the organic molecules, a decrease in the capacity. as against that in the pure supporting solution, is observed. With a further increase in the cathodic potential the organic substance is desorbed, which results in the appearance of characteristic peaks on the capacitance curves. Thus, on the capacitance-potential curves, there is a region of low capacity values limited on both sides by the adsorptiondesorption peaks, corresponding to sharp changes in the surface charge within a narrow potential range. In solutions containing hexyl alcohol (Fig. 2), instead of the two adsorption-desorption peaks, three capacity peaks were observed. The two outer peaks are considered to be due to the adsorption and complete desorption of the alcohol molecules from the electrode surface. The inner peak may be explained in terms of the adsorption of a second layer of molecules which may have formed a micellar film. On blowing an inert gas through the solution which slightly reduces the alcohol concentration, the differential capacity curves assume the usual form with only two peaks.

The capacitance-voltage curves of the brightening agents are quite different and far more complicated. There were no sharp adsorption or desorption peaks and the curves are not reproducible. This is probably because the brighteners are mostly sulfur containing compounds and are thus capable of strong chemisorption. This method is not suitable for measuring such strong bonding between the electrode and the additive.

The cathodic potential range over which silver is electroplated corresponds to the flat minimal in the adsorption curves (Figs. 1, 2, and 3). Therefore, the adsorption of leveling agents are maximized over this range and the deposition process is not complicated by additive adsorption-desorption transitions due to the cathodic potentials. When additive desorption occurs during deposition it involves interaction between adsorbents and other electrolyte components. Thus, the ease and the nature of adsorption must play a large role in determining the activity of the leveling agents since weak adsorption are usually potential dependent.

The non-Faradaic adsorption of foreign substances (other than the ions to be deposited and the molecules of the solvent) affects electrode kinetics considerably. In practice, very small quantities of such species may exert significant changes on chemical, physical, and morphological properties of the electrodeposit, and may even change the reaction mechanism¹⁴⁻¹⁶.

The adsorbed foreign substances cover varying fractions of the cathode surface area, thereby reducing the surface area available for the electrode process proper. In the case of full coverage of the electrode by the foreign substances, they would have to be displaced for electrodeposition to take place on the substrate surface. This 'desorption' process increases the energy requirement for the cathodic process¹⁷. Thus, in general, the adsorption of foreign substances exerts a retarding influence. Therefore, they are 'inhibitors'. With excessive adsorption of foreign compounds, passivity of the electrode surface may result. The transition from inhibition by adsorption to passivity is continuous in nature¹⁸. Large molecules, like organic compounds have been shown to exhibit inhibiting effects when adsorbed on the cathode surface.



Figure 1 - Differential capacitance curve of $0.5M Na_2SO_4$ containing $10^{-3}M$ 2-Butyne-1,4-diol measured at 1 KHz. The curve for additive-free Na_2SO_4 is represented by the dotted line.



Figure 2 - Differential capacitance curve of $0.5M Na_2SO_4$ containing $10^{-3}M$ Hexyl Alcohol measured at 1 KHz. The curve for additive-free Na_2SO_4 is represented by the dotted line.



Figure 3 - Differential capacitance curve of $0.5M Na_2SO_4$ containing $10^{-3}M$ Ethylenediamine measured at 1 KHz. The curve for additive-free Na_2SO_4 is represented by the dotted line.

By changing the composition or structure of the double layer, the adsorption of foreign substances may increase the activation energy for charge transfer. This may result in an increased transfer overvoltage and decrease in double layer capacitance¹³.

Since the adsorption of foreign substances retards lattice building and inhibits the growth of new lattice planes to various extents on different surfaces, newly formed and faster growing lattice planes may cover the adsorbed substances which occupy slower growing adjacent surfaces^{19,20}. Thus, the adsorbed substances may be occluded, buried or incorporated into the growing lattice, or between crystallises (if microcrystalline deposition occurs)^{19,20}.

Concluding Remarks

From the adsorption data it was deduced that leveling process is likely controlled by the prevailing electrochemical activities within the double layer of the cathode, unlike brightening process which has been shown to be due to the inhibition of crystallization process²⁰. The relation between the molecular structure of organic additives and their leveling and brightening action was explained. The empirical examples given in this paper are derived from the cathode behavior of the addition agents that impact common properties on silver, nickel, and gold electroplating systems. This study may in general be extended to other electroplating systems. It is intended that this should assist in the formulation of brightening and leveling organic additives.

References

- 1. M. Schloetter, U.S. Patent No. 1,972,693 (Sept. 4, 1934)
- 2. A. Iannelli, J. Richer, L. Stolberg, and J. Lipkowski, Plating and Surface Finishing, **77**, 47 (1990)
- 3. D. Gonnissen, A. Hubin, and J. Vereecken, Electrochim. Acta, **44**, 4129 (1999).
- 4. C. Gao, Y. Lu, S. Yue, and H. Wang, Trans. of the Institute of Metal Finishing, **77**, 75 (1999).
- 5. J.A. Harrison and H.R. Thirsk, Electroanalytical Chemistry, A.J. Bard, ed., Marcel Decker, New York, NY, 1971; p. 67.
- A.R. Despic', Comprehensive Treatise of Electrochemistry, B.E. Conway, J.O'M. Bockris, E. Yeager, S.V.M. Khan and R.E. White, eds., Plenum Press, New York, NY, 1983; p. 451.
- 7. J.C. Farmer and R.H. Muller, J. Electrochem. Soc., **132**, 313 (1985).
- 8. M. Beitowska-Brzezinska, E. Dutkiewicz and P. Skoluda, J. Electroanal. Chem., **181**, 235 (1989).
- 9. T. Hamelin, T. Vitanov, E. Sevastyanov, and A. Popov, J. Electroanal. Chem., **145**, 225 (1983).
- 10. O.A. Ashiru and J.P.G. Farr, J. Electrochem. Soc., **142**, 3729 (1995).
- 11. O.A. Ashiru and J. P. G. Farr, J. Electrochem. Soc., **139**, 2806 (1992).
- 12. J.P.G. Farr and O.A. Ashiru, Trans. of the Institute of Metal Finishing, **64**, 137 (1986).
- 13. D.C. Grahame, J. Amer. Chem. Soc., 68, 301 (1946).

14. O.A. Ashiru and S.J. Blunden, US Patent 5,378,346 (1995).

15. N. Cabrera and D.A. Vermilyea, Growth and Perfection of Crystals, Wiley, New York, p. 393 (1958).

16. W.P. Lorenz, T.J. O'Keefe, and C. B. Sonniono, Surface Technology, **6**, 179 (1978).

- 17. T. Erdey-Gruz, Kinetics of Electrode Processes, Adam Hilger Ltd., (1972).
- 18. H. Fischer, Elektrolytische Abscheidung und Elektrokristallisation von Metallen, Springer-Verlag, Berlin, (1954).
- 19. S.S. Kruglinov, Y.D. Gamburg, and N.T. Kudryavtsev, Electrochim. Acta, **12**, 169 (1967).
- 20. O.A. Ashiru, Surface and Interface Analysis, **23**, 618 (1995).