By O.A. Ashiru

This paper reports a study of the effect of gelatin (additive) on silver electrodeposition from an industrially viable iodide-based bath formulation. Gelatin is a grain refiner, as well as a leveling agent in the silver iodide plating system studied. The study is essentially an electroplating program whereby the electrode surface structure is related to the electrochemistry under well-defined experimental conditions, using a rotating disk electrode. DC polarization and *in situ* AC impedance techniques were utilized for monitoring adsorption and other surface relaxation processes. The resulting current-voltage curves and complex plane AC impedance spectra were used to elucidate the kinetic parameters of the additive-free and gelatin-containing silver iodide plating systems.

It is known that additives that modify the structure and properties of electrodeposited metals, such as microstructure, microthrowing, leveling and brightening, are generally inhibitors of the electrocrystallization process. In terms of electrode kinetics, these inhibiting effects may be monitored as a decrease in the overall rate of electrodeposition or as specific change in the rate of the various contributing interfacial reactions. In general terms, the phenomena associated with the adsorption of inhibiting molecules at the electrode interface have been studied traditionally by analyzing electrocapillary and differential-capacitance/potential curves.1-3 The specific mechanisms of adsorption and modification of the crystal growth processes by the adsorbates, however, require study by in-situ techniques. Adsorption and other reactions take place on the electrode surface, while the diffusive mass transport is a homogeneous phase phenomenon that must be carefully controlled. It is more useful to be able to study each elementary phenomenon in isolation from the others. Therefore, techniques capable of providing data that allow the different phenomena to be distinguished and quantified must be employed. In the past, some researchers have analyzed the adsorption kinetics of species in the electroplating baths by frequency dependence of the AC impedance of the electrode.⁴⁻⁷ This paper presents the results of a study of the effect of gelatin additive on the electrodeposition of silver from an

Effect of Rotation Speed of Rotating Disk Electrode Charge Transfer Resistance (Rct) & Double Layer Capacitance (Cdl) Of the Silver Iodide Bath

| Of the Silver louide bath | | | | |
|---|----------------|---------|----------------------------|---------|
| RDE | Rct (Ω-cm²) | | C _d (µF/cm²) | |
| SPEED | No | 0.4 g/L | No | 0.4 g/L |
| (RPM) | Additive | Gelatin | Additive | Gelatin |
| | | | | |
| 100 | 0.75 | 2.30 | 320 | 250 |
| 250 | 0.60 | 1.63 | 355 | 244 |
| 500 | 0.50 | 1.69 | 420 | 169 |
| 1000 | 0.45 | 1.70 | 458 | 234 |
| 2000 | 0.36 | 1.72 | 573 | 231 |
| With and without gelatin (0.4 g/L) : -77 mV vs. Ag. | | | | |

iodide electrolyte. To obtain meaningful kinetic information, advanced electrochemical techniques were used to monitor the plating system, under well-controlled hydrodynamic conditions, using the rotating disk electrode (RDE). This was necessary to obtain satisfactory understanding of electrode processes, which require an appreciation of mass transport at the cathode and the influence of both convection and diffusion. The objective of the study was to extend the interpretation of the data derived from the well-defined electrocrystallization and inhibiting processes, to understanding of the less well-controlled situation often encountered in practical electroplating systems.

Experimental Procedure

The electrolytes were prepared by treating silver nitrate with potassium iodide. The resulting silver iodide precipitate was washed thoroughly with double-distilled water, then dissolved in a large excess of potassium iodide. The electrolyte concentration was 0.05 M AgI and 0.8 M KI. This is within the concentration range proposed for industrial plating.⁸ When necessary, the required quantities of gelatin additive were weighed on a microbalance and added to the electrolyte. The respective concentrations of the additive and operating conditions are as indicated in the next section, along with the corresponding results. The pH of the solutions was usually ~10.5, and most experiments were carried out at temperatures between 20 and 60 °C, depending on the test.

The preliminary electrodeposition was carried out on cathode panels (usually 1.5 x 2 cm) cut from 99.9 percent pure copper sheet (buffed with emery paper) or gramophone record master plates. The panels were etched in 50-percent HCl for a few seconds and rinsed with doubly distilled water before electrodeposition. These copper and gramophone record master cathodes were used for assessment of microthrowing ability and leveling power of the cathode.⁹ The leveling measurements required assessment of roughness before and after plating. The leveling power is calculated as follows:

Initial substrate roughness - After plating roughness

Initial substrate roughness

Negative values indicate poor microthrowing power (*i.e.*, no leveling), and values greater than zero indicate leveling (the maximum attainable leveling is 1). During plating onto the panel cathodes, mild agitation of the silver iodide plating bath was achieved with an insulated magnetic stirrer. The RDE, cut from a copper cylinder, was used as the cathode (working electrode) for all kinetic studies. Deposition was conducted on the cross section of the copper cylinder with disk area of 0.70 cm^2 . To obtain reproducible results, the cathode surface was polished to a smooth finish, then cleaned, as described above, for the cathode panels prior to each plating. The counter electrode (anode) was a 99.9 percent pure silver sheet (5 x 10 cm). The reference electrode was a silver wire, corrected for ohmic drop and standardized with a saturated calomel electrode.

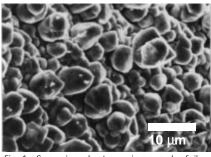


Fig. 1—Scanning electron micrograph of silver electrodeposit on copper panels from the additive-free iodide bath after plating for 20 min, 15 mA/cm² and 20 °C (nodular growth of silver deposit).

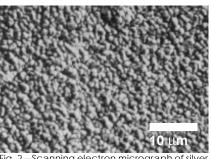


Fig. 2—Scanning electron micrograph of silver electrodeposit on copper panels from the iodide bath containing 1 g/L gelatin after plating for 20 min, 15 mA/cm² and 20 °C (suppression of nodular growth of silver deposit by gelatin inhibition).

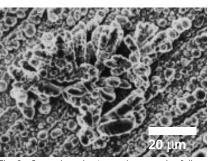


Fig. 3—Scanning electron micrograph of silver electrodeposit on copper panels from the additive-free iodide bath after plating for 1 hr, 30 min, 15 mA/cm² and 20 °C (roughening effects by nodules of silver deposits stacking).

The current-potential curves were plotted potentiostatically under steady-state. The complex electrode impedance was measured using a frequency response analyzer (FRA), with an electrochemical interface unit (ECI) for potentiostatic control of the process. Essentially, the FRA consisted of a programmable generator that provides a perturbing smallamplitude sinusoidal signal, a correlator to analyze the response of the system, and a data display. The generator was programmed to sweep from 50 kHz to 1 mHz at intervals of 4 points per decade. A computer was interfaced with the FRA to facilitate experimental control, data acquisition and data analysis. The impedance data were analyzed using a graphical operator with interactive capacity, which also included software for simulation of the equivalent circuit. In this study, the equivalent circuit models (from Armstrong et al.)¹⁰ were simulated for comparison with the experimental work. Some of the processes involved in the electroplating of silver displayed inductive loops in their complex plane impedance diagram. The methods usually employed for extracting kinetic parameters from such an inductive system require the use of a cumbersome, non-linear, least squares data fitting procedure.¹¹⁻¹² An algebraic method based on the idea proposed by Macdonald for estimating the equivalent circuit parameter from an impedance spectrum was used.¹³

The admittance function for the equivalent circuit is given by:

$$Y = \frac{1}{Z} = \frac{1}{R_{ct}} + j\omega C_{dl} + \frac{1}{(\rho + j\omega L)}$$
(1)

where Y is admittance, Z is impedance, R_{Ct} is charge transfer resistance, C_{dl} is double layer capacitance, ω is angular frequency, ρ is Faradaic resistance, L is inductance, and j is $\sqrt{-1}$.

This can be separated into real and imaginary impedances as follows:

$$\frac{1}{Z} = \frac{\rho + j\omega L + j\omega C_{dl}(\rho + j\omega L) R_{ct} + R_{ct}}{(\rho + j\omega L) R_{ct}}$$
(2)

Therefore,

$$Z = \frac{(\rho + j\omega L) R_{ct}}{\rho + j\omega L + j\omega C_{dl} (\rho + j\omega L) R_{ct} + R_{ct}}$$
(3)

Separating into real and imaginary values (*i.e.*, Z' = Z - jZ''

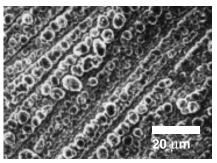


Fig. 4—Scanning electron micrograph of silver electrodeposit from the additive-free iodide bath (20 min, 15 mA/cm² and 20 °C). The plating was carried out on abraded copper cathode panels; the micrograph shows preferential alignment of bigger nodules at the peaks of the uneven surface.

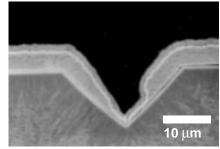


Fig. 5—Scanning electron micrograph showing electrodeposition of silver on gramophone record master grooves from additive-free iodide bath after plating for 20 min, 15 mA/cm² and 20 °C (poor microthrowing power revealed).

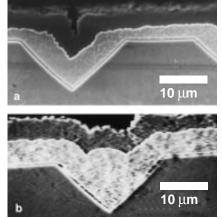


Fig. 6—Scanning electron micrographs showing the leveling process on gramophone record master grooves during silver plating from iodide bath containing 0.6 g/L gelatin. Preferential filling of the grooves and less deposition at the flat peaks revealed. Conditions: 15 mA/ cm² and 20 °C. Plating periods: (a) 20 min; (b) 1 hr.

$$Z' = \frac{\rho + R_{ct} + R_{ct}^2 \rho + \omega^2 L^2 R_{ct}}{[\rho + R_{ct} - \omega^2 R_{ct} C_{dl} L]^2 + \omega^2 [L + \rho R_{ct} C_{dl}]^2}$$
(4)

and

$$Z'' = \frac{\omega \left[R_{ct}^2 \rho^2 C_{dl} - L R_{ct}^2 \omega^2 L^2 R_{ct}^2 C_{dl} \right]}{\left[\rho + R_{ct} - \omega^2 R_{ct} C_{dl} L \right]^2 + \omega^2 \left[L \rho R_{ct} C_{dl} \right]^2}$$
(5)

Computer simulation of Z' and Z'' generated spectra that are similar to those obtained empirically. This model was tested and found satisfactory when applied to well-known behavior in other established metal plating systems. The electrode kinetics data (*i.e.*, charge transfer resistance, R_{Ct} and double layer capacitance, C_{dl}) were generated from the equations, using a computer for data acquisition and analysis to extract the frequency capacitive element of the equivalent circuit in the high-frequency region.

Results and Discussion

Effect of Gelatin

Generally, the silver iodide plating bath can be operated at current densities as high as 20 mA/cm^2 . This relatively higher operating current density, compared to the conventional or bright cyanide silver plating bath (12 mA/cm^2), means higher

productivity can be obtained from the iodide bath. Figure 1 shows the surface morphology of silver electrodeposited from the iodide bath in the absence of gelatin. The deposit was nodular over

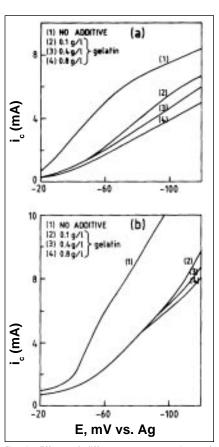


Fig. 8—Effect of different concentrations of gelatin on the current-voltage curves of silver iodide plating baths during deposition on RDE at 20 °C: (a) 1000 rpm; (b) 2000 rpm.

the entire optimum operating conditions (10 to 20 mA/cm^2 and 20 to 60 °C). The presence of gelatin (typically 0.1 to 2 g/L) suppressed the nodular growth, as revealed in Fig. 2. Silver depos-

silver deposits from the additive-free iodide bath often became dendrite-like, once the deposit thickness exceed

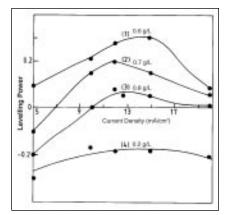


Fig. 7—Effect of current density and gelatin concentration on leveling power in silver iodide plating bath on gramophone record master at 20 °C.

thickness exceeded ~30 μ m. Scanning electron microscopy (SEM) of the surface topography revealed, as shown in Fig. 3, that the dendritic growth was caused by nodules of silver deposits mounting on top of each other, normal to the surface of the substrate. Thus, spikes were formed that continued to grow radially in a plane perpendicular to the surface of the flat

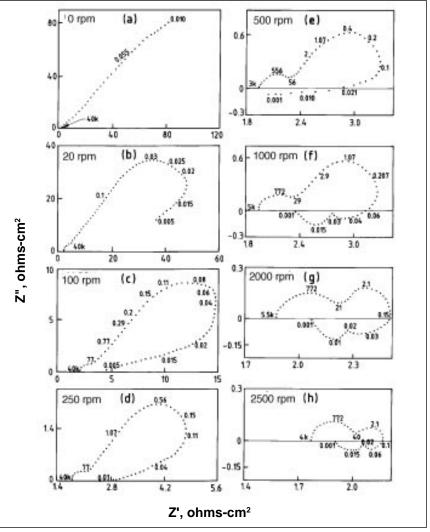


Fig. 9—Influence of RDE rotation speeds on the complex plane impedance spectra of additive-free silver iodide plating electrolyte during deposition on RDE (-77 mV vs. Ag, 20 °C).

substrate. The presence of gelatin in the iodide plating bath eliminated the characteristic dendrite-like structure.

SEM study revealed that bigger nodular grains tend to align themselves preferentially along the peaks of the crevices, as observed from deposition onto small-scale crevices produced by buffing the copper cathode substrate to 400 grit by emery paper (Fig. 4). This factor led to poor microthrowing power by worsening the roughness of the cathode after deposition. The poor microthrowing power of the additivefree silver iodide plating bath is also revealed by cross section in Fig. 5, which shows that deposition occurred preferentially at the peaks of the V-grooves of the gramophone record master substrate. Accordingly, these results confirm that the microthrowing power of the additive-free silver iodide plating bath is generally poor (*i.e.*, the deposition of silver from the electrolyte worsens the surface roughness of the substrate). In the presence of gelatin (0.1 to 3 g/L), the microthrowing power of the iodide bath was improved. In addition, gelatin was found to be a leveling agent, if employed under appropriate operating conditions, in the silver iodide plating bath. Figure 6 shows the cross section of leveled silver deposit from the iodide bath containing gelatin. The substrates were cut from a gramophone record master. The micrographs reveal the preferential filling of the grooves and less deposition at the peaks. The effect of current density and concentration of gelatin on the leveling power is shown in Fig. 7. The results show that for a constant concentration of gelatin in the iodide bath, the leveling power rises with increasing current density to a maximum, then decreases.

The current study revealed that the inherently poor microthrowing power of the silver iodide plating bath, which previously could not be improved by mere alteration of the operating conditions, can be ameliorated in the presence of gelatin. The study also produced leveled silver deposits with appropriate concentration of gelatin in the iodide bath at favorable operating conditions. These results are of paramount importance, in that they show encouraging leveling ability, which to the best of the author's knowledge, is novel in silver plating from an iodide bath. In view of the contemporary effort to replace the use of toxic chemicals, such as cvanide, the silver iodide bath in the presence of gelatin has merit for future industrial trials.⁸ The remaining part of this paper will focus on the use of electrochemical techniques to establish the electrode kinetic parameters relating to silver deposition from the additive-free and gelatin-containing iodide baths.

Polarization Curves

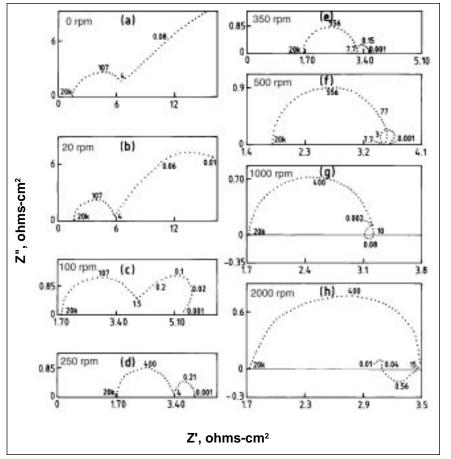
Figure 8 shows the influence of gelatin on the currentpotential (i-E) curves of the silver iodide plating bath during deposition processes on rotating disk cathodes operated at 1000 and 2000 rpm. The cathodic current is reduced for a given cathodic potential in the presence of gelatin in the iodide bath; this decrease is favored by an increase in gelatin concentration. This observation resembles the effect of leveling agents in the cyanide bath.⁹ A preliminary study, however, showed that only gelatin has this effect on the iodide bath; most other compounds reported as leveling agents in the

gelatin

0.5

140

(a)



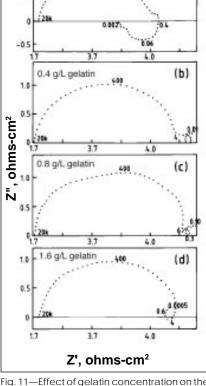


Fig. 10—Influence of RDE rotation speeds on the complex plane impedance spectra of silver iodide plating electrolyte containing 0.4 g/L gelatin during deposition on RDE (-77 mV vs. Ag; 20 °C).

Fig. 11—Effect of gelatin concentration on the complex plane impedance spectra of silver iodide plating electrolyte during deposition on RDE (-75 mV vs. Ag; 800 rpm, 20 °C).

cyanide bath did not have noticeable effect on the i-E curves in the iodide bath. Moreover, it can be seen from the currentpotential curves in Fig. 8 that the inhibiting effect is less at lower cathodic potentials.

AC Impedance Spectra

The impedance spectra obtained during this study are quite reproducible, inasmuch as repeated measurements gave identical spectra. Figure 9 shows a series of complex impedance analyses of silver deposition from the additive-free iodide bath at a cathodic potential of -77 mV (vs. Ag) and different rotation speeds. Figure 9a depicts the experimental result obtained without rotation. The spectrum can be approximately fitted (throughout the frequency range) to a straight line of 45° slope, with no obvious evidence of charge transfer. The main features of the spectrum obtained at 0 rpm, therefore, are: (1) the absence of the charge transfer semi-circle in the high-frequency range and (2) the spectrum can be conveniently extrapolated to fit a 45° slope straight line. These observations are characteristic of the Warburg impedance, attributable to an electrodeposition process in which diffusion of species dominates and the charge transfer contribution is negligible.¹¹

Figures 9b, c, d, e and f typify the effect of increasing the RDE rotation speed (up to 1000 rpm) on the AC impedance spectra obtained from the additive-free iodide electrolyte. The relevant features of the spectra are: (1) a charge transfer semi-circle in the high-frequency range; (2) a Warburg diffusion impedance in the intermediate-frequency range; and (3) vaguely defined quasi-relaxation processes in the very-low-

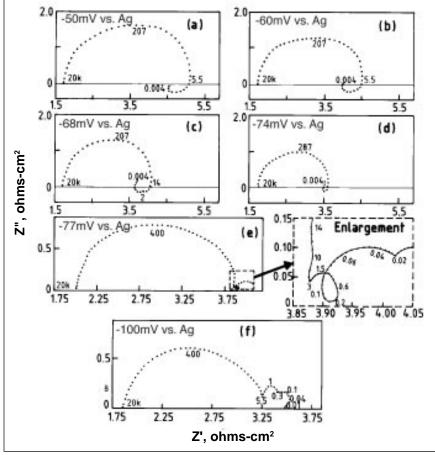


Fig. 12—The effect of plating potential on the complex plane impedance diagrams of silver iodide baths containing 1.2 g/L gelatin during deposition on RDE at 1000 rpm and 20 °C.

frequency range. Figures 9g and 9h are the impedance diagrams obtained at very high rotation speeds (2000 and 2500 rpm, respectively). The main features of the spectra are as follows: (1) in the high-frequency range (40 Hz to 40 kHz), the plot exhibits a charge transfer semi-circle; (2) the Warburg component is absent; and (3) in the lower-frequency range, there are three loops, made up of a capacitive loop coupled to two further terminal inductive loops. In an additive-free iodide electrolyte, therefore, rotation speeds must be as great or greater than 2000 rpm (Figs. 9g and 9h) to eliminate the influence of diffusion-control (Warburg component) of the deposition process. This suggests that, unlike the cyanide plating system,⁹ at very high rotation speeds, the diffusion of species in the solution (e.g., silver iodide complexes) still follows the applied sinusoid and, consequently, the electrode reactions are mass-transport-controlled. This is a major difference between the iodide and the cyanide baths; in the latter, classical diffusion components are not seen in the spectra when 500 rpm is attained. The persistence of the Warburg impedance in the iodide bath at higher rotation speeds (up to 1000 rpm) is associated with relatively large exchange current density, i, of the iodide bath, which implies that a high rate of transport of the species to the electrode is required as the electrode follows the electric vector.

In the additive-free iodide plating bath, the increase in rotation speeds produces a decrease in charge transfer resistance and an increase in double layer capacitance, as shown in the table and Fig. 9. It is noteworthy that the values of the double layer capacitance are very high, greater than 350 °F/ cm² in the additive-free iodide bath, compared with less than

 $100 \,^{\circ}\text{F/cm}^2$ in the cyanide silver plating bath.9 The large values of the double layer capacitance, C_{dl} (see table) obtained within a single high-frequency semi-circle suggest the adsorption of charged species and the possibility of discharge of the higher silver iodide complexes, such as AgI₃⁻² for the deposited silver metal.¹⁴ In addition, an increase in rotation speed gives a decrease in charge transfer resistance, with an increase in double layer capacitance. At very high rotation speeds (2000 and 2500 rpm) the influence of diffusion disappears in the complex plane impedance spectra (Figures 9g and 9h); instead, three low-frequency surface relaxation processes (one capacitive and two inductive loops) were exhibited.

Typical impedance diagrams obtained at varying RDE rotation speeds from the silver iodide plating bath containing 0.4 g/L gelatin operated at -77 mV (vs. Ag) are shown in Fig. 10. A comparison of the spectra in Fig. 10 and the corresponding additive-free iodide electrolyte in Fig. 9 shows that gelatin decreases the size of the impedance spectra. The Warburg diffusion impedance disappears at 250 rpm (Fig. 10d) in the gelatin-containing iodide electrolyte, unlike the additive-free bath, which exhibits diffusion impedance up to 1000 rpm (Fig. 9f). The

corresponding R_{Ct} and C_{dl} data for the iodide bath containing gelatin are listed in the table, along with the additive-free iodide bath, showing that charge transfer resistance, R_{C_1} , increases in the presence of gelatin. In addition, the kinetic data in the table reveal that, at specific rpm, the corresponding values of the double layer capacitance, C_{dl} are higher for the additive-free iodide electrolyte (>350 °F/cm²) compared with gelatin-containing electrolyte (<250 °F/cm²). Figure 11 shows the effect of varying gelatin concentration on AC impedance spectra of the iodide electrolyte on an RDE operated at 800 rpm. Correlation of the spectra in Fig. 11 and leveling ability revealed that the leveled silver deposits (leveling power > 0) exhibit a similar type of impedance spectra. The active concentration range of the gelatin additive is usually low in the iodide electrolyte; therefore, electrode activity and consumption rate will be controlled by convection and diffusion. Under such conditions, the number of adsorbed gelatin molecules and, consequently, their inhibiting effects, should be controlled by convective-diffusion. The leveling action of gelatin, therefore, was more effective at RDE speeds greater than 500 rpm (e.g., under the conditions that generated the spectra shown in Figs. 10g, 10h and Fig. 11).

Figure 12 shows the effect of plating potential on the impedance diagram. The lower cathodic potentials (Figs. 12a, b, c and d) exhibit only a high-frequency capacitive loop (corresponding to the C_{dl} - R_{Ct} circuit) and an inductive loop at lower frequency (*e.g.*, between 5.5 Hz and 0.004 Hz in Fig. 12a). Thus, intermediate-frequency capacitive loops that were observed in the additive-free iodide bath (Figs. 9g and 9h) are absent. These intermediate-frequency capacitive loops are usually ascribed to adsorption of charged silver iodide complexes, which is potential-dependent. As the plating potential is raised to more cathodic potentials, the capacitive loop starts to appear in the gelatin-containing iodide bath. The appearance of this loop (Fig. 12f) at higher potential (-100 mV vs. Ag) in the gelatin-containing iodide bath coincides with the retardation of the leveling process. This explains the experimental observation that the leveling action of gelatin reaches an optimum value with current-density increase (Fig. 7). This is because the adsorption of silver iodide complexes will be competing with the inhibition of gelatin at high cathodic currents and potentials.

General Discussion

Although a general mechanism for brightening in electrodeposition has been accepted, albeit on the grounds of rather slender experimentation, the process of leveling is clearly different and has not been explained satisfactorily. Accordingly, the main purpose of this discussion is to consider the nature of the leveling process. It can be said from practical experience that leveling involves weaker surface adsorption than does brightening. This renders it likely that leveling is system-specific; an understanding of the process studied here is not necessarily directly applicable to the deposition of other metals, or even to the deposition of silver from other solutions. Nevertheless, similar arguments may apply.

It is necessary first to summarize the characteristics of leveling as observed in the current studies. Second, consideration is given to the contribution of mass transport of the electrolyte species to the deposition reactions. This transport is determined by convection (*i.e.*, the prevailing hydrodynamics), and diffusion. Adsorption of the electroactive species has been demonstrated in the iodide bath to increase with increase in cathodic potential (Fig. 12), and to decrease in the presence of gelatin in the iodide bath. In the iodide plating system, however, adsorption of silver complexes dominates most other adsorption processes (Figs. 9–12). Adsorption of gelatin, and therefore its leveling action, occurs over a specific potential region and current density range. The impedance spectra indicate that the absorbed gelatin (leveling additive) has the ability to interfere with the electron transfer (*i.e.*, increasing R_{cl}) at the solution-cathode interface; also, it drastically reduces the double layer capacity by about 70 to 340 °µF/cm² (see table) in the silver iodide bath. The polarization curves indicate a cathodic reduction in the presence of gelatin (as shown in Fig. 8) in the silver iodide plating bath. Two possible explanations for these effects are:

- 1. Increase in ohmic resistance of the cathode film caused by the presence of gelatin in the plating solution.
- 2. Adsorption of the gelatin compound on the cathode with resultant retardation in the rate at which discharge processes occur,¹⁴ such as:

$$AgI_{2}^{-} + e^{-} \rightarrow Ag + 2I^{-}$$

The results of all the impedance spectra (Figs. 9–12) in the iodide plating baths, with and without gelatin, indicate that the solution resistance, R_{so} , is more or less constant (1.8 ±0.1 ohm-cm²), particularly for similar operating conditions. It is therefore concluded that IR contribution to the measured potential is not a major factor. The experimental evidence from i-E curves, double layer capacitance, and charge transfer resistance, support the second explanation that the change in the cathodic potential is caused by adsorption of the non-ionic gelatin molecules.

The above discussion clearly indicates that at the leveling cathode, various species are adsorbed competitively. For the iodide silver plating solution, there is competition between the anion (*i.e.*, Γ), silver iodide complexes, and the gelatin additive. The adsorption of the anion, Γ , is, however, likely to be chemisorption, but not involving the formation of strong covalent bonds, (i.e., specific adsorption).

The charge transfer resistance, R_{Ct} , of the iodide bath is very small, usually less than 1 ohm-cm² (see table), unlike the cyanide bath with usually very high R_{Ct}, up to 16 ohm-cm² in certain cases.9 Consequently, discharge processes are much easier in the iodide bath compared with the cyanide bath. Correspondingly, the exchange current density, i_o, of the iodide bath will be much higher than the cyanide bath. The cathode discharge of silver in the iodide bath has been shown to occur from adsorbed AgI or the higher silver complexes.¹⁴ This shows that iodine ions (I) are generated at a very high rate at the cathode through the discharge reactions, such as given above. Moreover, the large values of C_{dl} obtained from the iodide bath (see table) also indicate that I anions are likely adsorbed on the cathode. These are the major differences between the iodide and cyanide baths; the factors also partly explain why most of the conventional leveling agents found to be active in the low cyanide bath⁹ are inactive in the iodide bath.

The increase in "free" cyanide concentration in the silver cyanide bath shifts the i-E curves toward more cathodic potentials¹⁴ and is related to the fact that the cathodic polarization is dependent on the local CN⁻ concentration and the higher complexes. The i-E curves for the iodide bath are independent of I⁻ concentration in the bath, but dependent on AgI concentration.¹⁴ These clearly show that both the iodide and cyanide baths have essentially different adsorption and

desorption processes. Therefore, the same additive will be expected to behave differently in the two systems.

Findings

This study revealed that the inherently poor microthrowing power of silver iodide plating baths can be improved if silver is deposited in the presence of an appropriate concentration of gelatin additive, under favorable operating conditions. Gelatin, therefore, is a surface-active compound in this plating solution. The adsorption of gelatin in the iodide bath is potential-dependent and affects the diffusion of the reducing species to the cathode surface.

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