Leveling in Pulse Plating with Brighteners: Synergistic Effect of Frequency and Hydrodynamically Active Additives

By M. S. Aroyo

A method based on roughness measurements, providing reliable and precise estimation of the leveling power (LP) of d-c and pulsed electrodeposited metal coatings, has been developed. The maximum LP values were experimentally obtained at a pulse current frequency of 5 Hz for bright acid copper, bright Watts nickel and bright acid gold-cobalt plating processes, using commercially available brighteners and hydrodynamically active agent SA-LFPP. At this frequency, bright pulse electrodeposition is characterized by excellent leveling ability, about five, two and ten times better, respectively, than that of the corresponding bright d-c plating. Theoretical modeling considerations of the absorption-diffusion mechanism of leveling in low-frequency pulse plating with brightener additives are given. The results obtained prove that, under definite conditions of pulse electrodeposition, it is possible to combine the well-known advantages of pulse plating with those of conventional d-c bright electrodeposition, and to deposit metal coatings with better decorative and functional properties.

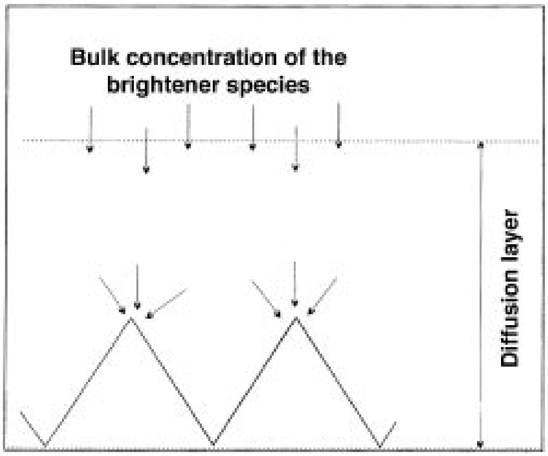

Fig. 1—Accessibility to brightener additives by diffusion for protrusions of microprofile.

Microthrowing power in electrodeposition is related to metal distribution on the electrode surface, which has a roughness depth or height less than 100 µm.[1] When dilute brightening additives are present in the plating electrolyte, metal deposition is accomplished in a way that leads to attenuation of rough surface features (i.e., to the leveling of the microprofile). According to adsorption-diffusion theory,[2-5] the brighteners act as inhibitors and the rate of electrodeposition is preferentially inhibited on those portions of the electrode surface that are more accessible to these agents by mass transport (Fig. 1).

As a result, protrusions that receive by diffusion more intensive flow of the leveling agent, become smaller as the deposit grows. Similarly, depressions receive less inhibitor and, consequently, become shallower. Obviously, the leveling power (LP) can be qualitatively characterized as ability to diminish the difference in height between protrusion peaks and recesses in an electrode microprofile. The greater this ability, the thinner the coating thickness required for achieving leveling. It is logical to make the assumption that in the case of good leveling, some specific coating properties, such as corrosion protection, optical appearance, wear resistance, electrical conductivity, etc. will be provided by coatings thinner than those having poor leveling performance.

The maximum value of the leveling power will correspond to the best value of a given coating property. For practical application of such a correlation, it will be necessary to choose and develop an exact, reliable and universal method of quantitative determination of the leveling power. This would create an opportunity to define the plating conditions for metal coatings with superior functional properties.

For quantitative leveling estimation in electrochemical coating applications, it is possible to use metal surface specimens (a) of regular (rectangular, quasi-sinusoidal, V-groove, etc) profile, and (b) of non-regular (random) profile, obtained by grinding the metal surface with emery paper. To define the leveling power in an electrodeposited coating on the surface of a nonregular profile, the following expression can be used:[6]

$$L = \frac{R_{a,o} - R_{a,c}}{R_{a,o}} \qquad (1)$$

where $\mathbf{R_{a,o}}$ and $\mathbf{R_{a,c}}$ are the roughnesses of the substrate and the plated surface, respectively. This formula does not take into account the leveling change as the coating thickness increases. It is suitable only for comparing the obtained values of the leveling power when the coating thickness is the same for all specimens investigated.

The reasons presented above have imposed a change in Eq. (1), namely, the substrate roughness, $\mathbf{R_{a,o}}$, in the denominator, is replaced by the actually obtained coating thickness **d**:

$$LP = \frac{R_{a,o} - R_{a,c}}{d} \qquad (2)$$

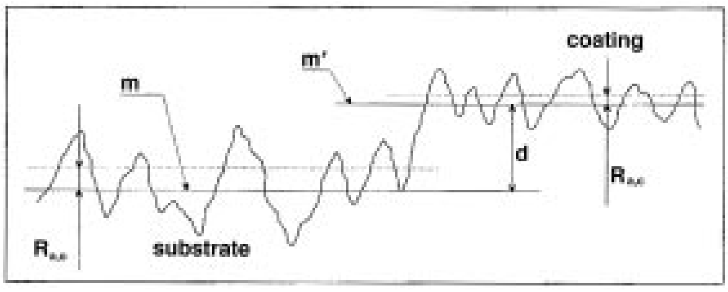

Fig. 2—Profilograms of bare and coated surfaces of rotating disk electrode.

Inasmuch as the metal quantities deposited on peaks and recesses of the non-regular surface profile are different, coating thickness is defined as the distance between the mean lines **m** and **m'** of the substrate and coating profiles, respectively (Fig. 2). The LP value calculated from Eq. (2) is independent of the coating thickness and leveling of coatings of different thickness can be compared.

Experimental Procedure and Results

The initial roughness, $\mathbf{R_{a,o}}$, was obtained by grinding the electrode surface in one direction only with grade 450 emery paper. The roughness measurements were made with a contact profilometer-profilograph. The plating of the metal coatings was conducted on a disc electrode (0.5 cm^2) with constant speed of rotation (250 rpm). The use of a rotating disc electrode guaranteed equal thickness of the diffusion layer in the vicinity of the cathode surface. Metal coatings of copper, nickel and gold were electrodeposited from standard bright acid electrolytes containing commercially available brighteners (patented Bulgarian products). Bath compositions and operating conditions are shown in the table.

The metal coatings were electrodeposited on half the disc electrode surface because the other half had been previously insulated with a thin film of photo-resist lacquer. After electrodeposition, this film was removed with the help of an organic solvent. As a result, it was possible to determine the coating thickness directly from the profilogram (Fig. 2).

The pulsed current frequency used in all plating processes ranged from 2.5 to 20 Hz, and the pulse duration was the same ($\mathbf{T_{on}}$ = 10 msec) for all frequencies used. For each pulse frequency a pulse current density $\mathbf{i_p}$ was calculated in accordance with the relationship:

$$i_p = \frac{i_m (T_{on} + T_{off})}{T_{on}} \tag{3}$$

where $\mathbf{i_m}$ was an average current density having a constant value for all plating processes in the experimental frequency range.

Figures 3, 4 and 5 demonstrate the relationship between LP and pulse frequency in three cases of electrodeposition: (a) without additives; (b) with brighteners; and (c) with brighteners and hydrodynamically active agent SA-LFPP. This agent is a water-soluble polymer of protein type HONH$_3$-R-COOH, where R is a CONH-containing chain. The concentration of SA-LFPP used in bright plating solutions is very low—only as much as 5x10^{-4} percent. It is obvious that in all three cases the maximum values of LP are at a pulse frequency of 5 Hz. This frequency is the same for the copper, nickel and gold deposits, although there are considerable differences in the contents of the electrolytes and the chemical nature of the brighteners used. As pulse current frequency increases above 5 Hz, the LP values go down gradually and, at 20 Hz, LP reaches values that are close to those of the coatings deposited from electrolytes without

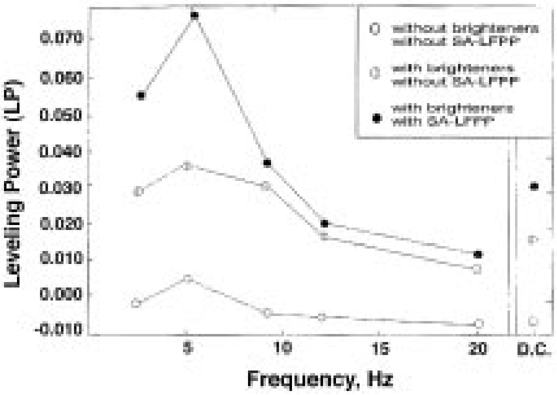

Fig. 3—-Leveling power (LP) dependence on pulse frequency in acid copper plating.

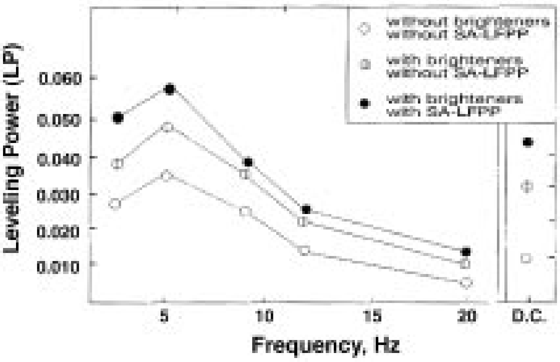

Fig. 4—Leveling power dependence on pulse frequency in Watts nickel plating.

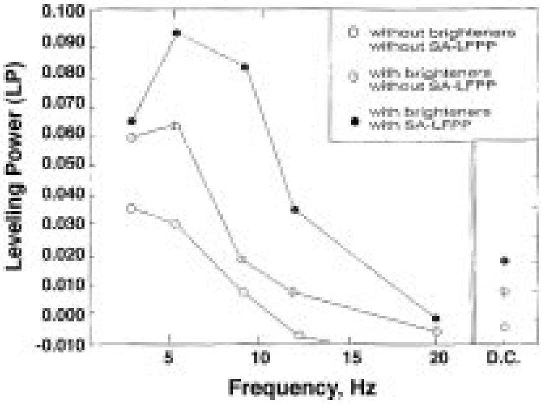

Fig. 5—Leveling power dependence on pulse frequency in acid gold plating.

Bath Composition and Operating Conditions for Copper, Nickel & Gold

Copper		**Nickel**		**Gold**	
$CuSO_4 \cdot 5H_2O$	220 g/L	$NiSO_4 \cdot 6H_2O$	250 g/L	Au, as $KAu(CN)_2$	8 g/L
H_2SO_4	60 g/L	$NiCl_2 \cdot 6H_2O$	30 g/L	Citric acid	25 g/L
NaCl	90 mg/L	H_3BO_3	40 g/L	Na citrate	80 g/L
Brighteners		**Brighteners**		**Brighteners**	
TD-I	3 mL/L	Saccharin	1.5 g/L	Aurolux	10 mL/L
TD-II	3 mL/L	Ferrassin-N	1 mL/L		
Cathode current dens. (average), A/dm^2	4	Cathode current dens. (average), A/dm^2	4	Cathode current dens. (average), A/dm^2	0.5
Pulse time, msec	10	Pulse time, msec	10	Pulse time, msec	10
Bath temp. °C	30	Bath temp. °C	55	Bath temp. °C	30
Plating time, min	5	Plating time, min	5	Plating time, min	10
pH		pH	4	pH	3.5

brighteners. In other words, from about 15 to 20 Hz pulse current frequency, electrodeposition takes place under the conditions of brightener deficit, although their bulk concentration is the same as that in d-c plating.

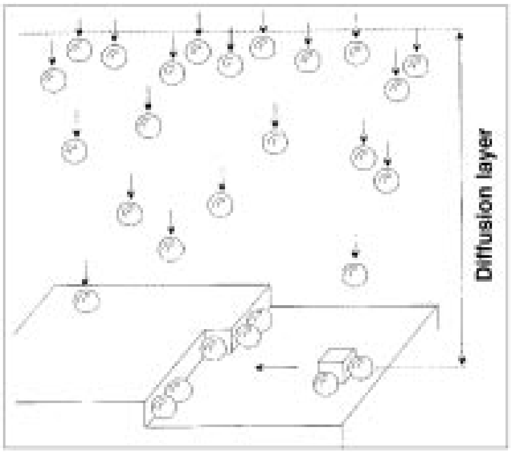

Fig. 6—Crystal growth by build-up of existing nuclei. Surface concentration of adsorbed brightener species is sufficient for inhibition of the crystallization process.

For pulsed copper electrodeposition in the presence of brighteners and the SA-LFPP agent, the maximum LP value (0.078) at 5 Hz is five times higher (0.016) than that of the corresponding d-c bright plating without the SA-LFPP additive in the electrolyte. By comparison, the addition of brighteners to the d-c plating bath improves the leveling performance of matte copper deposits, the corresponding LP values being increased from -0.006 to 0.016 (Fig. 3).

We can observe a similar relationship between leveling power and pulse frequency for pulsed bright nickel plating (Fig. 4). In the presence of brighteners and the SA-LFPP agent, the maximum LP value of a 5-Hz pulse plating is 1.7 times higher than that of d-c bright electrodeposition, using brighteners only. By comparison, in d-c plating, the addition of brighteners to Watts matte nickel electrolyte causes an improvement in LP of the same order (from 0.014 to 0.033). Addition of the hydrodynamically active agent SA-LFPP in bright plating baths gives the best results in the case of acid gold-cobalt pulsed plating (Fig. 5). The maximum LP value (0.096) at 5-Hz pulsed electrodeposition is 10 times higher than that of the conventional d-c bright acid, gold-cobalt plating (no SA-LFPP present).

Discussion

The mechanism explaining the leveling maximum, observed in the experimental curves (Figs. 3, 4 and 5) is based on the following principles:

1. The participation and consumption of various species $\mathbf{X}_1$, $\mathbf{X}_2$, $\mathbf{X}_3$... such as metal ions, organic molecules of additives, etc. in cathodic electrochemical reactions, create diffusion layers with respective thicknesses $\mathbf{d}_1$, $\mathbf{d}_2$, $\mathbf{d}_3$... In these layers, their concentration is lower than in the bulk solution. Consequently, each species consumed at the cathode has its own concentration gradient, representing the driving force of the different diffusion flows. In pulse plating with short pulse duration, these concentrations pulsate at the frequency of the pulse current, decreasing during the pulse and recovering in the intervals between them (off-time). During recovery, metal ions and other species consumed in the cathodic process are transported from the bulk solution for various times $\mathbf{t}_1$, $\mathbf{t}_2$, $\mathbf{t}_3$...

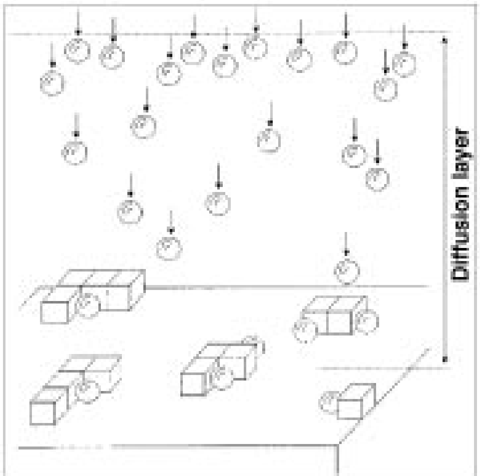

Fig. 7—Crystal growth by formation of new nuclei. Surface concentration of adsorbed brightener species is not sufficient for inhibition of the crystallization process.

2. Electrodeposition of high quality coatings from bright plating solutions depends on the degree of coordination between the rates of the different diffusion flows to the cathodic surface. If d-c or pulse plating parameters (current density, temperature, pH, pulse frequency duration $\mathbf{T}_{\mathbf{on}}$, agitation, etc.) are not within the range that guarantees a match of the rates of these flows, bright electrodeposits do not occur.

3. The electrocrystallization process is initiated either by further building-up of old crystals or by the formation and growth of new ones (Figs. 6 and 7). These two competing processes can be influenced by different factors. In pulse plating, inasmuch as the pulse current density and the overpotentials are considerably higher than those in d-c plating, the population of adatoms on the surface during pulse deposition is larger than that in d-c deposition. The crystallization process is predominantly carried out as a result of the formation and growth of new nuclei (Fig. 7).

Increase of pulse frequency is, on the one hand, related to an increase in the rate of nuclei formation. On the other hand, when the frequency goes up (at constant $\mathbf{T}_{\mathbf{on}}$), the off-time $\mathbf{T}_{\mathbf{off}}$, diminishes (i.e., the time available for the recovery of the bulk brightener concentration on the cathodic surface gets shorter as well.

At the same time, the active sites of adsorption of inhibiting species increase, as a result of the rising number of new nuclei. The higher the pulse frequency, the higher the need of an inhibitor (brightener). At a definite pulsed current frequency, the rate of brightener diffusion reaches the "limiting" value, above which nuclei growth takes place under conditions of brightener deficit.

Consequently, we reach the conclusion that in pulse plating with brighteners, there are two tendencies with different directions, one increasing with the pulse current frequency, and the other decreasing (Fig. 8). The first tends to increase the number of new nuclei, the second is related to the relative decrease in the surface concentration of brightener species. Evidently, the "limiting" value of pulse current frequency should be expected at the point where the upward line intersects the descending line. The optimum coordination of the rate of nuclei formation and the recovery rate of the brightener surface concentration for the pulsed electrodeposition processes considered was found at about 5 Hz.

It should be emphasized that the above mentioned principles account for the electrocrystallization process with brightener additives on a sub-microprofile scale. It means that while a certain value of this "limiting" frequency is optimal for the nuclei on the most accessible portions of the microprofile (Fig. 1), it will be too high for the recesses of the microprofile; the crys-

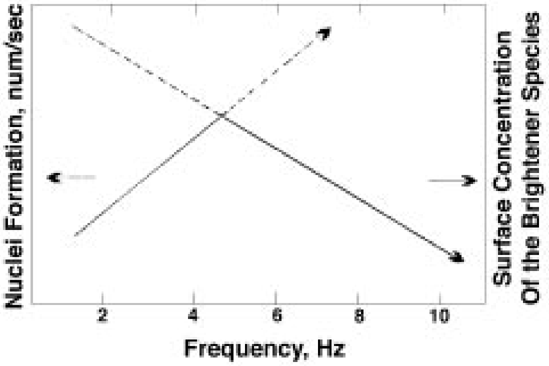

Fig. 8—Intersecting tendency lines, depending on pulse frequency.

tallization process there will take place under the conditions of inhibitor deficiency. As a result, the rate of crystal growth in the protrusions of the microprofile will be relatively low compared to that in the recesses. In other words, at this "limiting" frequency we observe an effect of leveling maximum.

Addition of a hydrodynamically active agent, SA-LFPP, to the bright acid copper, bright Watts nickel, and bright acid gold electrolytes leads to a considerable increase of the LP values, especially in the frequency range from 2.5 to 10 Hz. The explanation of these experimentally established facts is that the SA-LFPP addition leads to diminution of the dynamic viscosity μ. According to the Nernst-Einstein relation,[7] $\mathbf{D = kT/\mu}$, this increases the velocity of the diffusion flows of both kinds of species to the cathodic surface metal cations and organic molecules of the brightener additives. As a result, the curves for the three plating processes using SA-LFPP additive are shifted towards the higher LP values (Figs. 3, 4 and 5).

Given the fact that pulse plating at a fixed frequency can take place at different ratios of $\mathbf{T_{on}}$ and $\mathbf{T_{off}}$, it is important to define the ratio at which a maximum leveling effect is to be achieved. That is why Ibl's work[8] has been used as the theoretical basis for the explanation of the processes in the case of a single pulse. Before starting electrolysis, the concentration everywhere is $\mathbf{c_b}$. After the pulse current has been switched on, the concentration near the cathode drops and a diffusion layer is built up. The concentration profile can be approximately represented as a straight line, its slope being proportional to $\mathbf{i_p}$ and so remaining constant during a galvanostatic pulse (Fig. 9). Therefore, the increase in depletion with time **t** results in a parallel displacement of the concentration line toward lower concentrations. The full line shows the concentration profile at the end of the pulse ($\mathbf{t = T_{on}}$) The thickness of the diffusion layer increases with time and reaches the value $\delta_p = \mathbf{(2DT_{on})^{1/2}}$ at the end of the pulse. It can be seen that the thickness of the diffusion layer is independent of the concentration $\mathbf{c_p}$ as well as of the pulse current density $\mathbf{i_p}$. It depends only on the cation diffusion coefficient **D** and on the pulse duration $\mathbf{T_{on}}$. The interfacial concentration reached at the end of the pulse is $\mathbf{c_e}$. When the pulse duration $\mathbf{T_{on}}$ is equal to the so-called transition time τ, interfacial concentration drops exactly to zero at the end of the pulse (line OB in Fig. 9). Accordingly, for τ we obtain

$$\tau = (2F)^2 c_b^2 D/2i_p \tag{4}$$

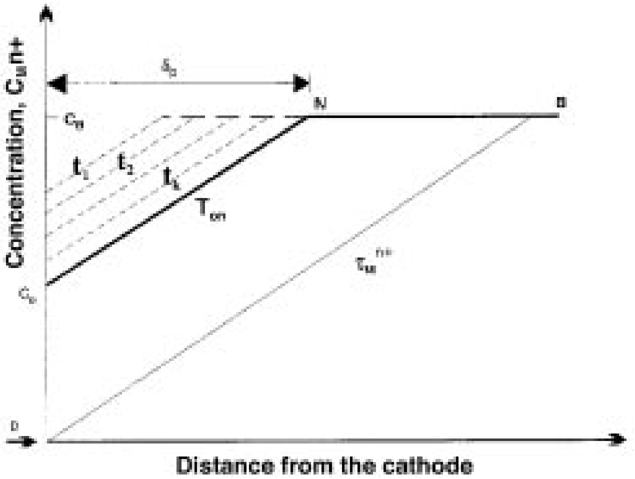

Fig. 9—Concentration profiles of discharged metal ions at various times ($t_1 < t_2 < t_k < T_{on}$) during a single pulse.

The considerably lower concentration of organic additives, as well as their limited mobility, account for their shorter transition time $\tau_{add} = t_k < T_{on}$. From this moment, until the end of the pulse, the crystallization process takes place in the complete absence of adsorbed brightener species. Now, one more condition can be defined for pulse electrodeposition of high-quality metal coatings:

$$T_{on} < \tau_{add} \tag{5}$$

At fixed pulse current frequency, the shortening of the pulse duration $\mathbf{T_{on}}$ is limited by the technological requirement for acceptable values of the duty cycle $\mathbf{t_d = T_{on}/(T_{on} + T_{off})}$ The inequality (5) can be satisfied by increasing the transition time τ_{add} (i.e., by increasing the mobility of the brightener species). In practice, this could be achieved with the use of hydrodynamically active additives that decrease the dynamic viscosity of the plating solution.

Conclusions

The pronounced maxima of LP values are obtained at 5 Hz pulse current frequency for bright acid copper, bright Watts nickel and bright gold plating processes, using commercial brighteners and hydrodynamically active agent SA-LFPP. At this frequency, the above pulse plating processes have an excellent leveling ability that is about five, two and ten times better, respectively, than the leveling performance of the corresponding d-c plating with brighteners only. The mechanism explaining the leveling power maximum permits a conclusion concerning the validity of this synergistic effect for all the other bright pulse plating processes.

Also, if the functional properties of metal deposits related to the leveling performance (e.g., corrosion resistance, electrical and tribological properties) could be improved to the same extent as that attained for the leveling power, these properties would be provided by coatings thinner than those produced in d-c bright deposition. In this case, the wide practical application of these plating conditions would lead to considerable reduction in the consumption of precious and expensive metals, such as Au, Ag, Pd, Sn, Ni, Cu, etc., especially in the electronics industry.

The results obtained prove that, under definite pulse plating conditions, that are the same for all plating processes, it is possible to combine successfully the well-known advantages of pulse plating with those of conventional bright d-c electrodeposition and to apply metal coatings with much better decorative and functional properties.

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