# The Influence of Pulse Frequency on the Hardness Of Bright Copper Electrodeposits

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The hardness of copper coatings deposited by direct and pulsed currents were measured. The proprietary bright acid solution used contains an agent, SA-LFPP, having high hydrodynamic activity. This additive, with a pulse frequency of 5 Hz, produced a synergistic effect on initial coating hardness values (about 230 HV). These values remained unchanged for more than 270 days. The results obtained prove the validity of the previously described mechanism of low-frequency pulse plating with brighteners. This mechanism predicts the occurrence of the maximum hardness values at a "limiting" frequency as a result of an optimal matching of the process rates of nuclear formation, brightener adsorption, and incorporation into deposits.

The addition of brighteners and surfactants into plating baths usually results in electrodeposition of bright coatings having hardness (HV) greater than that of coatings produced without additives.<sup>1-5</sup> Hardness is an important property of bright copper deposits, especially for coatings on gravure rolls in the printing industry.<sup>6.7</sup> Modern technologies for electronic engraving of gravure rolls have specific requirements for the properties of electroformed copper foils—a perfectly smooth surface and a hardness of  $205 \pm 20$  kg/mm2. This value must remain constant for a relatively long period. In many cases, however, the hardness of bright copper deposits rapidly decreases over time as a result of spontaneous processes of recrystallization and relaxation.<sup>8</sup>



Fig. 1—Time dependence of hardness for copper deposits from Electrolyte 1.

The research of Stoychev, et al.9 demonstrated that a number of factors, such as composition of the electrolyte, type and chemical nature of organic additives, and directcurrent density, can delay the processes of recrystallization to a considerable extent. These researchers have also observed that retardation of recrystallization is directly related to the amount of carbon-containing substances included in the copper coating. This paper reports the effect of pulse frequency on the hardness of bright copper coatings obtained from baths containing commercially available brighteners THB-6<sup>10</sup> and the specific additive SA-LFPP,<sup>11</sup> characterized by high hydrodynamic activity. Conditions of pulse plating were determined such that the recrystallization processes were maximally retarded and the high initial hardness maintained during the entire period of the research (more than eight months). These optimal conditions were based on a previously determined synergistic effect of pulse frequency, brighteners and the SA-LFPP additive.<sup>11</sup>

## Experimental Procedure

The composition of the electrolytes and the plating conditions are listed in the table. Deposition of copper from these electrolytes was done on rotating disc electrodes with a working area of 0.005 dm<sup>2</sup> and constant speed of 150 rpm. The pulse frequency used in all plating processes ranged from 5 to 40 Hz, and pulse duration (10 msec) was the same for all frequencies. Pulse current density  $\mathbf{i}_p$  was calculated by the relationship

$$i_p = \frac{i_m \left(T_{on} + T_{off}\right)}{T_{on}}$$

where  $\mathbf{i}_{m}$  was an average current density of 12 A/dm<sup>2</sup> for all frequencies used. Thickness for all coatings was about 75  $\mu$ m. Hardness of the copper coatings was measured with an indenter pressure of 50 g.

### Results & Discussion

Figure 1 shows the variation of hardness (HV) over time for deposits obtained from **Electrolyte 1**. The curves indicate that the hardness of copper deposits obtained with DC decreased from 232 kg/mm<sup>2</sup> to 150 kg/mm<sup>2</sup> within the first three days (curve 1), but remained stable at about 140 kg/mm<sup>2</sup> after the 15th day. The relationship of hardness with time changed dramatically with pulse plating. At 5 Hz (curve 2), the initial hardness remained constant for more than 240 days. At 10 Hz (curve 3), the initial hardness remained the same for the first 30 days, then decreased slightly to 210 kg/mm<sup>2</sup> within the following 25 days, remaining at that value until the end of the experiment (240 days).

Considerable changes in the rate of recrystallization took place at 20, 30, and 40 Hz. At 20 Hz, the initial hardness of 232 kg/mm<sup>2</sup> remained the same as that of coatings obtained



Fig. 2—Time dependence of hardness for copper deposits from Electrolyte 2.



Fig. 3—Time dependence of hardness for copper deposits from Electrolyte 3.

with DC and pulse plating at 5 and 10 Hz. It did not change for three days, then began to decrease and, by the end of the 15th day, reached 150 kg/mm<sup>2</sup>. After the 25th day, a stable value of 142 kg/mm<sup>2</sup> was reached that remained the same until the end of the experiment (240th day) (curve 4). With time, similar changes were observed for copper coatings obtained by pulse plating at 30 Hz. The initial hardness was slightly lower (222 kg/mm<sup>2</sup>) (curve 5). The results for 40 Hz (curve 6) were radically different. The coatings had considerably lower initial hardness, 136 kg/mm<sup>2</sup>, that remained stable for the entire period of 240 days.

Figure 2 shows the results of the use of **Electrolyte 2**. Copper coatings obtained with DC at 12 A/dm<sup>2</sup>had low initial hardness (106 kg/mm<sup>2</sup>) that did not change with time (curve 1). Coatings obtained by pulse plating at 5 Hz had initial hardness of 232 kg/mm<sup>2</sup>, similar to **Electrolyte 1** containing PEG. The hardness of these coatings remained stable for more than 270 days (curve 2). At 10 Hz, the hardness of the coatings was greater than those obtained with DC, but lower than those at 5 Hz. The initial hardness of 166 kg/mm<sup>2</sup> remained constant for more than 120 days. Increase of the pulse frequency to 30 and 40 Hz caused decreases in initial hardness, to 150 and 137 kg/mm<sup>2</sup>, respectively. These values showed no change for more than 120 days (curves 4 and 5).

Figure 3 summarizes the results of experiments with **Electrolyte 3**. Unlike **Electrolyte 1**, it contained  $4 \text{ cm}^3/\text{L}$  of the additive SA-LFPP. With this additive, the initial hardness was 232 kg/mm<sup>2</sup>, which did not change over the more than 240 days of the experiment, regardless of the plating method ( DC or pulse) (curves 1-6).

Comparative data analysis of these results, when one electrolyte (3) contained PEG and another (2) did not, led to these considerations:

- The experiments confirmed a conclusion reached by previous investigators<sup>9</sup> that the high values of hardness of bright copper coatings and the long periods of time (up to several months) during which these values remain constant, are related to the carbon incorporated into the coatings. Evidently, the main source of carbon is the PEG.
- 2. The additive SA-LFPP exhibits high hydrodynamic activity that becomes obvious in the reduction of dynamic viscosity  $\mu$  by several times.<sup>11</sup> According to the Nernst-Einstein relation and its modification<sup>12</sup>

$$D = \frac{KT}{\mu},$$

this reduction causes proportional increase of the diffusion coefficient **D** of less mobile organic molecules. As a result of increased diffusion flow of organic compounds to the cathodic surface, the amount of carbon incorporated in the copper deposited from Electrolyte 3 is more than sufficient to obtain high and stable hardness values. Under these circumstances, the hardness of the coatings is not practically dependent on the DC and pulse parameters. The relation between hardness and time is found to be a straight line parallel to the x-axis (Fig. 3). In other words, the presence of hydrodynamically active additives in bright plating baths causes incorporation of sufficient amounts of carbon in the copper deposits and provides for the maintenance of high and invariant (for more than eight months) HV values. If there is no SA-LFPP in the bath, as in Electrolyte 1, the high hardness values remain unchanged only for the 5-Hz pulse frequency. In all other cases, HV values decrease at different rates (Fig. 1).



Fig. 4—Intersection of tendency lines depending on pulse frequency.

Bath Composition & Operating Conditions

		Electrolyte	
	1	2	3
CuSO <sup>4</sup> 5H <sup>2</sup> O	220 g/L	220 g/L	220 g/L
$H^2SO^4$	60 g/L	60 g/L	60 g/L
NaCl	90 mg/L	90 mg/L	90 mg/L
Additives			
Saffronic dye	6 mg/L	6 mg/L	6 mg/L
Dialkyldisulfide derivative	8 mg/L	8Mg/L	8mg/L
Polyethylene glycol			
(MW 3000)(PEG)	220 mg/L	—	220 mg/L
SA-LFPP	_	4 cm <sup>3</sup> /L	4 cm <sup>3</sup> /L
Avg. current density	12 A/dm <sup>2</sup>	12 A/dm <sup>2</sup>	12 A/dm <sup>2</sup>
Pulse duration	10 msec	10 msec	10 msec
Temp	25 °C	25 °C	25 °C
Plating time	30 min	30 min	30 min

3. To explain the above results, it is useful to relate them to a previously described mechanism of leveling in pulsed electrodeposition with brighteners.<sup>11</sup> According to this mechanism, pulse frequency is a major controlling factor in the processes of nuclear formation, crystallization, adsorption, and incorporation of organic additives in the coatings. In this way, through scanning of the pulse frequency from 0 to 40 Hz, with  $T_{on}$  constant, the plating process can be divided into two simultaneous and related processes (Fig. 4). The rate of the first process, nuclei formation, increases with increase of pulse frequency. This results in an increase of active sites on the cathodic surface, where brightener molecules and other organic additives are adsorbed. In the second adsorption process, the surface concentration of brightener species gradually decreases with increase in pulse frequency. At a definite frequency, this concentration becomes insufficient for adsorption and inhibition of the increased number of nuclei. The abscissa of the point of intersection of the lines representing these opposing tendencies defines the pulse frequency optimally matching the rate of both processesnuclei formation on the one hand, and brightener adsorption and incorporation into the coating, on the other.

In these hardness measurements, as well as in leveling power determination, the maximum hardness values are obtained at a pulse frequency of 5 Hz. This coincidence is additional evidence for the assertion that both leveling power and hardness of bright coating are related to the same mechanism of electrocrystallization, adsorption and incorporation of brightener species.

### Conclusions

Under definite conditions, pulse plating of bright copper coatings confers considerable advantages over DC plating in terms of deposits with higher initial hardness (about 230 HV) that remains constant for periods of at least nine months.

The data obtained are another confirmation of the validity of a previously described mechanism of low-frequency pulse plating with brighteners that includes the processes of nuclear formation, brightener adsorption and incorporation in the deposit.

The addition of an agent with high hydrodynamic activity (SA-LFPP) in a bright plating bath enhances the effect of optimally matching the rates of the above processes. This synergism is manifested at a pulse frequency of 5 Hz, at which hardness values are found to be extremely high.

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