Studies of Acid Sulfate Copper Pulse Reversal Current Electrodeposition

By Show-Chin Kou & Aina Hung

Copper electrodeposition is a crucial process in the fabrication of high density build-up multilayer printed circuit boards (PCBs), thus the effects of additives and plating waveforms would provide useful information for future production of PCBs. The effect of additives AC90 and chloride ion on the redox potential and polarization resistance of copper electroplating were evaluated. This revealed an interesting synergistic effect of chloride ion and additive AC-90 with a substantial increase in the polarization resistance. Moreover, copper electrodeposition obtained by direct current, periodic pulse current and periodic pulse reversal current plating in the presence and absence of additive AD-90 were investigated. The thickness, surface morphology, texture, elongation percentage and tensile strength of the copper deposits were evaluated. The copper electrodeposit obtained by periodic pulse reversal current plating exhibited the best macroscopic throwing power among the three protocols based on thickness studies. The X-ray diffraction pattern of this copper deposit was a non-textured random deposit. In addition, this deposit showed desirable properties when compared to Class I copper foil (percent elongation 5.20 %; tensile strength 20.34 kgf/mm^2). With the presence of additive AC-90 in the plating solution, the microscopic throwing power of the copper deposit is improved and a smooth surface morphology of copper deposit was obtained. Copper electrodeposits obtained by periodic pulse reversal current plating would therefore be ideal for future manufacturing of PCBs.

Acid copper sulfate electroplating solutions are the predominant copper electroplating solutions used in the printed circuit industry and in the plating-on-plastics industry after an electroless strike.[1] As the size of electronic devices continues to shrink, high macroscopic throwing power copper electroplating is required to plate the blind microvias in the fabrication of high density build-up multilayer printed circuit boards, PCBs.[2-7]

To achieve high throwing power electroplating, the following basic operation conditions are required: (a) uniform air agitation; (b) equal anode and cathode distance; (c) chemical constituent control; (d) regular carbon treatment; (e) temperature control; (f) contaminant elimination; (g) current density control.[1] There has been a number of studies on the use of modified waveform techniques in presence of certain additives for improving throwing power.[8-13]

Moreover, employment of modern electronics and microprocessor control has permitted great flexibility for programming of the applied waveform in plating techniques. Several such modified waveforms have been available: superimposed alternating current, interrupted direct current, periodic reverse current, pulsed current, periodic pulse reversal current etc.[14,15] The general underlying theory for the effect of modified waveforms is that the double layer or diffusion layer next to the cathode is altered by the waveform, which will subsequently influence the mechanism of electrocrystallization. As the complexity of the waveform increases, it is more difficult to understand how a particular waveform affects the electrodeposition process. There have been many studies regarding the effect of special waveforms on the electrodeposit characteristics, including reduction of deposit porosity, higher purity, finer grain deposits, lower electrical resistance deposits, improved mechanical properties and enhanced throwing power.[8-13,16,17] In particular, various aspects of pulse plating have been investigated, such as limiting current density, power consumption, and the effect of pulse current on deposit properties.[9-13] Also, many studies have focused on periodic pulse reversal current plating, including the cathode efficiency, the polarization behavior and the mass transfer of copper deposition.[18-20] Although the basic principles governing the mechanism of pulse plating and periodic pulse reversal current plating remain controversial, we have previously demonstrated the utilization of periodic pulse reversal current plating for generating high macroscopic throwing power deposits in the plating of microvias.[21]

As miniaturization of electronic device continues, the importance of the copper deposition process increases because the copper deposit becomes a higher percentage of the finished laminate when compared to resin or glass, as the dielectrics become thinner. The production of high-quality electronic devices relies heavily, therefore, on the electrical and mechanical properties of the copper deposit. The texture of the deposit influences both electrical and mechanical properties, while the surface morphology is related to the downstream processing of the device. Thus, the texture, surface morphology, percent elongation and tensile strength of the electrodeposition of copper from acid copper sulfate electroplating baths by direct current plating, periodic pulsed current plating, and periodic pulse reversal current plating are presented in this report. Because additives such as sulfur- or nitrogen-containing organic compounds and chloride have been widely used in copper electroplating, the polarization resistance of electroplating solutions containing chloride and commercially available AC-90 were also studied as an indicator for the throwing power of the deposition and effectiveness of the corresponding additives.

Experimental Procedure

The copper electroplating solution employed in this experiment consisted of 75 g/L $CuSO_4 \cdot 5H_2O$, 95 g/L of 1.84 sp. grav. H_2SO_4 and 20 ppm chloride ion, purified by charcoal and dummy plated at 0.3 A/dm^2 for three hr. The additive used was 2.5 mL/L of AC-90.[a]

All the electrochemical studies were performed by a potentiostat interfaced with a personal computer. For cyclic voltammetry and polarization resistance studies, the working electrode was a copper disk of one cm^2 surface area, the reference electrode was an SCE and the counter-electrode was of platinum. The cyclic voltammograms were taken by scanning between -1.0 V and +1.0 V referred to open-circuit potential, with 100 mV/sec scan rate. The reduction potential of copper electroplating at fixed current density of 30 mA/cm^2 was recorded by chronopotentiometry during direct current electrodeposition.

Deposition of copper was performed at room temperature for one hr in a 267-mL Hull Cell, using a copper anode (containing 0.03% phosphorus) and an aluminum cathode, by direct current, periodic pulse current, or periodic reversal pulse current (Table 1). The direct current was 2 A. The pulse period of the periodic pulse plating was 21 msec, the duty cycle was 0.952, the cathodic current density was 2 A/dm^2, with dimensionless pulse current density of 3. The pulse period of the periodic reversal pulse plating was 21 msec, the cathodic duty cycle was 0.952, the cathodic current density was 2A/dm^2, with dimensionless anodic reversal pulse current density of 3. During deposition, the plating solution was stirred by air agitation. After deposition, the copper foil was separated from the aluminum cathode and divided into four equal sections. The thickness of each section was measured.[b] The measurement was made using a magnetic induction probe.[c] Each sample was measured more than four times and the average value was reported. The surface morphology of each section was examined by scanning electron microscope.[d] The texture of each section was investigated by scanning from 40° to 140° at a scan rate of 4°/Min with an X-ray diffractometer.[e]

The samples prepared for tension test were deposited at room temperature using an aluminum cathode and a 0.03% phosphor copper anode. The direct current was 3 A/dm^2. The pulse period of the pulse plating was 21 msec, the duty cycle was 0.952, the cathodic current density was 3 A/dm^2, with dimensionless pulse current density of 3. The pulse period of the periodic reversal pulse plating was 21 msec, the cathodic duty cycle was 0.952, the cathodic current density was 3 A/dm^2, with dimensionless anodic reversal pulse current density of 3. The percent elongation and tensile strength of the test specimen were measured according to the standard test methods of ASTM E-35-87 with a testing machine.[f] The load cell used was 2500 kgf and the speed of testing was 5.8 mm/min.

Results & Discussion

Electrochemical Study of Copper Electroplating Solution

The redox potential and polarization resistance of copper electroplating solutions in the absence and presence of additive AC-90 and chloride ion were measured. The reduction peak potential of the copper ion (-O.35 V) was not affected by chloride ion, but this potential was shifted to -0.42 V with the presence of additive AC-90 in the electroplating solution. The oxidation peak potential of copper was more positive and the oxidation current was higher in the presence of chloride ion (no chloride: 0.60 V, -0.73 A; with chloride: 0,65 V, -0.82 A). This indicates that the chloride ion affects the copper oxidation thermodynamically and kinetically. Interestingly, when both chloride and AC-90 were present in the copper electroplating solution, the reduction peak potential and the oxidation peak potential of copper were shifted and the oxidation current also increased (Fig 1). The average reduction potential of copper electroplating at a fixed current density of 30 mA/cm^2 was -0.4 V with no chloride or AC-90, but the average reduction potential was shifted to -0.52 V when AC-90 was added to the plating solution.

According to Ohm's law, the current distribution in plating is affected by the polarization resistance of the double layer as well as the relative position of anode and cathode. When the polarization resistance increases, the current is more evenly distributed, which would result in higher throwing power. The polarization resistance of the acid copper sulfate electroplating solution with no additive was approximately 10.0 Ω. The polarization resistance remained unchanged with the addition of chloride ion in the electroplating solution, but the polarization resistance increased significantly when AC-90 was added to the plating solution (56.7 Ω). When both chloride ion and AC-90 were added, the polarization resistance increased to 107.2 Ω. The synergistic effect of chloride ion and AC-90 resulted in a large increase of the polarization resistance of the double layer. This drastically improved the microscopic throwing power and yielded a bright deposit.

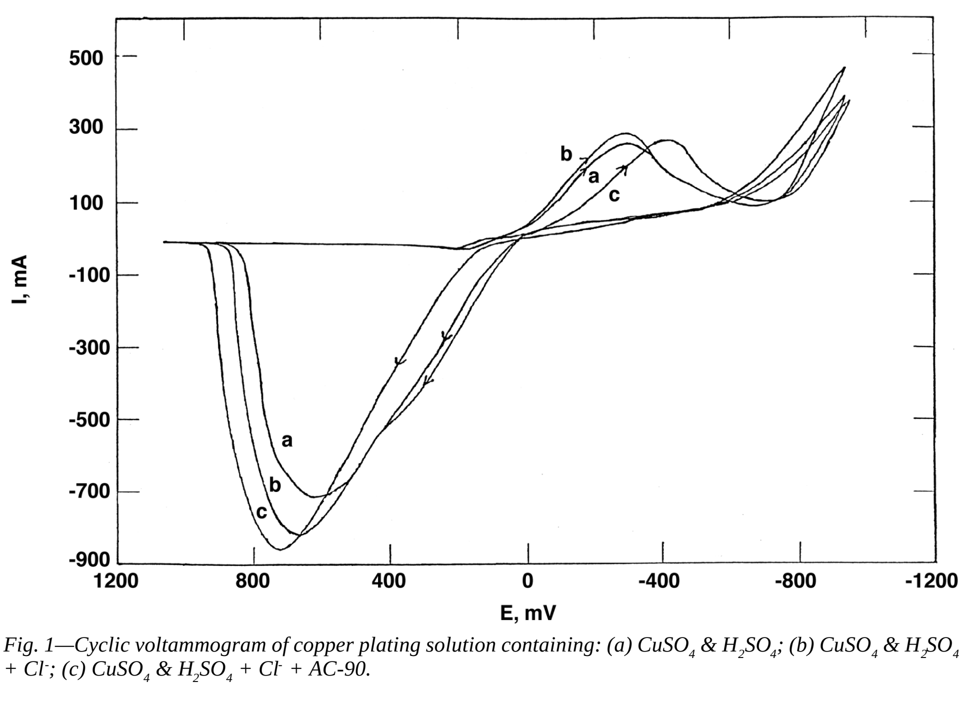

Fig. 1—Cyclic voltammogram of copper plating solution containing: (a) $CuSO_4$ & H_2SO_4; (b) $CuSO_4$ & H_2SO_4 + Cl^-; (c) $CuSO_4$ & H_2SO_4 + Cl^- + AC-90.

Thickness of Copper Electrodeposit

Direct current plating, periodic pulse current plating and periodic pulse reversal current plating were employed separately in the presence and absence of additive AC-90 for generating the copper deposits (Table 1).

[a] Uamura
[b] MP40 Dualscope, Fisher
[c] Model EGB1.3
[d] Model 5210, Bransonic
[e] Model XD-5, Shimadzu
[f] Model 4469, Instron

The average thickness of the copper electrodeposits is summarized in Table 2. The thickness of the copper deposits increased with current density for all deposition schemes, which is consistent with Faraday's law. For the same current-density section using the same plating solution, the order of thickness for copper electrodeposits was as follows: periodic pulse > direct > periodic pulse reversal. This trend was observed because the pulse current increased the thickness of the deposit during the pulse period by depositing more copper compared to direct current, and the periodic pulse reversal current decreased the thickness of the deposit during the pulse reversal period by dissolving some of the copper deposit. As anticipated *a priori*, the difference between the deposit thickness on the high-current-density section (80 mA/cm^2) and the low-current-density section (10 mA/cm^2) follows the trend: periodic pulse reversal current plating (scheme 1) < direct current plating (scheme 2) < periodic current plating (scheme 3). These results indicated that the periodic pulse reversal current increased the macroscopic throwing power of the copper solution and the periodic pulse current decreased it compared to direct current in the current density range of 10 to 80 mA/cm^2. Further, for the same current density and method of deposition, a brighter and thinner deposit was obtained with the presence of additive AC-90 in the plating solution. This suggests that addition of AC-90 improves the throwing power microscopically (see below).

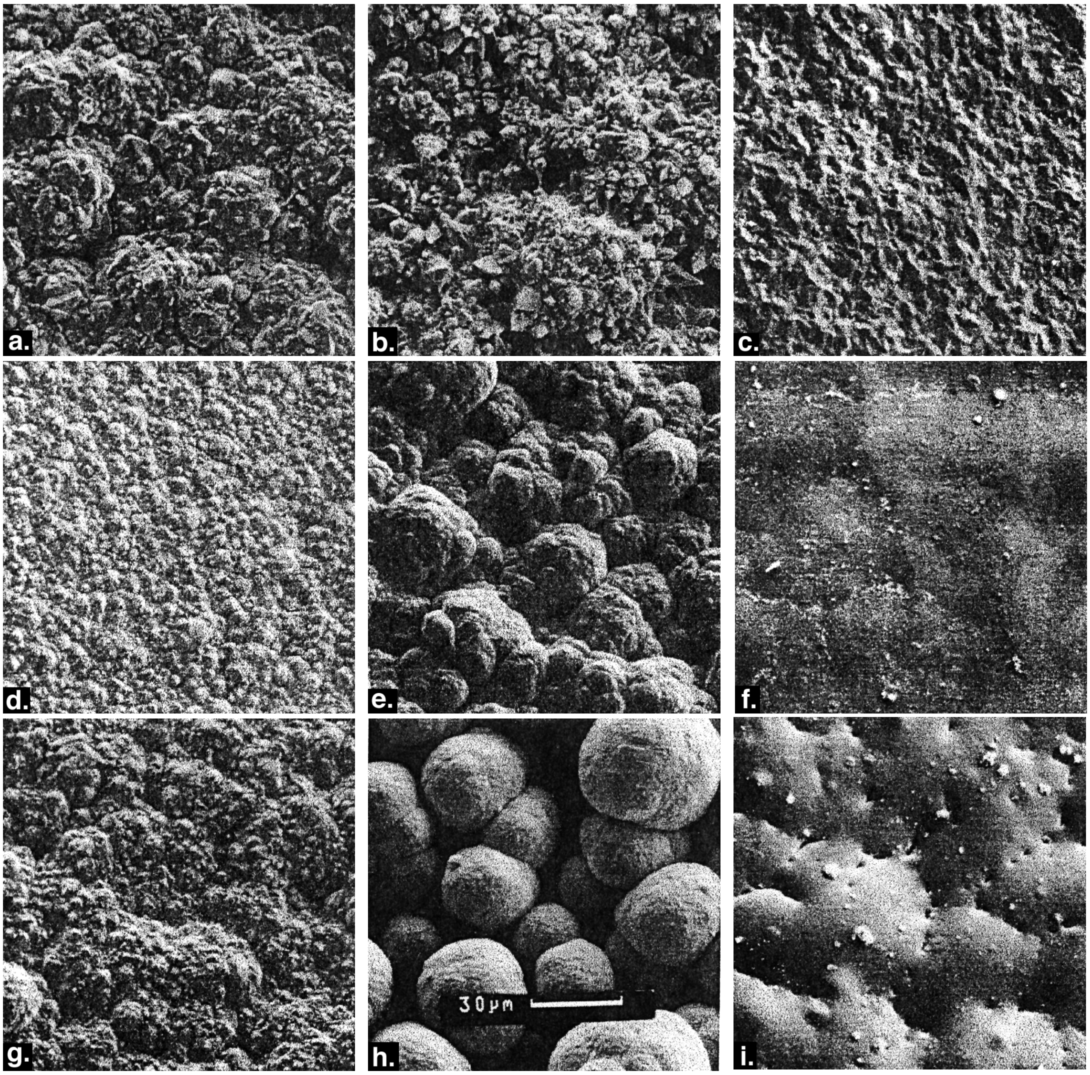

Fig. 2—Surface morphology of copper electrodeposits from:
At 10 mA/cm^2: (a) scheme 1; (d) scheme 2; (g) scheme 3
At 40 mA/cm^2: (b) scheme 1; (c) scheme 4; (e) scheme 2; (f) scheme 5; (h) scheme 3; (i) scheme 6.

Surface Morphology of Copper Electrodeposit

The surface morphology of the electrodeposits was studied by scanning electron microscopy to assess the microscopic throwing power (Fig. 2). Compact imperfect crystalline deposits were observed for the surface of samples deposited by direct current plating in the absence of additives (scheme 2) with a current density of 10 mA/cm^2 (Fig. 2d) and 40 mA/cm^2 (Fig. 2e). Moreover, the grain size increased with increasing current density. Additionally, the copper grains were hemispherical and nodular when plated in the current density section of 40 mA/cm^2 (Fig. 2e). With additive AC-90 in the plating solution (scheme 5), the direct current plating deposits were bright in the current density range of 10 to 60 mA/cm^2. A smooth surface morphology for the copper deposit was obtained by scheme 5 in the current density section of 40 mA/cm^2 (Fig. 2f), corroborating that the influence of additive AC-90 on throwing power is microscopic.

With periodic pulse current in the absence of additives (scheme 3), the copper grain size increased considerably with increasing current density. The individual crystals of the copper deposit from scheme 3 in the current density section of 10 mA/cm^2 were imperfect (Fig. 2g). Also, the copper deposit from scheme 3 with current density of 40 mA/cm^2 contained loose spherical grains (Fig. 2h). Additive AC-90 also modified the surface morphology of the copper deposit microscopically. With additive AC-90 in the plating solution (scheme 6), the pulse current deposits were bright with a current density between 10 and 60 mA/cm^2. The surface morphology of the copper deposit by scheme 6 with a current

Table 1
Schemes for Copper Electrodeposition

Scheme	Additive AC-90 in Plating Solution (2.5 mL/L)	Method of Copper Plating
1	None	Periodic Pulse Reversal Plating
2	None	Direct Current Plating
3	None	Periodic Pulse Current Plating
4	Yes	Periodic Pulse Reversal Plating
5	Yes	Direct Current Plating
6	Yes	Periodic Pulse Current Plating

Table 2
Average Thickness of Copper Electrodeposits
μm

Current Density (mA/cm^2)	Scheme 1	2	3	4	5	6
10	33	42	44	33	37	43
20	40	46	55	36	43	51
40	48	60	67	46	56	60
80	61	76	N/A*	59	72	82

* Powder

Table 3
Average Percent Elongation & Tensile Strength

Scheme of Deposition	1	2	3	4	5	6	Class 1 Copper
Percent Elongation	5.20	4.65	—	5.16	4.19	2.71	3.00
Tensile Strength (kgf/mm^2)	20.34	31.62	—	17.89	30.06	25.55	21.14

density of 40 mA/cm^2 is shown in Fig. 2i. There were some pinholes on the smooth surface and hemispherical grains beneath could also be noticed.

With periodic pulse reversal current, the individual crystals of the deposits were more perfect than those obtained by either direct or periodic pulse current plating using the same solution. In the absence of additives (scheme 1), there was no significant difference in the size of the crystallite between the deposit from the 10 mA/cm^2 section (Fig. 2a) and the deposit from the 40 mA/cm^2 section (Fig. 2b), indicating that such deposits have a higher microscopic throwing power compared to those obtained by direct or pulse current plating. Additionally, both hemispherical and secondary nucleation of copper deposits were observed. With the presence of additive AC-90 in the plating solution (scheme 4), the surface of the periodic pulse reversal current deposit was dull and concave when it was obtained with a current density between 10 and 80 mA/cm^2. The surface morphology of the copper deposit obtained by scheme 4 in the 40 mA/cm^{2}current density section is shown in Fig 2c. The deposit was smoother than those obtained from the plating solution without additive. This again supports the conclusion that additive AC-90 serves to modify the surface morphology of the copper electrodeposit and influence the throwing power microscopically. These results indicate that the copper plating solutions used for electrodeposits obtained by periodic pulse reversal current plating exhibit the highest microscopic throwing power compared to direct or periodic pulse current plating.

Texture of Copper Electrodeposit

To determine the degree of preferred orientation, all the relative intensities of the X-ray diffraction patterns were acquired and compared with the Powder Diffraction File (PDF) number 4-836 of the Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data card for randomly oriented powder copper.[22] The X-ray diffraction patterns were similar for the same scheme of electrodeposition used in the 267-mL Hull Cell at various different current density sections except that the degree of preferred orientation for scheme 2 and scheme 4 were stronger at the higher-current-density section.

When there was no additive in the plating solution, direct current plating resulted in a textured deposit (scheme 2). The X-ray diffraction pattern of this deposit showed that the major preferred grain orientation was 220, and the minor preferred orientation was 331. The copper deposit obtained from periodic pulse reversal current plating in a plating solution without additive (scheme 1) was random, probably because in the pulse reversal interval, the copper deposit was redissolved, mostly at the high-current-density section, (*i.e.*, the crystal fast-growing, low-resistance section). The deposit obtained from periodic pulse current in a plating solution without additive (scheme 3) was also random, possibly because during pulse periods, the electron transfer rate was much faster than the mass transport rate. The crystal could not, therefore, be grown continuously in a certain direction. The adsorption of additives on the high-current-density site increased the polarization resistance, thus slowed deposition at the high-current-density site, resulting in a randomly oriented copper deposit for direct-current plating and pulse plating (schemes 5 and 6, respectively). In other words, the leveling effect of the additive resulted in randomly oriented copper deposits for periodic reversal current and pulse current. With additive in the plating solution, however, adsorption of the additive on the high-current-density site prohibited the redissolution of copper from that site during the pulse reversal interval (scheme 4), resulting in a textured deposit. The major preferred grain orientation was 220, and the minor preferred orientation was 331 for this deposit.

Deposit Properties

In the production of high-density multilayer PCBs, the higher elongation and tensile strength of a copper electrodeposit can provide more fatigue resistance to copper cracking during thermal cycling or thermal shock of the board and improve the process window for manufacturing. The average percent elongation and tensile strengths of the various copper electrodeposits are listed in Table 3. The properties of Class 1, one-ounce, traditional electrodeposited copper foils that meet the requirements of IPC-ML-150 are also listed for comparison.[2]

The percent elongations of copper obtained by different plating schemes exhibit the following trend: periodic pulse reversal current plating (schemes 1 and 4) > direct current plating (schemes 2 and 5) > periodic pulse current plating (scheme 6). The copper electrodeposit obtained by periodic pulse current plating without additive in the plating solution (scheme 3) was extremely fragile. The percent elongations of all the copper electrodeposits obtained from periodic pulse reversal current plating and direct current plating were higher than that of Class 1, one ounce traditional electrodeposited copper foils. The tensile strengths of copper electrodeposits obtained from periodic pulse reversal current plating (schemes 1 and 4) were comparable to that of Class 1 one-ounce traditional electrodeposited copper foils. The tensile strengths of copper electrodeposits obtained from direct-current plating (schemes 2 and 5) and periodic pulse current plating (scheme 6) were greater than Class 1 one-ounce traditional electrodeposited copper foils. In comparison with the properties of such foils, the high throwing power copper electrodeposits obtained from periodic pulse reversal current plating are potentially useful for the manufacture of high-density PCBs.

Conclusions

Periodic pulse reversal current improved the macroscopic throwing power of the plating solutions and periodic pulse current decreased it, compared to direct-current plating in the current density range of 10 to 80 mA/cm^2. The synergistic effect of chloride ion and additive AC-90 resulted in a large increase of polarization resistance of the double layer. Moreover, with the presence of additive AC-90 in the plating solution, the microscopic throwing power of the solution was improved and a deposit with brighter and smoother surface morphology was obtained in the current density range of 10 to 60 mA/cm^2 for all methods of electrodeposition. The copper deposit obtained from periodic pulse reversal current plating in the plating solution without additive was a non-textured random deposit. Addition of additive AC-90 resulted in a textured deposit with a major preferred orientation of 220. The percent elongation and tensile strength of the deposit obtained from periodic pulse reversal current plating was 5.20 percent and 20.34 kgf/cm^2, respectively. Thus, the high throwing power copper electrodeposit obtained by periodic pulse reversal current would be ideal for the manufacturing of high density PCBS.

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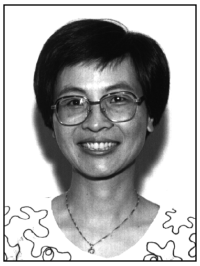

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