A Robust Palladium-Free Activation Process for Electroless Copper Plating

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ABSTRACT

A new activation process for electroless copper plating has been developed, which does not require the use of a palladium-based activation bath as typically employed in the plating industry. The activation bath of the new process described herein is entirely free of palladium and is based on colloidal metallic copper particles, which are nanoscopic in size. This bath can also be readily analysed and controlled. The new copper-based activation bath can be operated in such a way that colloid agglomeration and colloid oxidation are efficiently and effectively suppressed, while electroless copper plating quality and electroless copper bath stability is maintained. In addition, the new activation bath can be operated for several weeks without any detectable deterioration in electroless copper plating performance. Furthermore, acrylonitrile butadiene styrene (ABS) and FR4 coupons treated with the new copper-based colloidal activation bath can be vigorously rinsed with water for several minutes prior to immersion in the electroless copper bath without loss of plating quality. The new activation process performs comparably to an established palladium-based process operated at typical vertical equipment immersion times. Even though the electroless copper plating initiation is somewhat delayed for the new copper-based activation process, the final electroless copper deposit thicknesses are the same for both the new process and the palladium-based reference process. The adhesion of the electroless copper deposit obtained with the copper-based activation process is also similar to that obtained with the palladium-based reference activation system. Moreover, the electroless copper coverage performance of the new copper-based activation process, as determined by the backlight test, is comparable to that of the palladium-based reference process.

INTRODUCTION

Electroless copper plating is an indispensable part of printed circuit board (PCB) manufacture and its application ranges from the production of relatively simple double-sided boards for the low-cost electrical device market to the production of highly sophisticated boards for the package substrate sector. Regardless of the complexity of the PCB to be processed, electroless copper plating cannot take place without prior activation of the PCB, which invariably entails contact of the PCB with a solution containing palladium, either in colloidal or in ionic form. If the latter form is used, an additional step is required to reduce the palladium to its elemental form so that it may function as an activator.

Although the use of palladium-based activators in the production of PCBs spans several decades, the high cost and unpredictable price development of palladium metal persist as large thorns in the sides of PCB manufacturers. In 2018 and 2019, the price at which palladium was sold repeatedly exceeded that of gold and hence the interest in alternatives to palladium as activators has been rekindled.

Anyone familiar with electroless copper plating might conclude that copper is an obvious alternative to palladium for the purpose of activation due to the autocatalytic properties of electroless copper baths. These properties, along with the significantly lower price of copper metal compared to palladium, have been and continue to be reason enough for researchers to explore the capacity of copper to function as an activator for electroless copper plating. An activation system based on a copper-tin colloid was patented more than 40 years ago. [1] Luke wrote of the merits of copper colloids in the manufacture of PCBs in the early 1980s. [2] A brief review of the younger literature also reveals examples in which copper and other metals have been investigated as activator alternatives to palladium. [3-10]

Even though the aforementioned copper-tin colloid [1] has seen some commercial success, [11] to the best of our knowledge, practically all industrially relevant activators for the electroless copper plating of PCBs still rely exclusively on palladium. This suggests that the palladium-free systems are lacking in one or more aspects compared to palladium-based systems and are therefore not fully satisfactory substitutes.

We have been exploring the suitability of colloidal and ionic copper as activators for electroless copper plating in our laboratories since the late 2000s and although we have been able to develop at least transiently functioning copper-based activation systems, our efforts have been repeatedly thwarted by the lack of activator bath stability and the poor resistance of activated coupons to rinsing with water. Recently, we focused our attention on the development of a stable colloidal copper activation system and were able to resolve the issue of copper colloid agglomeration in the activator bath as well as the issue of water-rinse-induced deactivation of the copper colloid adsorbed on the PCB coupons. The electroless copper plating results obtained using this new, stabilized and rinse-resistant copper colloid activation system are presented herein.

EXPERIMENTAL DETAILS

Test Coupons

Acrylonitrile butadiene styrene (ABS) and FR4 test coupons (Table 1) were used for the assessment of the quality of the electroless copper deposit. The parameters tested were appearance, blistering, deposit thickness and coverage.

TABLE 1. BASE MATERIALS USED FOR THE ASSESSMENT OF ELECTROLESS COPPER DEPOSIT QUALITY AND THE CORRESPONDING PARAMETERS TESTED.

Material Name	Material Type	Desmeared	Test Parameter
Metak	ABS	Yes[a]	Appearance; Blistering
Panasonic MC100EX	Bare FR4[b]	No	Appearance; Deposit thickness
NanYa NP140	Copper-clad FR4[c]	Yes[a]	Coverage
Isola IS410	Copper-clad FR4[c]	Yes[a]	Coverage

[a]Desmear conditions are given in the following subsection. [b]Unstructured and no copper inner layers. [c]1 mm through holes without copper inner layers.

Desmear Conditions

Coupons requiring desmear were desmeared using the Securiganth® series of treatment baths listed in Table 2, which were operated on a beaker-scale (1-2 L) at typical bath settings. [12]

TABLE 2. DESMEAR CONDITIONS APPLIED TO ABS AND FR4 COUPONS.

Step[a]	Bath	Immersion Time [s]
1	Securiganth® P Sweller	120 (ABS); 300 (FR4)
2	Securiganth® P P-Etch	240 (ABS); 600 (FR4)
3	Securiganth® P Reduction Cleaner	120 (ABS); 300 (FR4)

[a]Tap water rinse of approximately 60 s between each step.

Pretreatment, Activation and Electroless Copper Conditions

Palladium-Based Reference System: All reference system coupons were subjected to treatment with the Securiganth®, Neoganth® and Printoganth® series of baths shown in Table 3, which were operated on a beaker-scale (1-2 L) at typical bath settings. [12]

Palladium-Free Test System: All test system coupons were subjected to treatment with the baths shown in Table 4, which were operated on a beaker-scale (1-2 L). The commercially available Securiganth® and Printoganth® baths were operated at typical bath settings. [12] All other baths are not yet commercially available and were operated as indicated in Table 4. The colloidal copper activator was prepared *in situ* by adding a certain reducing agent to a stirred solution comprising copper sulfate and a certain ligand. [13]

Dynamic Light Scattering (DLS) Measurements

Samples of the neat colloidal copper activator bath solution were transferred to disposable cuvettes and analyzed using a Zetasizer Nano-ZS instrument (Malvern Instruments Ltd., Malvern, UK). Measurements were performed at a measurement angle of 173° (backscatter mode) at a constant temperature of 21 °C (equilibration time = 120 s). Z-average and polydispersity index values, as well as intensity-size and volume-size distribution graphs were recorded. The presented plots are averages of 3 individual measurements with a delay of 10 s in between, each measurement typically consisting of 5 runs with run durations of 10 s.

TABLE 3. PRETREATMENT, ACTIVATION AND ELECTROLESS COPPER CONDITIONS APPLIED TO ABS AND FR4 REFERENCE SYSTEM COUPONS.

Step[a]	Bath	Immersion Time [s]
1	Securiganth® 902 Cleaner	240
2	Securiganth® Etch Cleaner SPS	60
3	Neoganth® B Pre Dip	60
4	Neoganth® 834 Activator	240
5	Neoganth® Reducer P-WA S	180
6	Printoganth® PV Electroless Copper	1200

[a]Tap water rinse of approximately 60 s between each step, except between steps 3 and 4.

TABLE 4. PRETREATMENT, ACTIVATION AND ELECTROLESS COPPER CONDITIONS APPLIED TO ABS AND FR4 TEST SYSTEM COUPONS.

Step[a]	Bath	Conditions	Immersion Time [s]
1	Securiganth® 902 Cleaner	Typical[b]	240
2	Securiganth® Etch Cleaner SPS	Typical[b]	60
3	Conditioner	pH 11.5; 50 °C[c]	240
4	Colloidal copper activator	pH 4.5; 22 °C[c]	240
5	Printoganth® PV Electroless Copper	Typical[b]	1200

[a]Tap water rinse of approximately 60 s between each step. [b]See reference [12]. [c]See reference [13].

RESULTS AND DISCUSSION

Colloidal Copper Activator

The challenge in working with metallic copper colloids is to overcome their tendency towards oxidation and agglomeration. We have succeeded in developing a system in which the oxidation and agglomeration of the copper particles are effectively suppressed, thereby enabling activator baths based on these particles to be operated for several weeks. [13] The size of the copper particles in the bath can be directly and easily determined by DLS measurements and the concentration of copper in the bath can be readily determined by atomic absorption spectroscopy (AAS).

The intensity-size and volume-size distribution graphs of a sample of the colloidal copper activator bath are depicted in Figure 1. It is evident from these graphs that the copper colloid consists almost exclusively of particles of nanoscopic dimensions. The Z-average and polydispersity index values are 13 nm and 0.271, respectively.

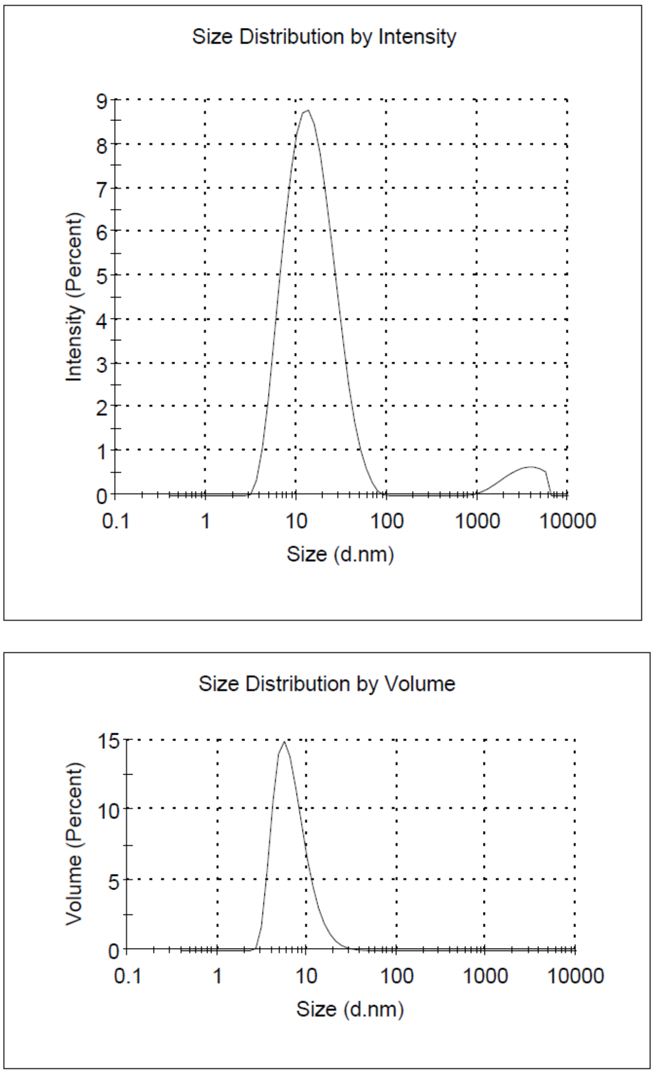

FIGURE 1. AVERAGED INTENSITY-SIZE (TOP) AND VOLUME-SIZE (BOTTOM) DISTRIBUTION GRAPHS OF A COPPER COLLOID BATH SAMPLE.

Electroless Copper Deposit Quality

The appearance of the electroless copper deposit obtained using the colloidal copper activator is illustrated in Figure 2. The deposit colour on the copper-activated ABS and FR4 coupons is indistinguishable from that of the palladium-activated reference coupons. The deposit thickness on the FR4 coupons, determined by complexometric titration, is 1 µm, both for the palladium-activated as well as the copper-activated coupons, even though the copper-activated coupons demonstrate a somewhat delayed electroless copper initiation.

Table 5 contains the electroless copper coverage results on copper-activated FR4 material, as determined by the backlight test. The colloidal copper activator bath was operated for several days and backlight coupons were activated and plated at given intervals. The coverage results of the copper-activated coupons are typically between D9 and D10 (D10 = perfect coverage; D1 = no coverage) and therefore comparable to those of the palladium-activated reference coupons (D9-D10).

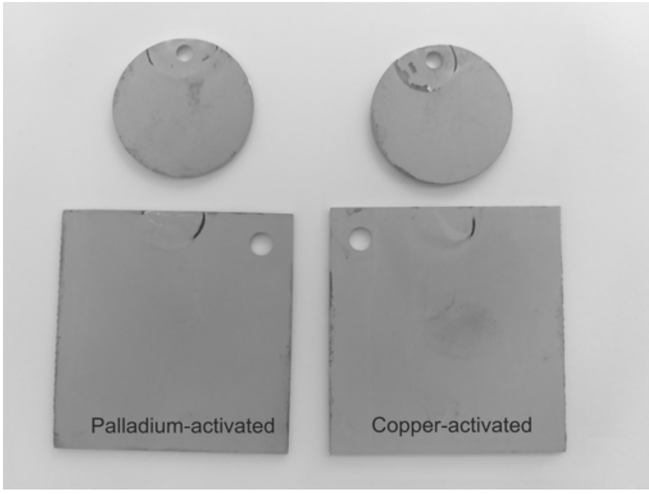

FIGURE 2. ELECTROLESS COPPER APPEARANCE ON ABS (TOP) AND FR4 (BOTTOM) COUPONS.

TABLE 5. COVERAGE RESULTS OF COPPER-ACTIVATED FR4 COUPONS.

Day	Coverage Result [D][a]
1	10
4	9.5
6	9.5
10	9.5
12	9.5

[a]Palladium-activated reference coupons typically show coverage results between D9 and D10.

Images of copper-activated coverage coupon through holes after plating and cross-sectioning, as observed during the backlight test, are compared with those of a palladium-activated through holes in Figure 3 (see next page). It is clear from the images that the coverage performance of the copper-colloid-based system is indistinguishable from that of the palladium-based system.

SUMMARY AND CONCLUSIONS

The results presented herein demonstrate that a robust, copper-colloid-based activation system for electroless copper deposition has been developed. The new palladium-free system yields electroless copper plating results comparable to a commercially established, ionic-palladium-based system regarding coverage and deposition rate performance. Furthermore, the tendency of the colloidal copper to agglomeration in the activator bath and to oxidation on the activated PCB during rinsing are effectively suppressed. The colloidal copper activation system presented herein may therefore be regarded as a viable substitute for palladium-based activation systems.

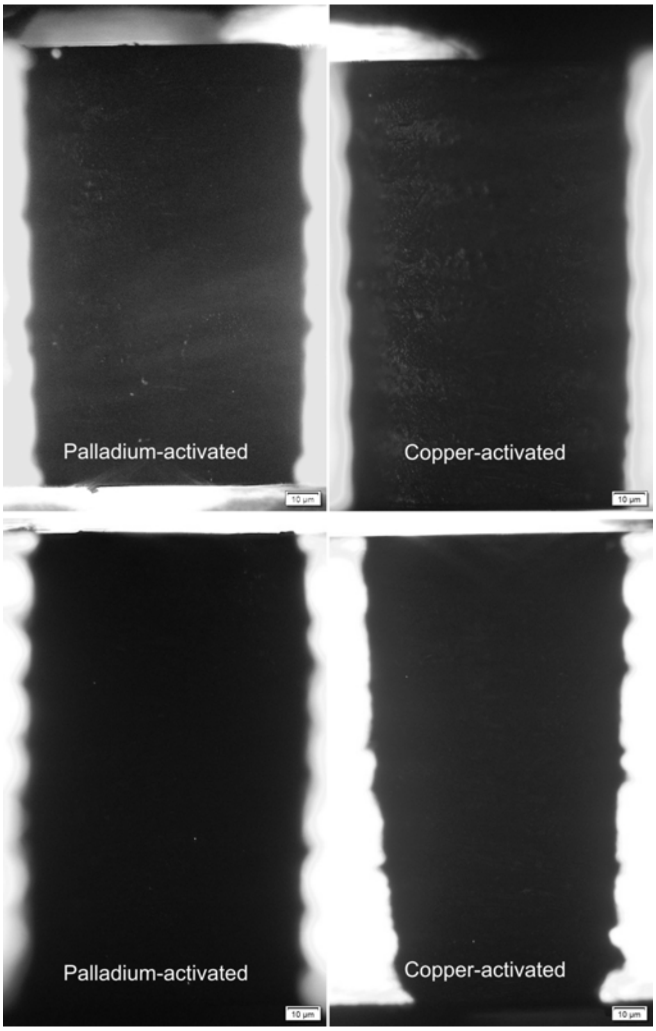

FIGURE 3. IMAGES OF ISOLA IS410 (TOP) AND NANYA NP140 (BOTTOM) COVERAGE COUPON THROUGH HOLES AFTER PLATING AND CROSS-SECTIONING, AS OBSERVED DURING THE BACKLIGHT TEST.

REFERENCES

[1] N. Feldstein, U.S. Patent 3,993,799, 1976.

[2] D. A. Luke, *Transactions of the Institute of Metal Finishing*, 1982, vol. 60, pp. 97-101.

[3] M. Charbonnier, M. Romand, Y. Goepfert, D. Leonard, M. Bouadi, *Surface and Coatings Technology*, 2006, vol. 200 (18-19), pp. 5478-5486.

[4] M. Charbonnier, M. Romand, Y. Goepfert, *Adhesion Aspects of Thin Films*, Ed.: K. L. Mittal. Leiden: VSP, 2007, pp. 111-137.

[5] N. Inagaki, H. Kimura, *Journal of Applied Polymer Science*, 2009, vol. 111(2), pp. 1034-1044.

[6] X. Wang, *Advanced Materials Research*, 2012, vol. 548 (Material and Manufacturing Technology III), pp. 54-57.

[7] L.-M. Luo, Z.-L. Lu, X.-M. Huang, X.-Y. Tan, X.-Y. Ding, J.-G. Cheng, L. Zhu, Y.-C. Wu, *Surface and Coatings Technology*, 2014, vol. 251, pp. 69-73.

[8] R. E. Litchfield, J. Graves, M. Sugden, D. A. Hutt, A. Cobley, *IEEE 16th Electronics Packaging Technology Conference*, 2014, pp. 235-240.

[9] J. E. Graves, M. Sugden, R. E. Litchfield, D. A. Hutt, T. J. Mason, A. J. Cobley, *Ultrasonics Sonochemistry*, 2016, vol. 29, pp. 428-438.

[10] N. Nobari, M. Behboudnia, R. Maleki, *Applied Surface Science*, 2016, vol. 385, pp. 9-17.

[11] C. A. Deckert, *Plating & Surface Finishing*, 1995, March issue, pp. 58-64.

[12] The products and technical data sheets required for making up and operating the commercial treatment baths named herein are available from Atotech Deutschland GmbH.

[13] A patent application has been filed and further details on bath compositions and modes of operation cannot be revealed at this point in time due to confidentiality reasons.