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Optimization of Decorative Acid Copper Plating Solutions for Plating on Plastics Applications

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Introduction

Acid copper electrodeposition is an important metal finishing operation used extensively on both metal and plastic substrates, in a wide variety of industrial and electronic applications (1).

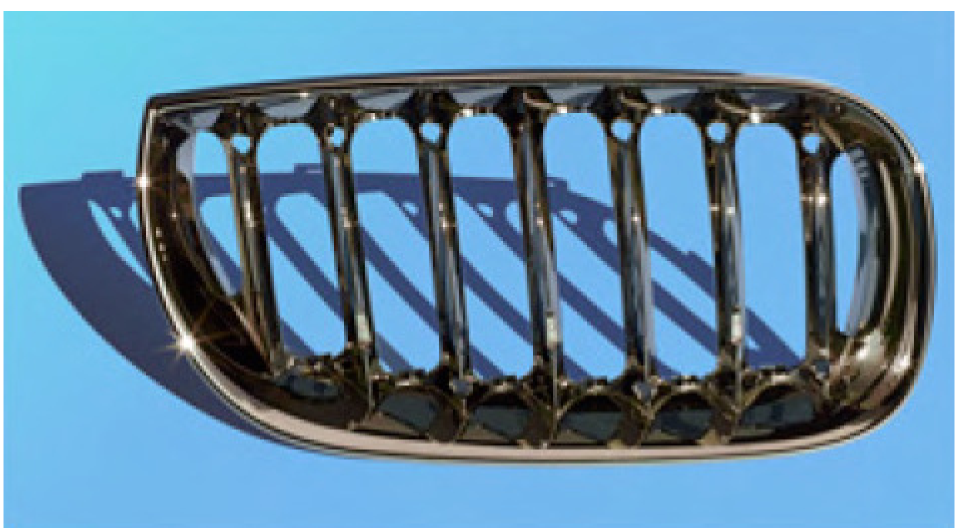
The physical and cosmetic properties of the plated copper deposit are controlled by the presence of specific combinations of organic additives, functioning in combination with the electrolyte inorganic components and bath operating conditions. The deposit's physical properties, which can be adjusted by these means, include tensile strength, ductility, hardness, stress, resistivity and grain structure. In addition, deposit cosmetic properties, such as brightness, throwing power and leveling are profoundly influenced by the combination and concentration of organic additives in the system.

For decorative plating on plastics applications, a combination of an initial deposit of electroplated copper with a subsequent layer of electrodeposited nickel is very widely used for industrial and automotive components. The copper layer applied is typically thicker than the nickel layer, with a ratio of copper to nickel of approximately 1.35:1.

In such applications, the copper layer is primarily responsible for improving the surface smoothness, brightness and coating ductility of the part and also plays a larger role in ensuring that the ductility of the overall coating meets both physical durability and corrosion resistance requirements.

Since plastic parts often have complex geometries (as illustrated in Figure 1), it is necessary for the copper electroplating system to be capable of providing a uniformly bright and smooth surface on a combination of external and recessed areas. Since the external and recessed areas will plate at substantially different local current densities (CD), copper electroplating baths that are capable of delivering excellent leveling and uniform brightness, even at low current densities and, consequently, low deposition thicknesses, are particularly suitable for plating on plastics applications.

Figure 1: Example of Plating on Plastics Substrate



Proper selection of the appropriate copper electroplating system for a particular application first requires a clear definition of the physical performance properties necessary to meet the end-customer needs. Table 1 shows examples of attributes that electrolytic copper plating baths for plating on plastics applications are required to possess.

Table 1: Electrolytic Copper: Critical Attributes for Plating on Plastics Applications

Attribute	Requirement Target
Surface Leveling	Rapid leveling, even at low deposit thicknesses
Surface Brightness	Highly reflective surface across wide plating CD range
Bath Life	Long life, with consistent deposit properties
Run to Run Variability	Uniform surface appearance of finished parts
Surface Smoothness	Plated surface free of cosmetic defects
Process Compatibility	Compatible with subsequent plating processes
Process Control	Precise and accurate methodologies
Adhesion after Baking	Meet end-user specification

Once a list of requirements has been created, assessment of plating system performance versus those targets must be carried out.

Such assessments are very often carried out in two phases. Initially, samples plated in freshly prepared baths are compared and the data used to differentiate between those products that meet all the requirements and those that fail to meet one or more of the critical performance aspects. Once a "short list" of potentially capable systems has been identified, more extensive testing can be carried out, including assessments of the impact of extended bath cycling and bath control on consistency of performance.

While process control is listed as the last item in Table 1, the selection of techniques for bath analysis often has a major impact on bath performance, particularly on the ability to maintain a process so that it can continue to deliver the same properties as a new bath, over extended usage time and under a wide range of operating conditions.

While the traditional approach to copper bath control has been to replenish additive components based on plating throughput (most conveniently measured as Amp.Hours) and to monitor performance using periodic Hull Cell testing, the introduction of advanced analytical control methods for electrolytic copper plating for plating on plastics applications has been found to bring valuable increases in productivity and deposit consistency, enabling production of enhanced quality copper coatings.

The combination of two well established, simple control techniques, which allows separate measurement of the concentrations of brightener and leveler components in the plating solution, provides an enhanced bath control system that is easily implemented in plating shops. Application of this approach has been found to improve the ability to predict bath performance, speed up troubleshooting and ensure the most economical utilization of process additives. The approach also facilitates easy start up after plating solutions have been idle for an extended period.

This article will outline the process control methods and present quantitative bath performance data obtained from baseline testing of a number of commercial copper plating systems, demonstrating how the application of these can enhance plating bath performance.

Experimental

Initial screening tests were carried out on eight commercial acid copper systems [A – H], differing in the specific additives used, but operated with similar inorganic electrolyte compositions. Five of the baths tested contained organic dyes, in addition to other organic additives. Three baths were dye-free (A, B, E). While organic dyes have been found useful in LCD brightness and leveling in these plating systems, the dye (or its breakdown products) may leave a film which interferes with subsequent electroplating steps and can also require additional maintenance of the bath and tank environment. These screening tests were designed to illustrate the variation in deposit properties associated with alternate plating baths. Evaluations were carried out on freshly prepared plating baths in Hull Cells, using brass test substrates.

A more detailed evaluation was then carried out on one of the systems. This evaluation was carried out in 700 liter tanks and involved extended bath cycling, during which periodic evaluations of deposit properties were carried out.
These cycling tests provided a comparison of the relative performance of a bath replenished solely on Amp.Hour throughput with that obtained from a bath controlled using quantitative analysis techniques.

The bath replenished based on Amp.Hour throughput was cycled from 0 to 40 Amp.Hours per liter, while the bath controlled with quantitative analysis techniques was tested over an extended range of 0 to 70 Amp.Hours per liter.

Evaluation of deposits from the 700 liter tests was carried out using a combination of brass Hull Cell test panels and standard ABS plastic test plaques. The ABS plaques were prepared using a typical POP pre-treatment, with a chromic-sulfuric etch.

The inorganic electrolyte composition used for all screening and cycling tests is shown in Table 2.

Table 2: Inorganic Component Composition

Component	Concentration
Sulfuric Acid	60 – 70 grams / liter
Copper Sulfate ($CuSO_4.5H_2O$)	190 – 200 grams / liter
Chloride Ion (Cl^-)	60 – 100 mg / liter

The deposit properties measured on the plated test coupons were as follows:

1) Brightness (gloss)
   a. At high and low CD
   b. At short and long plating time

2) Surface Leveling
   a. At high and low CD
   b. At short and long plating time

3) Micro-pitting value

Measurements of gloss (Gloss Units, GU) were made using a BYK Gardner 60 degree angle gloss meter.

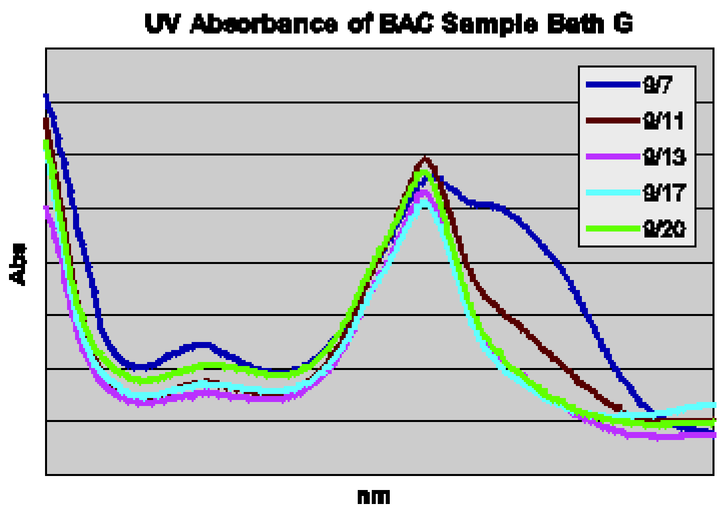
The substrates used for the leveling tests were brass panels, pre-abraded with 600 grit sandpaper. Measurements were made using a KLA Tencor profilometer (Model P-15). Roughness values were recorded before and after plating at two current densities (0.6 and 4.0 ASD) and two plating durations (5 and 20 minutes).
Percent leveling was calculated from the ratio of surface roughness before and after plating.

Micro-pits were counted visually using a microscope at 50x magnification. Samples were evaluated after both 5 and 20 minute plating cycles and measurements were made in both high and low current density areas of each sample. The micro-pit counts were reported as a single “Pit Number”, calculated by multiplying the number of pits by a factor based on the size of the pits and summing the values for both the 5 and 20 minute plating times.

Process Control Methods

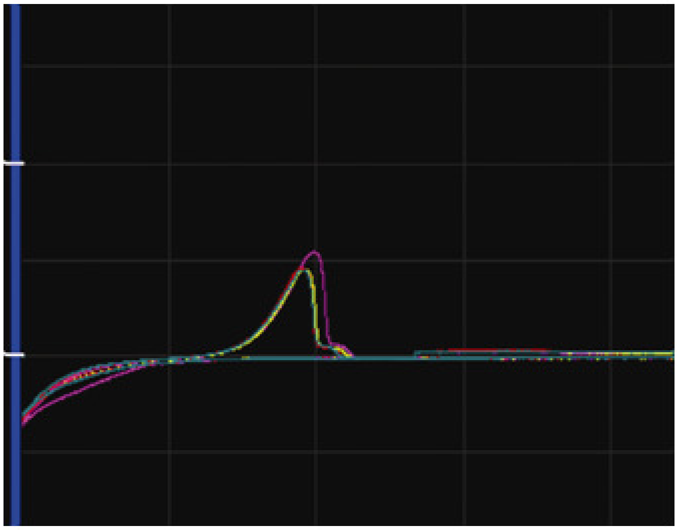
Two separate analytical methods were used to control additions of individual replenishment components. The first technique measured the UV absorbance of an additive component after solvent extraction from a bath sample. Additive concentration was determined based on the sample absorbance at the appropriate wavelength. Figure 2 shows the UV spectra obtained from a bath controlled using this technique over a period of several weeks.

Figure 2: UV Spectra of Additive Concentration in a Cycled Bath



The second method used for bath control was cyclic voltammetric stripping (CVS) analysis. The popularity of this electro-analytical technique has grown rapidly in recent years, as the capabilities of such methods have become better appreciated. Such systems allow additive concentrations to be measured based on their impact on the quantity of metal deposited and stripped under defined time and potential conditions. Figure 3 shows a series of such scans obtained from a bath over the period from 0 – 40 A.Hr/liter

Figure 3: Acid Copper Plating Bath Control using CVS: Bath Age - 0 – 40 A.Hr/liter



A wide variety of plating baths used for both functional and decorative applications can be controlled using this technique, including acid copper systems used for plating on plastics, electronics and circuit board technologies (2). A variety of different types of automated equipment is available to perform this analysis. A typical unit is illustrated in Figure 4.

Figure 4: Cyclic Voltammetric Stripping Analysis Equipment (image provided by ECI Technology Inc.)

Use of the UV absorbance measurement and CVS analysis method to immediately determine the appropriate individual additions of the two bath replenishment components allows rapid restoration of bath performance after idle periods, without the need to perform multiple Hull Cell tests and bath adjustments.

Results - Screening Evaluation

In the Hull Cell testing, a 20 minute plating time combined with high and low current densities of 4 A/dm^2 and 0.6 A/dm^2 corresponds to plated thicknesses of approximately 30 microns and 4.6 microns. Thirty microns represents a very typical plated thickness on significant areas of parts for typical industrial applications.

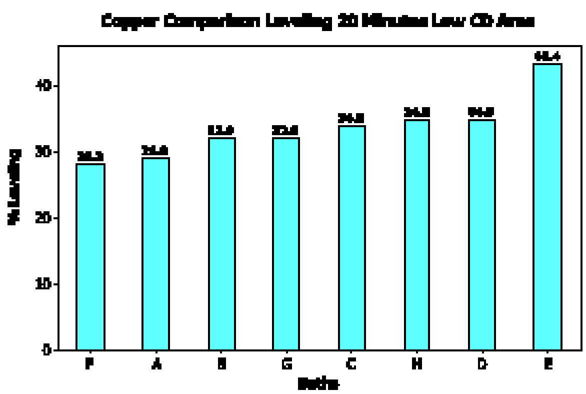
Figures 5 a) and b) show the differences in surface leveling after 20 minutes plating time between the eight acid copper plating systems. In low CD areas, Bath E was the only one with significantly better performance, with the remaining seven products showing comparable behavior. As would be expected, given the low plated thickness in this area, overall leveling was only moderate, with values ranging from 28 – 49%.

In high CD areas, almost all the baths had leveling values in the 80 – 90% range, with only baths F and H falling below this range. Bath F showed the poorest leveling at both conditions tested.

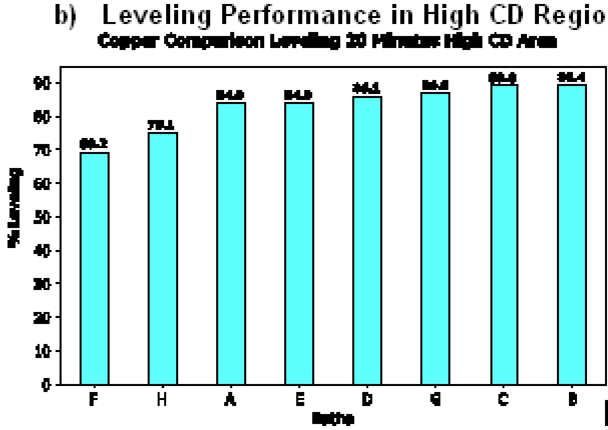
Combining both high and low CD performance, Bath E had the best overall leveling capability.

Figure 5

a) Leveling Performance in Low CD Region



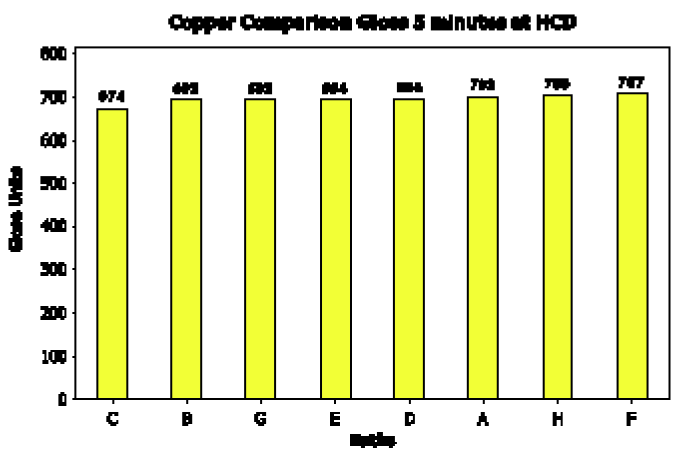
b) Leveling Performance in High CD Region



Figures 6 a) and b) show the variation in brightness between low and high plating thickness at high CD for the eight plating baths. While the absolute values for a given bath were quite close, there were some differences between the different baths tested. Deposits from Bath C had the lowest values of brightness of the eight baths screened and visual differences were discernible between deposits with Gloss Unit (GU) differences of 10–15 units.

Figure 6:

a) Deposit Brightness: 5 Minutes Plating at 4 A/dm^2



b) Deposit Brightness 20 Minutes Plating at 4 A/dm^2

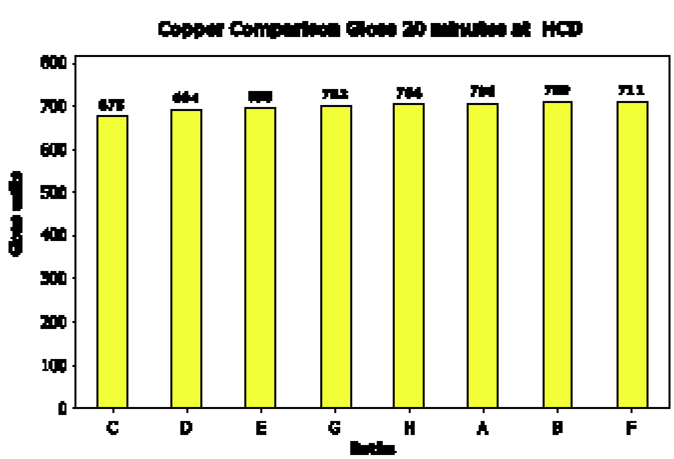
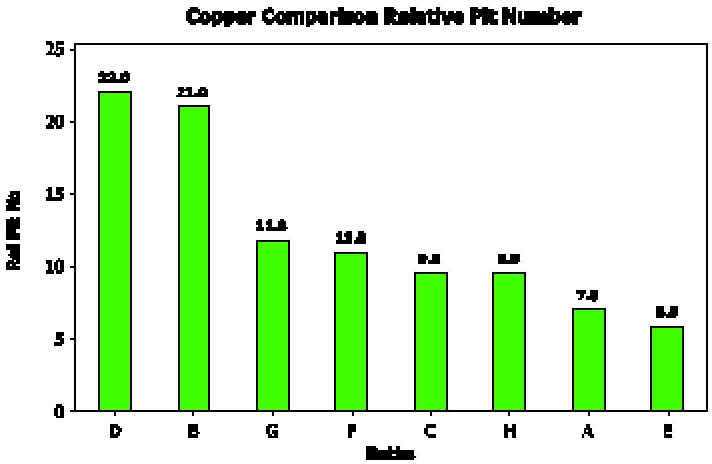


Figure 7 shows the relative pit number for the eight deposits tested. Baths D and B had much higher degrees of pitting, while Baths A and E were the best of the remaining baths.

Figure 7:



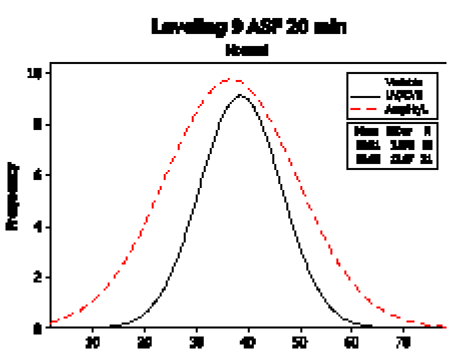
Results - Comparison of Control Methodologies: Bath C

The results for the control method comparison are shown in Figures 8 – 10.

Figures 8 a) and b) allow a comparison to be made of leveling at low and high CD areas during a 20 minute plating cycle. The median values for leveling at high CD are again higher than those at low CD. In both high and low CD areas, the use of the combination UV / CVS control methodology provides more consistent performance. In particular, at both current densities, the bath replenished by UV / CVS has significantly fewer occurrences of abnormally poor leveling, a defect that might lead to part rejection. Use of the UV / CVS control also has a positive effect on the average leveling at high CD.

Figure 8: Effect of Bath Control on Surface Leveling

a) **Low CD: 20 Minute Plating Time**



b) High CD: 20 Minute Plating Time

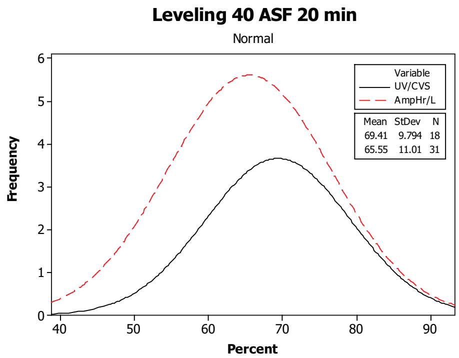
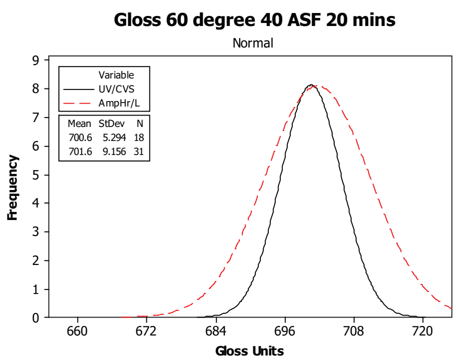


Figure 9 demonstrates a substantial reduction in variability of surface brightness when the UV / CVS control methodology is used, although the average brightness is not affected. Again, the tighter distribution reduces the probability that production parts will fail to meet end-customer cosmetic appearance requirements.

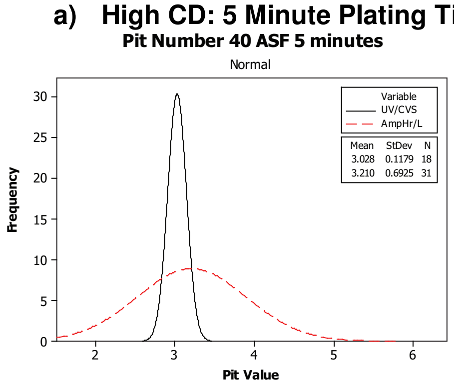
Figure 9: Effect of Bath Control on Surface Brightness



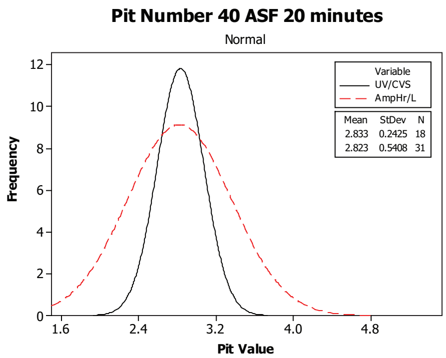
Figures 10a) and b) show a similar, positive impact of the UV / CVS control method on deposit pitting, with significant reduction in variability.

Figure 10: Effect of Bath Control on Deposit Pitting

a) High CD: 5 Minute Plating Time



b) High CD: 20 Minute Plating Time



Overall, the variance for all properties was found to be lower when employing instrumented analytical controls than when using the amp hr/liter dosing method. In some cases, the median performance is also improved.

The benefits of this approach are particularly evident after long idle periods. In addition, the economy of bath operation can be improved by reduction in additive consumption. Table 3 illustrates the differences noted in our comparison tests between consumption rates, depending on the control method employed.

Table 3: Impact of Bath Control Methodology on Additive Consumption Rate

Actual Consumption UV/CVS Controlled Bath	
Part A	0.08 ml/Amp.Hr
Part B	0.20 ml/Amp.Hr
Actual Consumption Amp.Hr/Liter Controlled Bath	
Part A	0.18 ml/Amp.Hr
Part B	0.27 ml/Amp.Hr

Summary

Screening and long term plating simulation under statistically sound data logging conditions allow for comparisons and selection of appropriate acid copper formulations for decorative plating applications. In addition, the use of instrumental analytical tools to monitor and control replenishment of an acid copper system has proved particularly useful, providing improved performance consistency and lower consumption of additive components.

Acknowledgements

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