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ELECTROCHEMICAL CONTROL OF  
BRIGHTENER IN ACID COPPER  
SULFATE PLATING SOLUTIONS

M. J. Bronson, KCD,  
and M. Dale Hawley,  
Kansas State University

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Final Report  
M. J. Bronson, Project Leader

Project Team:  
Tony Robinson, Kansas State University

Technical Communications  
Kansas City Division

**Allied-Signal Aerospace Company**



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Prepared by M. J. Bronson, KCD, and M. Dale Hawley, KSU

Electrochemical methods have been evaluated that attempt the indirect measurement of the effective concentration of a brightener additive in acid copper sulfate plating baths. The procedures all employed electrodeposition of copper on a platinum working electrode under carefully controlled conditions of mass transport, time, temperature, and potential, followed by the measurement of the charge that was required to strip the copper deposit from the working electrode. The amount of charge that was required to strip the copper deposit at a given concentration of additive varied significantly from fresh to production baths and from lot to lot of the additive. The feasibility of using electrochemical methods to control brightener additive in acid copper sulfate plating baths is discussed.

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P.O. Box 419159  
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## SUMMARY

Electrochemical methods have been evaluated that attempt the indirect measurement of the effective concentration of a brightener additive in acid copper sulfate plating baths. The procedures all employed electrodeposition of copper on a platinum working electrode under carefully controlled conditions of mass transport, time, temperature, and potential, followed by the measurement of the charge that was required to strip the copper deposit from the working electrode. The amount of charge that was required to strip the copper deposit at a given concentration of additive varied significantly from fresh to production baths and from lot to lot of the additive.

A potential application of the multi-potential step coulometric stripping analysis (MPSCSA) method is the quality testing of the acid copper bath additive. A second potential application involves the indirect measurement of the brightener concentration and the possible control of the brightener concentration in production baths. In order to implement this second application, the upper and lower stripping charge limits must be ascertained for satisfactory performance of the production bath. Once this relationship has been established, on-line control of the effective brightener concentration in the production bath should be feasible.

This project was sponsored by Allied-Signal Inc., Kansas City Division (KCD), with the work being done by the Department of Chemistry, Kansas State University (KSU), Manhattan, KS.

## DISCUSSION

### SCOPE AND PURPOSE

The presence of organic additives in acid copper sulfate plating baths has pronounced effects on such important deposit properties as ductility, tensile strength, uniformity of the deposit thickness, brightness, and solderability. In spite of their importance to the quality of the deposit, the analysis and the subsequent control of the several organic additives in production baths have been difficult to achieve because of the relatively low concentrations of the additives in the bath (0.01 to 0.05% of the brightener), interferences from additive decomposition products and other bath contaminants, and the low sensitivity of most instrumental methods of analysis to polymeric additives.

Although the mechanisms by which the additives exert their actions are not well understood, extensive experience has shown that the presence of nonionic polyethylene glycol surfactants and other additives in amounts up to several tenths of one percent affords beneficial effects on the deposit's tensile and morphological properties. Because the additives alter the rate at which the copper is deposited, a number of electrochemical procedures have been devised that relate the amount of copper stripped from a suitable working electrode to the effective concentration of the additive. Such methods are indirect and are affected by the presence of decomposition products of the additives, bath contaminants, the rate of mass transfer, electrode pretreatment, working potentials, and other factors.

This study evaluates multi-potential step coulometric stripping analysis [also called cyclic pulse voltammetric stripping (CPVS)] as an indirect method for measuring the concentration of a proprietary organic additive in an acid copper sulfate plating bath. The study was restricted to several samples of a single additive in fresh and production baths at concentrations that varied from 0.0 to 1.0 v/v%. In addition, a literature search was conducted for all papers and documents that are relevant to this work and that are included in the CAS ONLINE and STN INTERNATIONAL databases.

### ACTIVITY

#### Background

Most commercial acid copper plating baths contain two major classes of organic additives which function in concert to affect the quality of the deposit. Typically, the first class of additives consists of nonionic surfactant wetting agents such as

polyethylene glycols and polyoxyethylene alkyl and aryl ethers.<sup>1</sup> The surfactants, which have molecular weights that normally range from 200 to 20,000, are believed to form an adsorbed monolayer on the copper cathode and to enhance the throwing power by suppressing the electrodeposition current at a given potential.<sup>2</sup>

The second class of additives functions as brighteners and enhances the electrodeposition current. Although the compositions of acid copper sulfate plating bath additives are proprietary, one, which functions similarly to several other commercial additives including the brightener considered here,<sup>3</sup> may contain a sulfoniumalkanesulfonate as the brightening agent.<sup>4</sup> Neither the mechanism by which the brightener functions nor the pathways by which the brighteners are decomposed are well understood. In the case of one commercially available brightener of this type, the brightener was decomposed by air oxidation, electrochemical oxidation at the anode during plating, and slow catalytic decomposition at unpolarized copper surfaces.<sup>5</sup> Neither the several decomposition products nor their possible roles in brightening action were studied.

The long-accepted method for assessing the efficacy of the additive in the acid copper sulfate plating bath is the Hull cell. However, because the test is relatively time-consuming and the interpretation of the results relies heavily on the operator's judgement, this method cannot be incorporated into automatic control of the additive level. More recently, electrochemical methods have been developed that attempt to measure the effective concentration of the organic additive.<sup>6-10</sup> The most widely accepted procedures employ deposition of copper on a platinum working electrode under carefully controlled conditions of mass transport, time, and potential, and the subsequent measurement of the charge that is required to strip the copper deposit from the working electrode. The stripping charge is then related to the effective concentration of the brightener by means of a working curve.<sup>7,10</sup>

## Experimental Details

### Instrumentation

Experiments were performed either with a Shipley Electroposit Bath Analyzer or a KSU-designed and -constructed, computer controlled potentiostat that emulated the Shipley analyzer in its operation.<sup>11</sup> Both instruments used a programmed sequence of potential steps that is a slightly modified version of the original Tench and White multi-potential step coulometric stripping analysis procedure.<sup>7,10</sup> The method involves stepping the potential of the stationary platinum disk working electrode sequentially among those required for the plating of copper (-0.25 V versus AgCl/Ag for 2 s), stripping of the copper deposit

(0.20 V for 10 s), cleaning of the electrode (1.6 V for 5 s), and equilibration of the electrode (0.425 V for 5 s). This was followed by a 30-second period of open-circuit operation. The charge (millicoulombs) that was required to strip the copper deposit was recorded. In the absence of brightener, the value for a fresh copper solution (*vide infra*) at 26°C with a Shipley Electroposit Bath Analyzer was typically 42 to 45 millicoulombs. The mode of mass transfer was forced convection and was furnished by a stir bar which was rotated at constant rate.

The stationary planar platinum electrode was furnished either by Shipley or by BAS (Model MF-2013). A double-junction Ag/AgCl electrode and a copper rod were used as the reference and auxiliary electrodes, respectively.

#### Chemicals and Solutions

The fresh acid copper sulfate bath consisted of 210 g/L H<sub>2</sub>SO<sub>4</sub>, 80 g/L CuSO<sub>4</sub>, and 50 ppm Cl<sup>-</sup>. All inorganic chemicals are commercially available and were of reagent-grade quality. When the brightener additive was present, the appropriate amount of additive was added to the fresh copper solution prior to dilution with deionized, distilled water. Two different samples of the additive were furnished to KSU by KCD. The particular lot numbers of these samples were not provided.

#### Test Results

Multi-potential step coulometric stripping analysis (MPSCSA) results for a fresh acid copper bath in which the concentration of additive was varied systematically from 0.0 to 1.0 v/v% are shown in Figure 1. Initially, the incremental addition of this additive up to a total amount of 0.01% causes the stripping charge to decrease abruptly from 45 to 2 millicoulombs. (This may be explained as wetting component effects.) This region is then followed by a broad minimum in which there is little variation in the amount of charge stripped as the concentration of the additive is increased from 0.01 to 0.2%. In the third region, the amount of charge stripped increases monotonically as the concentration of the additive is varied from approximately 0.2 to 1.0%. (This may be explained as brightening effects.)

Although the precision of the measurements on this particular sample of additive in a fresh acid copper bath was excellent, the sensitivity of the stripping charge to the concentration of the brightening component (that is, the component that enhances the stripping charge) varied markedly from sample to sample and from fresh to production baths. As shown in Figure 2, a second sample of additive in a fresh acid copper bath afforded only the expected sharp decrease in stripping charge because of

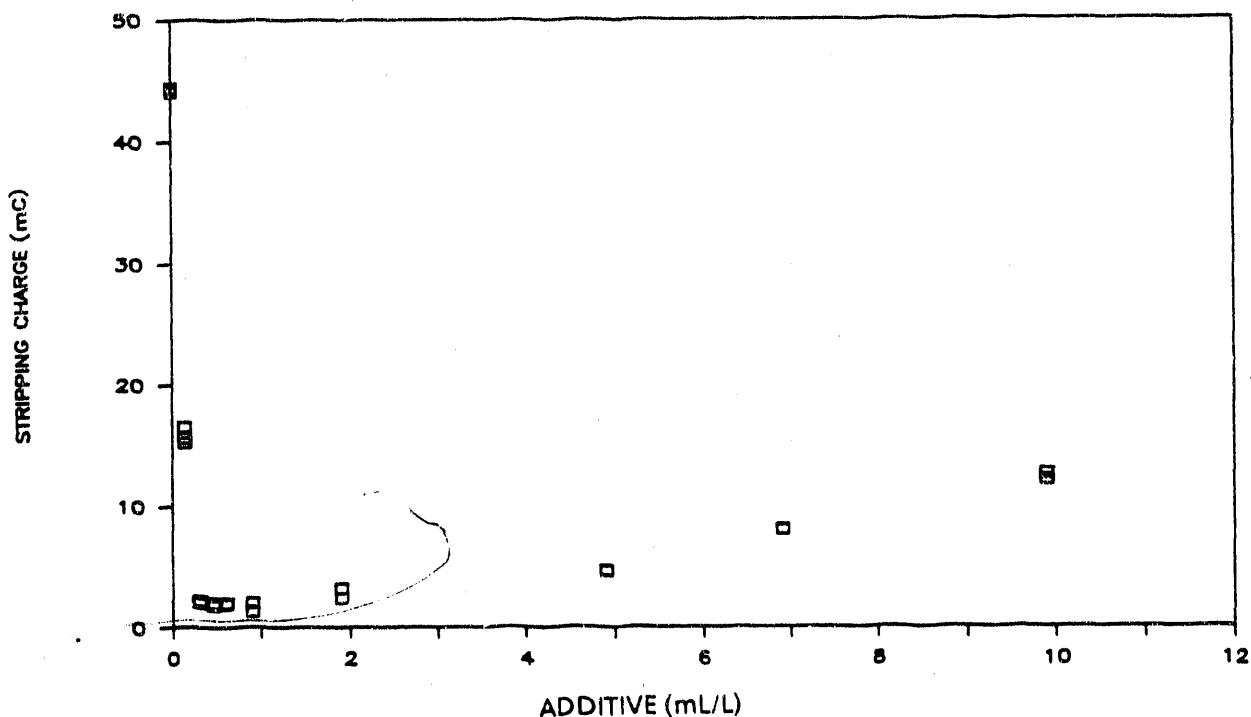


Figure 1. Plot of Stripping Charge as a Function of Additive Concentration for a Fresh Acid Copper Sulfate Bath (Lot 1 of Additive)

the presence of the wetting component; there was no discernible enhancement of the stripping charge at higher additive concentrations because of the anticipated effect of the brightening component(s). In Figure 3, aliquots from the first sample of the additive have been added to a sample of a production bath (86 g/L  $\text{CuSO}_4$ , 212 g/L  $\text{H}_2\text{SO}_4$ , and 47 ppm  $\text{Cl}^-$ ). Although there is a monotonic increase in the stripping charge with additive concentration in the range from 0.2 to 1.0%, the variation of the stripping charge with additive concentration is approximately one-half that for a fresh acid copper bath for the same concentration of additive. The low stripping charge with zero additive added to the production bath is presumably caused by the presence of unconsumed wetting agent.

### Conclusions

The general response of the stripping charge versus concentration of the first sample of the additive is similar to the behavior reported by Tench and White<sup>7</sup> for a Lea Ronal Copper Gleam PCM and Fisher and Pellegrino<sup>10</sup> for Shipley Company's Electrodeposit 276. As long as all parameters that affect the quantity of copper deposited and stripped from the platinum working electrode are carefully controlled, it is apparent that it should be feasible to measure the effective concentrations of the current suppressing agent and the brightener in a fresh acid copper



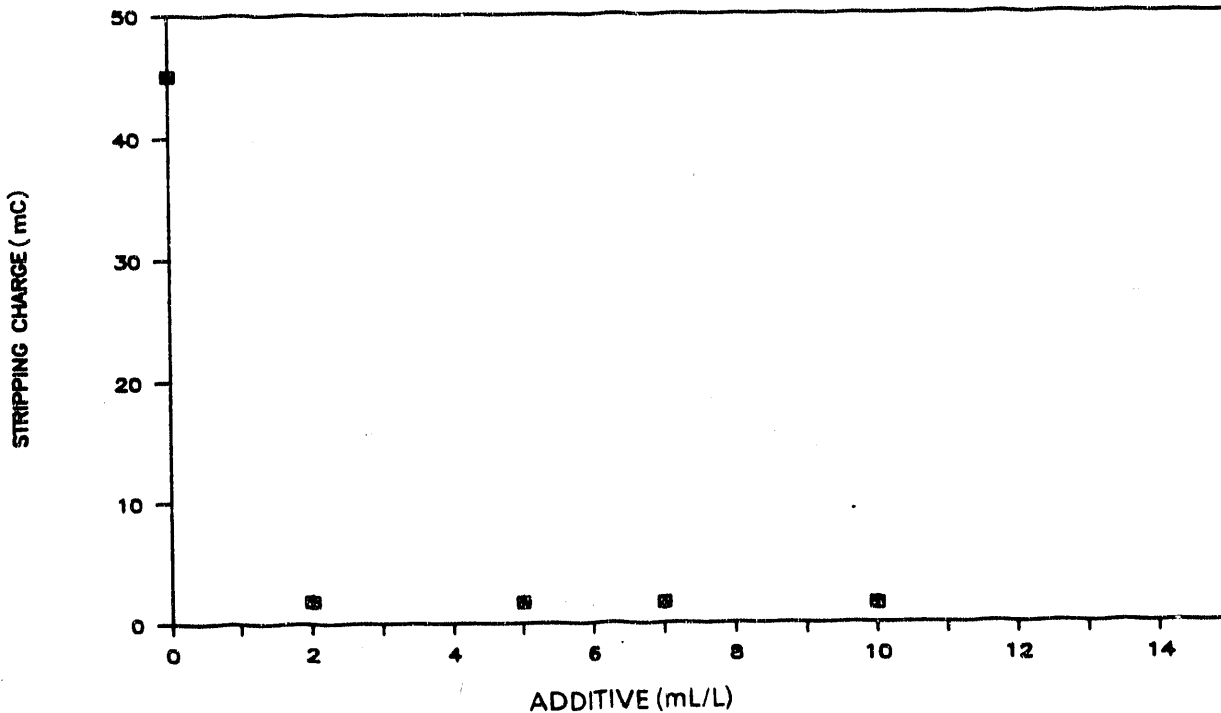


Figure 2. Plot of Stripping Charge as a Function of Additive Concentration for a Fresh Acid Copper Sulfate Bath (Lot 2 of Additive)

bath. As demonstrated by the significant difference in response from the first to the second sample of additive in fresh acid copper baths (see Figures 1 and 2), one potential application of the method might be the assessment of the additive's quality.

The decrease in sensitivity of the MPSCSA method to brightener concentration upon going from a fresh acid copper bath (Figure 1) to a production bath (Figure 3) poses a slightly more serious problem for the use of this method for the on-line measurement and control of the brightener additive. A literature report has shown that a proprietary brightener additive which is similar to this one<sup>3,4</sup> is consumed both by air and anodic oxidation and by contact with copper metal.<sup>5</sup> Furthermore, the effectiveness of the additive may also be affected by the products that arise from decomposition of the brightener and from adventitious contaminants that are introduced into the bath during the circuit board plating process. Because the presence of these contaminants indicates either that brightener has been consumed or that the brightener's effectiveness has been diminished, the results of the MPSCSA method should be correlated with results from Hull cell or production tests. Results from plating tests should then permit the establishment of upper and lower MPSCSA values between which satisfactory plating performance can be expected. Once a relationship has been established between the amount of charge consumed during the stripping of the copper deposit and the

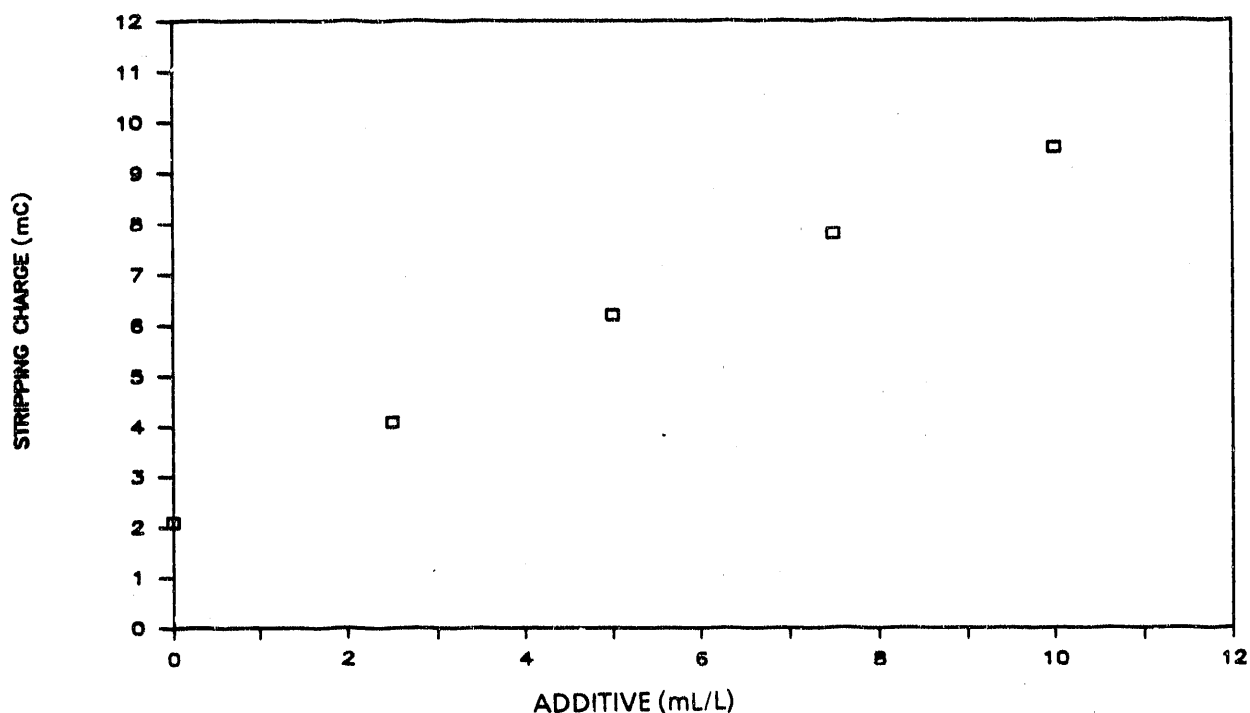


Figure 3. Stripping Charge Versus Additive Concentration for a Production Bath

effective brightener concentration, it should be possible to ascertain the amount of brightener that is required for the replenishment of the production bath.

It must be emphasized that all electrochemical methods that relate the amount of the copper stripping charge to brightener concentration are indirect and that the electrochemical measurements are affected also by brightener decomposition products and by contaminants which may have been introduced into the bath during the circuit board plating process. The most effective control of the production bath will result when the identities of the brightener and all decomposition products and contaminants are known and analytical methods are developed that will permit the direct determination of each of their concentrations. If the brightener and the other organic materials cannot be made electrochemically active, then nonelectrochemical methods, such as chromatography, should be sought.

#### ACCOMPLISHMENTS

A literature search was conducted to find electrochemical methods that attempt to measure the effective concentration of organic

additives in acid copper sulfate plating solutions. The search revealed that methods employing deposition of copper on platinum working electrodes were most commonly used. The charge required to strip the copper from the electrode is related to the effective brightener concentration.

An electrochemical method, namely cyclic pulse voltammetric stripping (CPVS), a multi-potential step coulometric stripping analysis, was determined to have some potential usefulness in assessing the quality or effectiveness of a brightener additive in acid copper sulfate plating solutions. Experimentation with two vendor lots of the brightener indicated variations in stripping charge between the two supplied lots relative to the concentration of each brightener added to the copper plating solution.

Because electrochemical methods are indirect, their usefulness for measurement of this brightener additive concentration in production copper sulfate plating solutions was not demonstrated. Brightener decomposition products and/or external contamination is presumed to have consumed brightener or to have caused diminished effectiveness to the stripping charge.

Determination of the usefulness of electrochemical methods for measurement of effective brightener concentration for additive control in production copper sulfate plating solutions would require that the following additional studies be performed:

- Establish upper and lower stripping charges,
- Establish a relationship between the stripping charge and effective brightener concentration, and
- Correlate stripping charge with Hull cell tests.

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