PLATING BATH ANALYSIS AND CONTROL BY CVS

A REALITY

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Introduction

A variety of analytical methods have been described to measure the activities or concentrations of **additives in electroplating baths.** These include, for example, the venerable Hull cell, HPLC, Ion Chromatography, UV spectrophotometry, hanging mercury drop voltammetry and cyclic voltammetric stripping (CVS) at a rotating platinum electrode.

Over the last decade, the availability of CVS analysis equipment specifically designed for the industrial electroplating shop has made this technique second only to the Hull cell, and the predominant choice for platers concerned with meeting assured quality standards. This very success has brought forth additional needs: the desire to use CVS for "closed loop" automatic additive dosing, the desire to maintain records for statistical process control (SPC), the desire for more frequent analyses with less demands on the analyst's time, the desire to have the instrument double as a desktop computer, and - from the additive suppliers - the desire for improved portability. **These desires have generated an unprecedented explosion of new commercial CVS products.**

A number of new CVS products have recently been introduced - some evolutionary and others revolutionary. The technique has also been extended to additional additives.

This presentation focuses on two revolutionary products: **online CVS-based analyzer/controllers**, one for acid copper sulfate additives and one for copper pyrophosphate additives. Methods, procedures and instrumentation will be reviewed, and production bath experience described. Analytical advantages of this form of CVS will be highlighted.

CVS Background

Voltammetry is an electrochemical technique in which the electric current arising from reactions at an electrode surface is measured as a function of the electrode voltage. In **cyclic voltammetry**, the applied potential is cycled back and forth between potential limits. We use the convention that the current is positive when the working electrode is the anode, and negative when it is the cathode (plating metal, for instance). Applied to a copper electroplating bath, as in Figure 1 for example, cyclic voltammetry reveals cathodic current in the most negative potential region of the cycle, due to metal plating onto the electrode. Later in the cycle, at more positive potentials, anodic current occurs when the metal is electrochemically stripped off (redissolved into solution).

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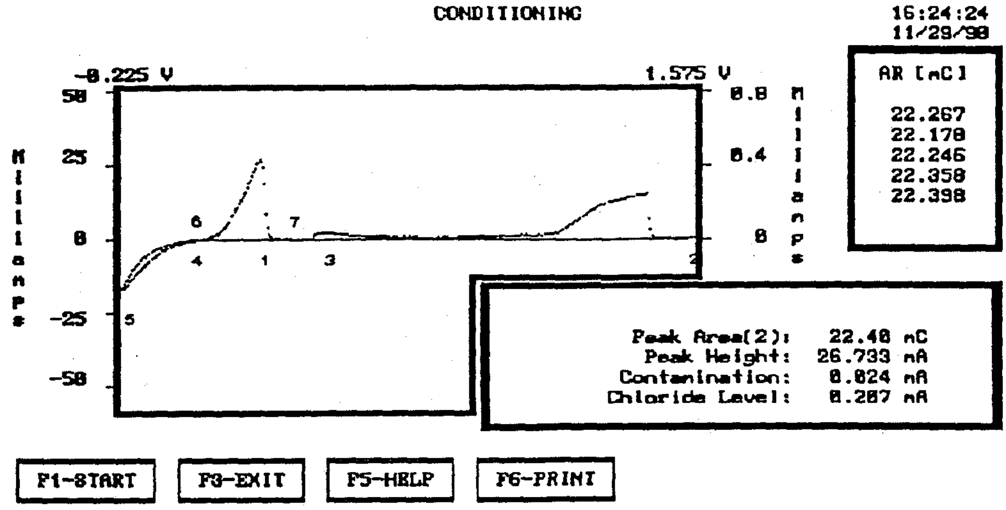


AR [mC]
22.267
22.170
22.246
22.350
22.390

Peak Area(2): 22.40 mC
Peak Height: 26.733 mA
Contamination: 0.024 mA
Chloride Level: 0.207 mA

Figure 1. Typical CVS voltammogram with major analytical processes

Cyclic Voltammetric Stripping (CVS) is a similar type of cyclic voltammetry, except that the variable of interest is the stripping current peak, or in our case, the stripping charge (the area under the striping peak) in mC. Usually the electrode is rotating during the measurement of the stripping charge. Then it is referred to as A_R, or Area, Rotating.

As noted previously[1,2], the various chemical compounds added to electroplating baths to improve mechanical and electrical properties of the deposit affect the CVS A_R parameter as well. In both cases these compounds modify the electrochemical mechanisms of the electroplating process. Since additives and contaminants affect the electroplating of parts and the CVS determination in similar ways, CVS yields the "activity" of additives, which is more relevant than the analytical concentrations of specific compounds.

Figure 2 shows the CVS A_R value plotted versus concentration for a typical additive. The shape of such a curve differs from one additive to the next.

Since the electroplating is affected by other variables besides the additive components, and since the CVS voltammogram contains a multitude of complex information, commercial CVS instruments utilize a variety of CVS techniques. These techniques are used to simplify the information, as well as eliminate interferences. They make use of dilutions, standard additions or alternate approaches to improve accuracy and reproducibility. A number of these techniques have been previously described[3].

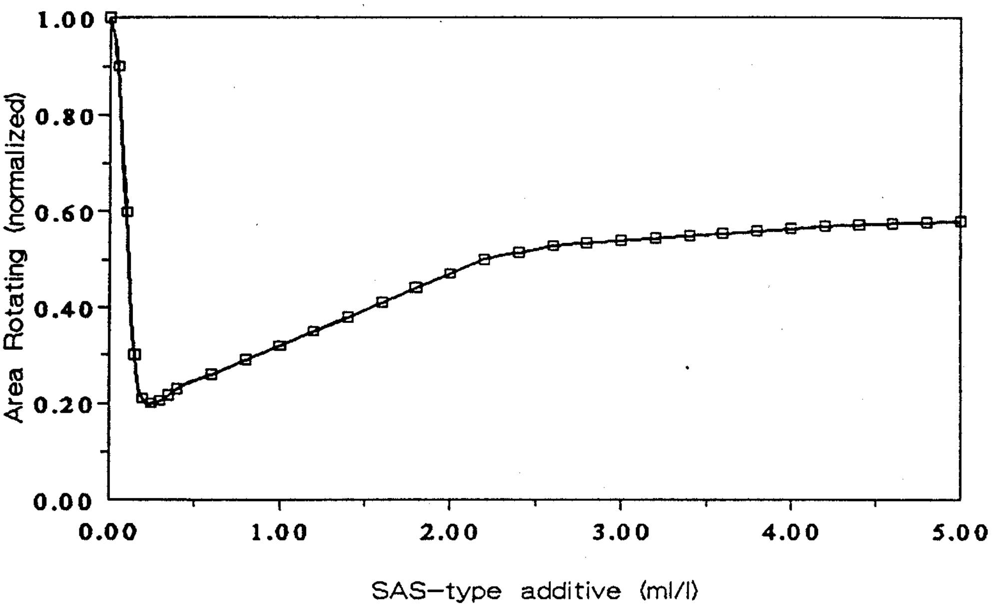


Figure 2. Plot of A_R versus concentration for a typical SAS-type additive in acid copper sulfate plating solution.

The simplest techniques involve measuring the A_R value of a sample and dividing it by either the similar value, A_R^0, for an additive-free reference solution or by the A_S value (Area, Stationary) obtained using a stationary electrode in the same sample. This is effective if the electroplating is only affected by one compound (as in copper pyrophosphate). This ratio can be used as a control set-point, or interpreted using a calibration curve.

Additive control in copper pyrophosphate plating baths is especially challenging for two reasons. This bath is used primarily for PC boards that must meet tight MIL specs, so the acceptable window of additive activity is narrow. And, additive activity changes relatively rapidly in this system, partly due to its complex dimer equilibria. The mechanisms and control of pyrophosphate copper additive have been described earlier[4-6]. With the introduction of CVS over a decade ago, more and more manufacturers have abandoned the practice of running unbrightened baths. The conversion to the use of additive coupled with frequent CVS analysis has improved quality and dramatically decreased reject rates. The CVS A_R/A_S ratio technique is relatively fast, allowing for the frequent analyses needed.

Acid copper sulfate baths are more complex. The functions performed by additive components include carrier, leveler, brightener, wetter, etc. For simplicity and uniformity, CVS divides such components into two classes: plating suppressors and antisuppressors. Suppressors reduce A_R, while antisuppressors increase A_R in a suppressed solution.

Suppressors are generally the leveler and wetter components that increase the amount of energy needed to plate copper, increasing throwing power and improving deposit uniformity. Generally polyglycols, suppressors that work with chloride ions in the bath, have been found to influence mechanical properties of the deposits[7]. Their activities do not change as rapidly as those of antisuppressors, since they are not as readily electrolyzed and the breakdown products are also often antisuppressors. This causes them to tend to increase with the addition of mixed additives, and increasing attention is being given to monitoring them.

Antisuppressors, which are generally brighteners or "carriers", decrease the energy required to deposit copper in the presence of suppressors. Measuring the brightener activity independently and controlling it has long been important, because it has a smaller range of acceptable variation than suppressors, yet it varies considerably since it is partially electrolyzed. Recent experiences with high aspect ratio boards indicate lowering brightener levels coupled with frequent, almost continuous, dosing leads to higher quality boards than does large batch dosing. However, this strategy requires tight control of the antisuppressor activity at all times.

CVS is also useful in monitoring levels of oxidizable contaminants and chloride ions, allowing early detection of accidental contamination or chloride overdosing.

Available Instrumentation

Apart from general research-grade electrochemical analyzers, there are currently about five generations of CVS instrumentation designed for industrial electroplating use.

Even the early units are useful improvements over the Hull cell. However, they have restricted display, hardcopy and data storage, and they are dead ends concerning improvements and upgrades. Despite their limitations, they are important analytical tools in many electroplating shops throughout the world.

The modern CVS analyzers are PC based, and the newest can also function as a modern desktop computer. A portable version has recently been released. These models have such improvements as real-time voltammogram display (with different parts in colors), automatic syringe control for additions, storage of results in groups for statistical summary, printout of reports and voltammograms on plain paper, and context-sensitive, detailed on-screen help.

Two online CVS analyzer/controllers have recently been introduced. **These are the first commercial instruments to use CVS for automatic online analysis and closed loop additive dosing.** They are based on over a decade of developments and experience with laboratory CVS analyzers. Requiring only infrequent attention from the analyst, these units are located directly in the plating shop, where they automatically draw and analyze samples from up to four separate tanks. Cell cleaning, electrode conditioning and solution temperature control, as well as the entire analysis sequence, are automatic and repeated exactly.

Dose adjustments and additive activity corrections are made automatically based on CVS analysis. The operator has considerable flexibility in structuring the dosing, within the desirable framework of small, frequent additions.

Each set of analyses begins with thorough cell and electrode preparation, including rinsing and conditioning to provide reproducible analytical conditions. The online unit then draws a sample from a plating tank (as far as 75 feet from the unit) and begins the analysis.

Results are stored by the unit, available at any time to an operator directly on the plating shop floor. Reports include summaries of results (including amp-hours), SPC charts, recent voltammograms and chronological histories of alarms. Multiple levels of alarms and warnings can be triggered by various hardware problems, suspicious results or SPC pattern analysis. Results can be transferred to an external computer, printed out, or stored on floppy disks for future reference.

To validate the results, the analysis cycle includes a standard, prepared using known amounts of brightener and suppressor components (supplied by the additive manufacturer).

An important consideration now, especially with a high frequency of analyses, is the absence of any waste generation by the online unit. This is possible because only chemicals used for plating are used for analysis, and all solutions, including rinse water, are returned back to the tanks. Special care is taken to ensure that samples are returned to their proper tanks. In addition, the total volumes of chemicals used for analysis are essentially negligible compared to the tank volumes, even for relatively small tanks.

The copper pyrophosphate version of the online unit is designed to monitor and control the activity of the monocomponent additive, and monitor contamination levels.

The more sophisticated acid sulfate copper version can use the full range of CVS techniques to monitor brightener and suppressor activities and contamination and chloride currents, and controls brightener or a premixed additive.

Analytical Advantages of Online CVS

The wide acceptance of CVS for additive analysis reflects the need for a fast and accurate quantitative measurement. As leading-edge printed circuit board manufacturers began to use more ambitious quality criteria, with stringent testing of the mechanical properties of the plated metal, increased demands were placed on bath performance and analysis. Coupled with increased use of Statistical Process Control, even the previously reasonable variance of CVS analysis came under scrutiny.

Several shortcomings of lab analysis were revealed. Samples analyzed promptly gave better results than samples sent out for analysis. A few percent variation could be attributed to temperature changes. Equipment, especially electrodes, used infrequently gave larger variance. Some analysts achieved tighter variance than others. In addition to great care in measurement and mixing, these analysts were characteristically consistent in their regimens of cleaning, conditioning, analysis and even record keeping.

Automating the processes of cleaning, conditioning, sampling, temperature adjustment, dispensing, analyzing and data storage, addresses almost all of these issues. Reduced analyst dependence also makes more frequent analyses practical, providing a truer picture of the bath conditions, greater opportunity to catch bath problems early, and more data points for proper use of statistical process control and for checking self-consistency. The availability of current analytical information during late work shifts is a valuable improvement. In addition, these online units offer a reproducible environment in which the programmed sequences can be adjusted and meaningfully evaluated - a perfectible analytical environment.

Automated checking can also correct for batch-to-batch variability of additives, differing usages of additives due to seasonal factors or varying plating conditions, as well as human errors. This should lead to more timely warnings, improved product quality and a lower costly reject rate.

Production Bath Experience

Continuing field testing of the copper pyrophosphate and acid copper sulfate online units indicate that they will prove to be invaluable tools in managing copper electroplating tanks.

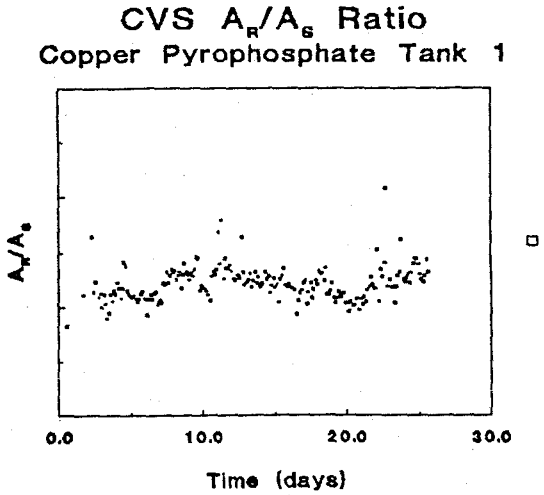


Figure 3. Pyrophosphate A_R/A_S Ratios from Production Bath

The expectations of good reproducibility were borne out by the performance of the pyrophosphate unit, Figure 3. The relative simplicity of the A_R/A_S measurement is well-suited to the pyrophosphate environment, since it allows frequent measurements and the activity of the pyrophosphate additive is rather variable. The additive is thermally activated with a time lag of hours, so measurements after baths have been idle are especially useful.

Figure 3 shows a 30 day plot of A_R/A_S ratios for an actual production plating tank. During this period, the tank was used for plating circuit boards. A number of outliers have been linked to uncontrolled additions of water and ammonia. A close examination of this graph, correlated with records kept for additions of all chemicals and water, for plating activity, for temperature changes, and for air sparging periods revealed clear causes of some of the fine structure in the graph. A more detailed description of these tests will be published later.

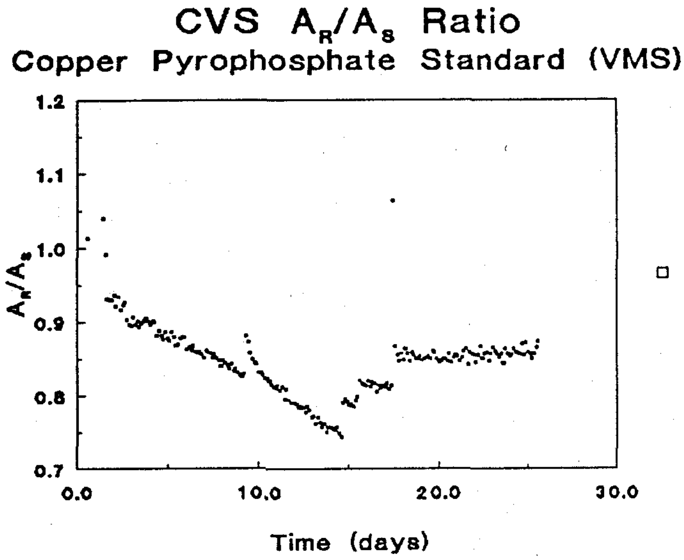
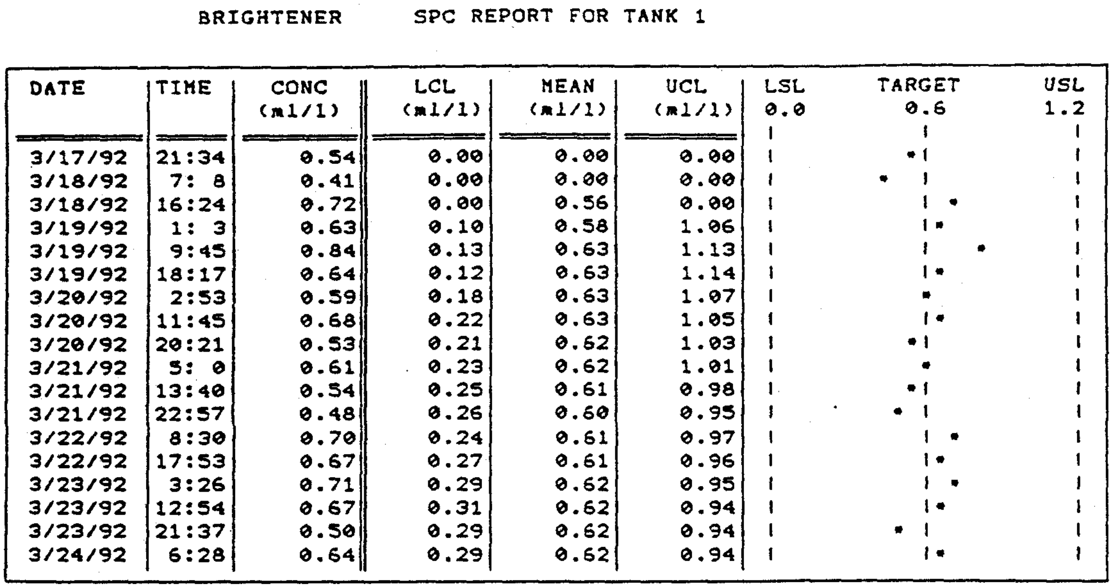


Figure 4. Copper Pyrophosphate VMS Used as Standard: See Text

Figure 4 indicates the analysis of additive-free copper pyrophosphate plating solution (Virgin Makeup Solution or VMS), which is analyzed in sequence along with the four production tanks. Replenishment of the VMS is clearly visible, as is the drift due to solution deterioration. After some experimenting, solution chemistry was stabilized, as is evident from the graph.

Similar tests are occurring with the acid copper sulfate online unit. This unit is more complex, since it independently monitors both brightener and suppressor activities. Results from tests using tanks of 100 gallon volume are shown in Figures 5-7. Figure 5 shows brightener activity in a functioning production tank, while Figure 6 and Figure 7 show brightener and leveler monitoring on a second tank during the same period. During this



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                       BRIGHTENER      SPC REPORT FOR TANK 1

 DATE     |TIME  |  CONC  ||  LCL   |  MEAN  |  UCL   | LSL         TARGET        USL
          |      | (ml/l) || (ml/l) | (ml/l) | (ml/l) | 0.0          0.6          1.2
========= |===== |======= ||======= |======= |======= | |            |            |
 3/17/92  |21:34 |   0.54 ||   0.00 |   0.00 |   0.00 | |           *|            |
 3/18/92  | 7: 8 |   0.41 ||   0.00 |   0.00 |   0.00 | |        *   |            |
 3/18/92  |16:24 |   0.72 ||   0.00 |   0.56 |   0.00 | |            | *          |
 3/19/92  | 1: 3 |   0.63 ||   0.10 |   0.58 |   1.06 | |            |*           |
 3/19/92  | 9:45 |   0.84 ||   0.13 |   0.63 |   1.13 | |            |    *       |
 3/19/92  |18:17 |   0.64 ||   0.12 |   0.63 |   1.14 | |            |*           |
 3/20/92  | 2:53 |   0.59 ||   0.18 |   0.63 |   1.07 | |            *            |
 3/20/92  |11:45 |   0.68 ||   0.22 |   0.63 |   1.05 | |            |*           |
 3/20/92  |20:21 |   0.53 ||   0.21 |   0.62 |   1.03 | |           *|            |
 3/21/92  | 5: 0 |   0.61 ||   0.23 |   0.62 |   1.01 | |            *            |
 3/21/92  |13:40 |   0.54 ||   0.25 |   0.61 |   0.98 | |           *|            |
 3/21/92  |22:57 |   0.48 ||   0.26 |   0.60 |   0.95 | |          * |            |
 3/22/92  | 8:30 |   0.70 ||   0.24 |   0.61 |   0.97 | |            | *          |
 3/22/92  |17:53 |   0.67 ||   0.27 |   0.61 |   0.96 | |            |*           |
 3/23/92  | 3:26 |   0.71 ||   0.29 |   0.62 |   0.95 | |            | *          |
 3/23/92  |12:54 |   0.67 ||   0.31 |   0.62 |   0.94 | |            |*           |
 3/23/92  |21:37 |   0.50 ||   0.29 |   0.62 |   0.94 | |          * |            |
 3/24/92  | 6:28 |   0.64 ||   0.29 |   0.62 |   0.94 | |            |*           |
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Figure 5. Acid Brightener Concentration from Production Bath

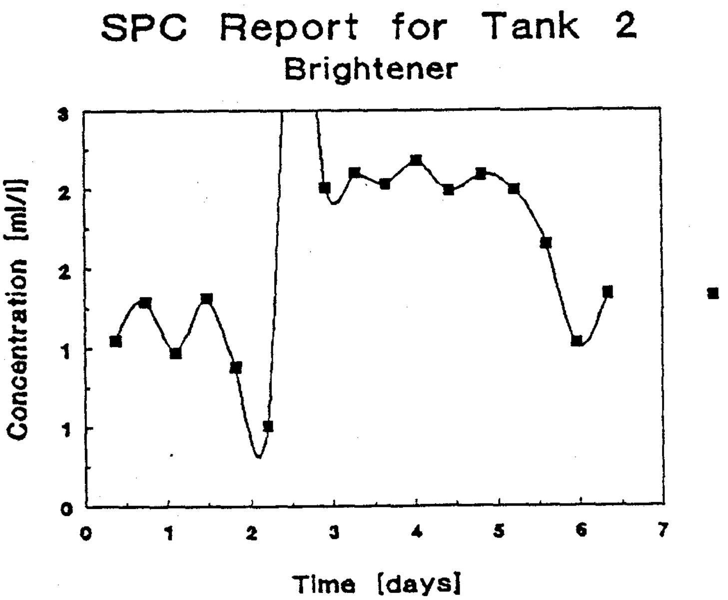

Figure 6., Acid Copper Brightener Activity

period, the second tank was carbon filtered, dosed with additive and dummy plated. The carbon treatment on day one is used to bring down high levels of built-up organics, but it removes brighteners and levelers as well. Figures 6 and 7 show the drastic decrease of both

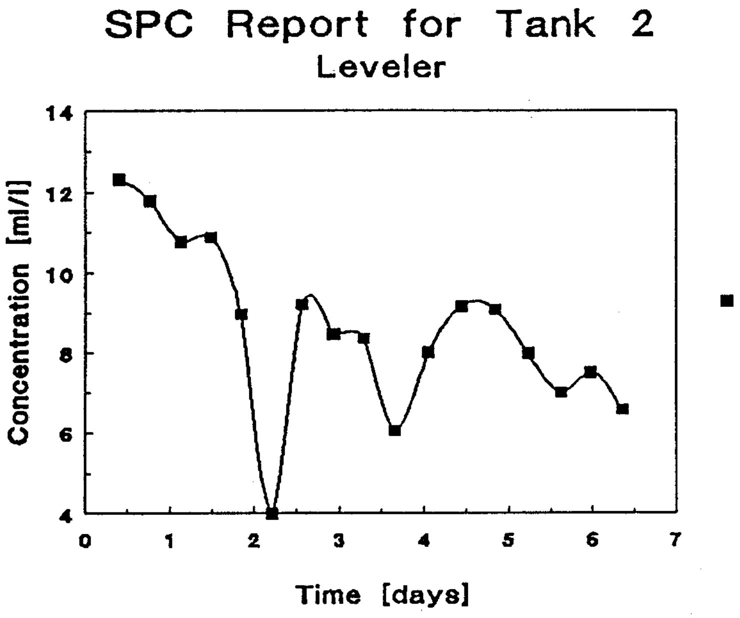

Figure 7. Acid Copper Leveler Activity

brightener and leveler components. Replenishment is done with a dose of mixed additive to bring the suppressors close to their normal steady state levels, which overdoses the brightener. The figures show a sharp increase on day two from this replenishment dose. After a weekend of inactivity (days 3 - 5), dummy plating was used to preferentially destroy brightener until the normal steady state balance is achieved. Later additions of the mixed additive based on usage will maintain this approximate balance.

Conclusion

The use of CVS methods for analysis of additives in copper electroplating baths is enhanced significantly in usefulness and reliability when the analyses are performed using an intelligent online analyzer, which can also be used for automatic additive dosing.

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