Inexpensive, Light-Emitting, Diode-Based Photometer For Determining Copper In Hard-Chromium Plating Baths

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An infrared-light-emitting-diode-based photometer has been developed for use in measuring copper concentrations in hard-chromium and other plating baths. This device provides accuracy comparable to that of more sophisticated techniques, is easy to operate, requires no sample preparation, creates no waste, and can be assembled from a small number of simple and inexpensive components.

In recent years, there has been a large amount of work directed toward reducing waste in hard-chromium plating operations. This work has been motivated in large part by the EPA, which had estimated that hard-chromium plating operations accounted for 160 tons/year of chromium air emissions alone.¹ Of the many strategies that have been developed to address various aspects of the waste problem, one of the most straightforward involves simply ensuring that the bath is operating under optimized conditions. If contaminants or trivalent chromium build up to high levels, or if the ratio of essential bath components is changed, both current efficiency and deposit quality can be adversely affected. As the current efficiency drops, plating times must be increased. This leads to greater release of hexavalent chromium through misting and generation of more lead chromate sludge through decomposition of the anodes. It also raises plating costs by increasing energy consumption and reducing the number of parts that can be plated per day.

Build-up of trivalent chromium and transition-metal impurities can lead to poor-quality deposits, in the worst cases requiring grinding and replating of the part. All of these problems can be minimized if care is taken to maintain the bath at optimum conditions through frequent analysis and the use of any of several methods of removing impurities. Unfortunately, frequent bath analysis is not always possible. Many of the common methods of bath analysis, such as atomic absorption spectroscopy, ion chromatography, or ICP, require relatively expensive equipment, as well as trained operators. Sending bath samples out for analysis can be costly and in some cases can involve unacceptably long



Fig. 1—Absorption spectra of new chromium plating solution (approx. 250 g/L CrO₃, 2.5 g/L H_2SO_4). Top trace represents undiluted plating solution in 1-cm path length cuvette; bottom trace is plating solution diluted 1:10,000.

turnaround times. We are currently involved in a program to develop a low-cost analyzer for hard-chromium plating baths. The analyzer is based primarily on photometric detection. In this paper, a simple and inexpensive method of determining copper in chromium plating solution is offered. In future publications, we will describe methods of determining other common impurities and primary bath constituents.

Copper is one of the most common transition-metal impurities in hard-chromium plating baths. It is generally introduced through dissolution of bus bars, brushes, and/or copper-containing base metals. The method is one of determining copper based simply on direct absorption of near-infrared light. Although this method has been used before,² it does not appear well known and, in fact, no mention of a method of determining copper, based on near-infrared absorption was found in any common text or reference books on chromium plating, plating bath analysis, or spectrophotometric/colorimetric determination of the elements.³ The primary difference between our method and those presented previously is cost. Because the photometer uses only inexpensive solidstate components and substitutes batteries for power supplies, it is significantly less expensive than other photometric, as well as non-photometric, instruments used to determine copper. In addition, it is easy to operate, requires no sample preparation, offers rapid turnaround times, and creates no waste. Finally, since the primary components are all solid state, the unit should be extremely rugged and reliable.

Background

It might at first seem unlikely that a colorimetric sensor could be used to monitor copper in a hard-chromium plating solution. Chromium plating solutions are very strongly colored deep wine-red when new and often closer to black after extended use. In contrast, copper solutions tend to be pale blue even at relatively high metal-ion concentration. Examination of the spectra of chromium plating and copper solutions shows, however, that a simple absorption sensor can indeed be used to determine copper. As seen in Fig. 1, the primary absorption bands of the hexavalent chromium spe-



Fig. 2—Spectrum of aqueous copper sulfate solution containing 2500 mg/ L copper metal in 1-cm path length cuvette.

cies present in hard-chromium plating solutions appear in the ultraviolet region of the spectrum; the red color of the solution results from the long-wavelength tail of these bands. On the other hand, the primary absorption band of copper, shown in Fig. 2, is located in the near infrared and the blue color of copper is caused by the short-wavelength tail of this band. Therefore, there is virtually no interference at the main copper absorption peak because of hexavalent chromium. Moreover, most of the other primary colored species commonly found in hard-chromium baths, including trivalent chromium and iron, also have absorption bands widely separated from that of copper. Consequently, it is reasonable to assume that a simple absorption sensor, using a light source having the same wavelength as the copper absorption maximum, should be well suited to measuring copper in chromium plating solutions.

Experimental Procedure

The experimental apparatus is shown in Fig. 3. An 808-nm light-emitting diode (LED) was used as a light source. This LED was chosen because its emission wavelength corresponds approximately to the copper absorption maximum (see Fig. 2). The detector is an integrated photodiode/ transimpedance amplifier. As shown in Fig. 4, the diode is powered by a 6-V lantern battery and the detector/amplifier by two 9-V batteries. Because of the low currents drawn by the LED/resistor and detector/amplifier, the batteries are suitable power sources even for extended use.

A 1-cm path length absorption cell was positioned between the LED and detector/amplifier. Because this apparatus is intended to serve as part of a larger automatic analyzer, we used a glass flow cell, a peristaltic pump to control flow through the cell, and a computer to record voltage from the detector/amplifier and calculate copper concentrations. To minimize cost, however, an inexpensive static glass or plastic cuvette could be substituted for the flow cell, which would eliminate the pump, and the computer could be replaced with a voltmeter.

The apparatus must first be calibrated, using the following procedure. The cell is filled with new plating solution containing no copper and a background voltage, V_{bkgnd} , is measured. Next, the cell is filled with a sample of plating solution containing a known amount of copper and a second voltage, V_{std} , is measured. (It is important that all solutions be at the same temperature when measurements are made.) The output voltages of the detector/amplifier, V_{bkgnd} and V_{std} are proportional to the intensity of light transmitted through the respective solutions. They can be related to the concentration of copper through Beer's law,⁴ which in our case takes the form

$$\log_{10} \frac{\mathsf{V}_{bkgnd}}{\mathsf{V}_{std}} = \epsilon \, \mathrm{lc}$$

where l is the path length of the cell, c is the concentration of copper and ϵ is the extinction coefficient. Because l and c are both known, Beer's law is solved to give ϵ . Once ϵ is known, samples of plating solution can be analyzed, using essentially the same procedure: The cell is first filled with new plating solution to obtain a background voltage, and next with a bath sample to obtain a sample voltage. Once these voltages have been measured, the Beer's law equation is solved to give the copper concentration, c.

Results

As in the case of previous work,² tests of laboratory standards containing various amounts of copper showed agreement with Beer's law. Some potential bath contaminants, however, such as nickel, have absorption bands that overlap those of copper.⁵ To evaluate the photometer under more realistic conditions, therefore, we used samples obtained from a number of different plating shops. For purposes of comparison, the samples were also sent to two independent laboratories for analysis. The choice of plating shops and baths was intended to reflect the wide range of hard-chromium plating operations. The shops are located in diverse geographic locations and specialize in widely varying parts and base metals, the latter ranging from brass through advanced Inconel alloys. The samples were taken from both Sargent and fluoride-catalyzed baths and varied widely in concentrations of CrO₂ (from 166 g/L to approximately 240 g/L), trivalent chromium, and impurities. The analytical labs both used the same technique, ICP, to determine copper.

Figure 5 shows the results of our measurements along with those obtained by the two analytical labs for six samples provided by five different plating shops. These results are representative of those obtained from all the samples. If each

of the measurements is assumed accurate to within ± 10 percent (the level of accuracy estimated by one of the analytical labs), then the results of all measurements are in good agreement. More importantly, since transition-metal con-



Fig. 3—Schematic of optical system.



Fig. 4-Schematic of LED and detector/amplifier circuits.



Fig. 5—Comparison of copper concentrations in hard-chromium plating solutions, determined by two independent laboratories and by the method of this study.

centration measurements are generally used to form the basis of a "go/no-go" decision on bath usage or clean-up, the measurement accuracy is more than adequate for hard-chromium plating applications.

Summary

We have developed a photometer, based on a near-infrared light-emitting diode and demonstrated its utility in measuring copper impurities in hard-chromium plating solutions. The photometer is inexpensive and easy to use. It requires no sample preparation and creates no waste because all solutions can be returned to the plating tank after use.

Editor's note: Manuscript received, September 1995.

Acknowledgments

This work was supported by ARPA under Grant #MDA-97293-1-0006. We thank the numerous platers who supplied us with samples.

References

- EPA 453/R-93-030a, Chromium Emissions from Chromium Electroplating and Chromic Acid Anodizing Operations—Background Information for Proposed Standards, July 1993.
- 2. J.E. Freeman, A.G. Childers, A.W. Steele and G.M. Hieftje, *Analytica Chimica Acta*, **177**, 121 (1985).
- For example, Metal Finishing Guidebook and Directory Issue, Elsevier Science, New York, NY, 1995; D.G. Foulke and F.E. Crane, Electroplaters' Process Control Handbook, Reinhold, New York, NY, 1963; F.A. Lowenheim, Electroplating, McGraw-Hill Book Co., New York, NY, 1978; T.H. Irvine, The Chemical Analysis of Electroplating Solutions, Chemical Publishing Co., Inc., New York, NY, 1970; P. Morisset, J.W. Ostwald, C.R. Draper and R. Pinner, Chromium Plating, Robert Draper Ltd., Teddington, Middlesex, England, 1954; Z. Marczenko, Spectrophotometric Determination of Elements, Ellis Horwood, Sussex, England, 1976; H. Onishi, Photometric Determination of Traces of Metals, Pt. IIA, 4th Ed., John Wiley & Sons, New York, NY, 1986.
- D.G. Peters, J.M. Hayes and G.M. Hieftje, *Chemical Separations and Measurements*, W.B. Saunders, Philadelphia, PA, 1974.
- 5. R. Lehrmann, J. Burck, and H.-J. Ache, *Process Control and Quality*, **4**, 139 (1993).





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