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LIQUID CHROMATOGRAPHIC ANALYSIS OF ORGANIC ADDITIVES IN COPPER PLATING BATHS

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SUMMARY

A new method is described for the analysis of organic additives in copper plating baths. Liquid chromatography, utilizing an ion-pair reversed-phase technique, was found to be most suited for this purpose. Ion pairing neutralizes the brightener components, thereby enabling the use of moderate conditions during analysis, *i.e.*, a pH of 4–5 and isocratic elution. Preceding the chromatography, a solid-phase extraction process was used to decrease the copper ion concentration and the acidity of the bath. Active copper plating baths were investigated and the results are given and explained.

INTRODUCTION

Electrical copper plating is one of the most important steps in the manufacture of printed circuit boards. The pattern of the copper on the board is responsible for the conductivity between the electronic components mechanically attached to the board surface. During the copper electroplating, close control is required so that neither too much nor too little copper is plated on the board or in the plated-through holes, and that the copper deposit has a bright shiny uniform appearance with high ductility and tensile strength. It has been found that the rate of electrodeposition of the copper is important in respect of efficient and repeated formation of an uniform continuous smooth layer of bright shiny metal having a controlled depth or thickness with good physical properties. Organic additives, commonly known as "brighteners" (or "copper gleam" in acidic copper baths), are used in electroplating baths to regulate the rate of metal deposition and thus to maintain control over the physical properties of the plated metal. Therefore, it is very important to be able to monitor both changes in the concentration and the chemical composition of the additives in the bath.

The concentrations of the additives fluctuate due to their electrochemical destruction during the plating process and to their inclusion in the copper plate. As the additive concentration changes, it affects the quality of the plating. If the brightener

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concentration is too low, the copper electroplate becomes coarse grained or burned and powderly; if it is too high, the electroplated copper shows a burned deposit with a brittle or non-uniform surface.

Increasing demands for high reliability in the manufacture of printed circuit boards with high aspect ratios, specifically on very dense multilayer substrates, necessitate the definition control of the range of allowed concentrations of the additives in the copper plating solutions. In view of the importance of the additives, the paucity of published reports describing their analysis is most surprising. The few reports which can be found describe methods such as cyclic voltammetric stripping, high-performance liquid chromatography and ion chromatography. The oldest and most common test of additive concentration is the "Hull-cell" test which consists of a small electrodeposition cell through which a current is passed. The nature of the electroplated copper layer is monitored as function of the current density. However, this test does not provide a direct measurement of the additive concentration.

More recently, a polarographic technique known as cyclic voltammetric stripping (C.V.S.) has been used for the analysis of organic additives in baths, *e.g.*, ref. 1. The C.V.S. technique provides direct evidence of the influence of additives on the overvoltage for copper deposition. The measurement of the charge required to strip a plated deposit is indicative of the concentration of the additives. However, the C.V.S. technique is influenced by the electrolyte species, contaminant concentration, temperature and chloride concentration due to their effects on the stripping charge. Several papers and technical notes describe various modes of chromatographic analysis of the brighteners. An application note from Dionex[2] concerns an ion chromatographic method for the analysis of the major component in a commercial Copper Gleam solution. LeaRonal, a manufacturer of such solutions, described the reversed-phase liquid chromatographic analysis of a particular brightener solution[3]. The method used a solid-phase extraction step to pre-isolate the organic compounds from the acidic copper bath, a column containing a polymeric packing and step gradient elution. The resulting chromatogram was rather complex, making the quantitation difficult. Reid[4] also described a reversed-phase liquid chromatographic system utilizing a column packed with a polymeric packing. Although he used an UV detector, most of the work employed an electrochemical detector. He monitored the concentration of brighteners in an acidic copper bath under a variety of conditions. Since the detector used was selective, only one or at most two peaks were observed.

The characterization of organic additives is difficult due to the complex nature of the bath. A typical acidic copper bath contains copper salt (15–22.5 g/l), sulphuric acid (170–230 g/l), chloride ion (30–80 ppm) and organic agents at various concentrations, usually less than 1%, depending on the system used. Therefore, the accurate analysis of the additives requires intensive pretreatment prior to the chromatographic injection. The present work examines the concentration and behaviour of the organic additives in a typical acidic copper bath.

EXPERIMENTAL

Materials

The mobile phase was prepared using 18-mΩ water and HPLC-grade acetonitrile (Bio-Lab, Jerusalem, Israel). The mobile phase components were filtered

through a 0.2-μm filter. Tetrabutylammonium hydrogensulphate was obtained from Sigma Israel (Tel Aviv, Israel). The samples of the organic additives were stored at 4°C to prevent decomposition. They, and samples from active copper plating baths, were obtained from Tadiran Printed Circuits.

The column (250 mm × 4.5 mm I.D.) was a LiChrosorb RP-18 cartridge (Merck, Darmstadt, F.R.G.). An open column (10 mm × 0.5 mm I.D.) packed with 40-μm reversed-phase particles was used for extraction.

The mobile phase used consisted of 91% water, 9% acetonitrile and 3 m*M* tetrabutylammonium hydrogensulphate.

Instrumentation

The chromatographic studies were carried out using a Series 4 liquid chromatograph (Perkin-Elmer, Norwalk, CT, U.S.A.) and either a Perkin-Elmer 85B UV–VIS detector or a Chrom-A-Scope rapid scanning UV detector and integrator (Barspec, Rehovot, Israel).

Sample preparation

It was necessary to reduce the high concentration of the copper as its strong UV absorbance obscured that of the organic components. The high acidity of the original bath is also harmful to the analytical column. In order to decrease the concentration of copper ions and of sulphuric acid in the samples from the concentrations that can be found in the bath, a solid-phase extraction process was used. A 20-ml volume of the original bath solution was passed through the extraction column followed by 3 ml water and 5 ml acetonitrile. The acetonitrile fraction was collected and its volume was adjusted to 4 ml.

RESULTS AND DISCUSSION

In this work the organic additives used were of a type commercially available in Europe, suited to work with titanium baskets and containing mainly surfactants such as sulphonic alkanes. Because of the highly ionic nature of the brightener components, they cannot be retained using conventional reversed-phase chromatography. To retard the solutes, ion-pair chromatography was used with tetrabutylammonium cations added to the mobile phase.

Fig. 1 shows a chromatogram of the additive standard as supplied. The chromatogram shows two main peaks, A and B, corresponding to two of the

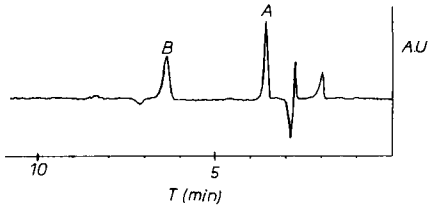

Fig. 1. Chromatogram (at 210 nm) of 7.5 ml/l of a basic additive standard showing two peaks due to the organic modifier components, A and B.

components in the organic modifier. A third component, called the "carrier" or "wetting agent", does not appear in the chromatogram since it absorbs in the UV range only below 200 nm.

Of the two other components, the second peak shows a significant decrease after bubbling of air through a sample of the brightener over an extended period, and a third peak, C, appears. The sum of the areas of peaks B and C does not equal that of the original peak B. This variation in the total peak areas might be due to the different absorption coefficient of the degradation product (peak C).

With further oxidation over 1 month, peak B decreases until it finally disappears, Fig. 2. Concurrently, there is a corresponding increase in peak C. The rate of formation of the degradation product is dependent on the rate of bubbling of air and on the temperature; when refrigerated, there is no apparent change in the second peak.

Using the Hull-cell technique, it was found that as the second component (peak B) decreases and peak C increases, the brightener solution shows a poor plating quality. This confirms the significance of the second component of the organic additive in the plating process.

Fig. 3 shows a chromatogram of the organic additive in an acidic copper bath after the solid-phase extraction. Even after the extraction process, a copper peak can still be noticed before the solvent peak. Its short retention time is due to the fact that the reversed-phase column is acting as an anion exchanger (because of the ion-pairing reagent) which will not retard the positive copper ions.

To examine the utility of the method for determination of the concentration of the additive in acidic copper baths, a calibration graph was prepared for various concentrations of the organic additive, ranging from 2.5 to 15 ml brightener per litre bath solution. Such graphs were plotted for both peak A and peak B. They were linear in this concentration range. For peak A, the relationship between the peak height and the concentration, C (in units of ml additive per litre bath solution), is:

$$\text{Height} = 0.527C - 0.239$$

The correlation coefficient is 0.9979. For the second component the equation is

$$\text{Height} = 0.899C - 0.0644$$

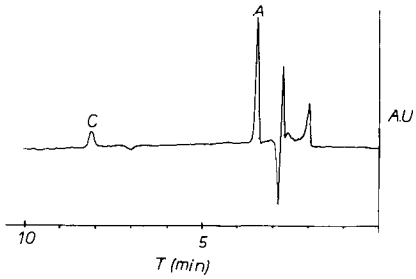

Fig. 2. Chromatogram (at 210 nm) of the same sample as in Fig. 1 after bubbling of air over an extended period. Note the disappearance of peak B and the appearance of a third peak, C.

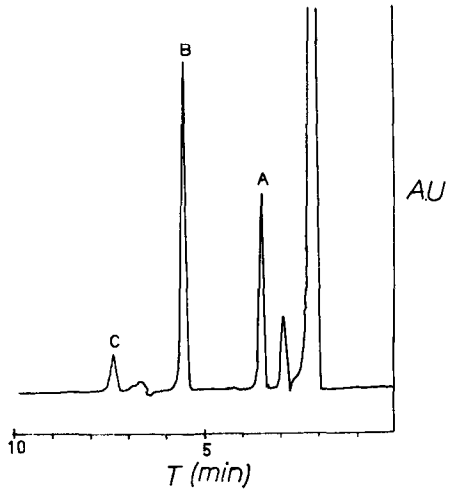

Fig. 3. Chromatogram (at 210 nm) of the organic modifier in an acidic copper bath after solid-phase extraction.

with a correlation coefficient of 0.998. The results indicate that ion-pair reversed-phase liquid chromatography can be used for quantitation of the brightener in acidic copper bath.

A chromatogram of an active bath is shown in Fig. 4. Two important points

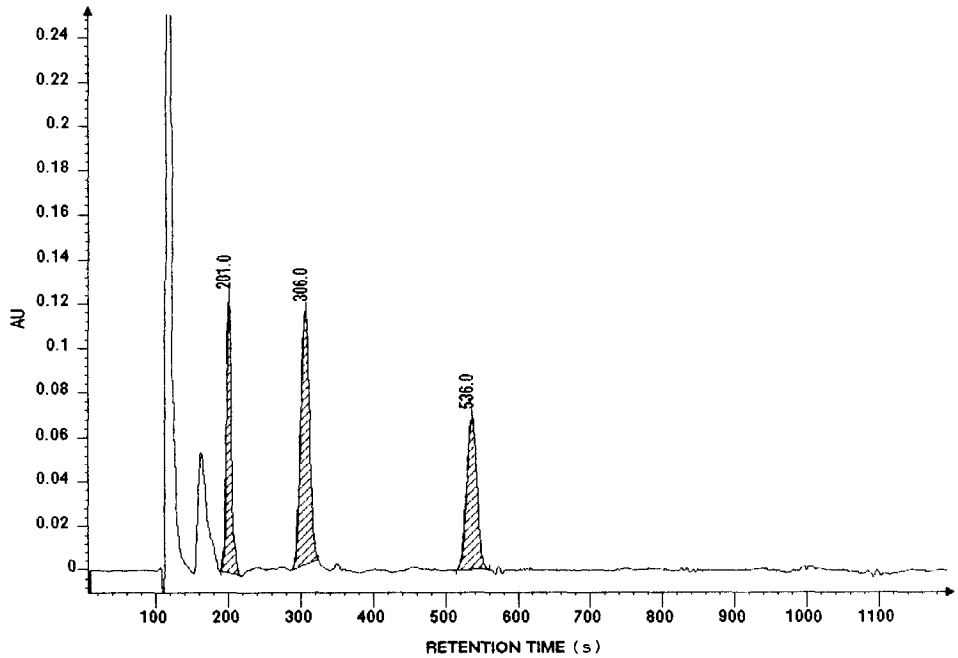

Fig. 4. Chromatogram (at 200 nm) of an active bath. Note the increased height of peak C.

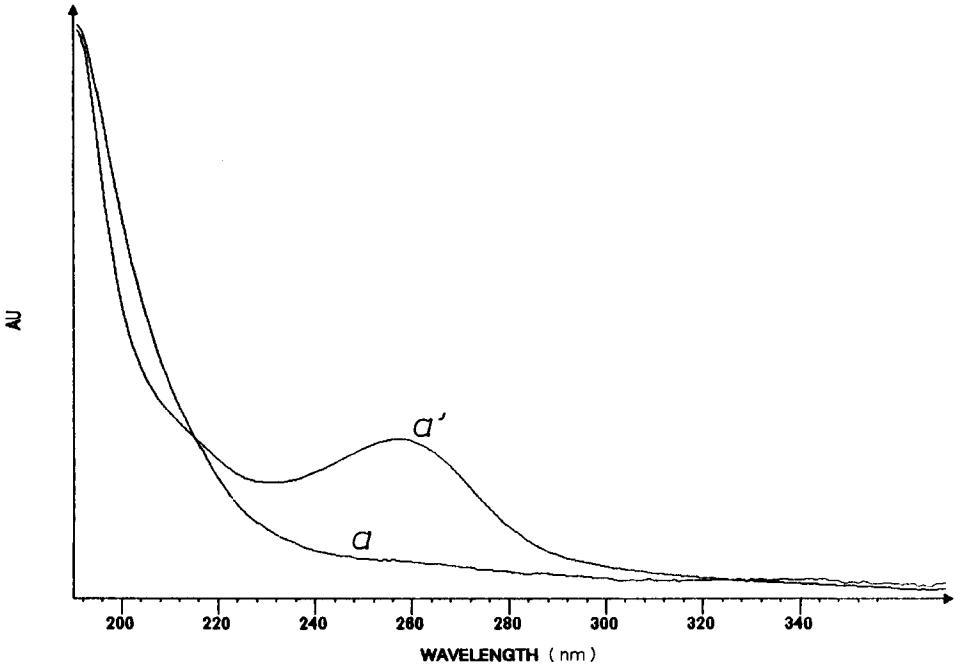

Fig. 5. Spectra of peak A in a new (a) and an activated (a') bath.

should be noted. The first is the appearance of an increased amount of the degradation product, peak C. At a first glance, it may seem that the concentrations of components B and C are equal, corresponding to their equal heights and areas. However, as mentioned above, the absorbance coefficient of the degradation product may significantly differ from that of the second component. Therefore, its relative concentration, as shown in the chromatogram, may differ from that of its source (peak B). Furthermore, the concentration of peak C seems to increase in proportion to the activation time of the bath. This is expected as new brightener is added periodically to the bath to replenish its diminishing concentration.

The second point of interest is the change in the absorbance spectrum of the first peak (peak A) in the chromatogram of the brightener before and during activation of the bath. Fig. 5 shows a spectrum, obtained with the Barspec detector, of peak A in a new bath and in an active one. An absorption peak at 260 nm appears in the spectrum of the component in an active bath. The reason for the change in the spectrum is not known at this stage of the research.

CONCLUSIONS

The liquid chromatographic method described allows the determination of the concentration of a brightener solution in an acidic copper bath, and the monitoring of changes in the composition of the brightener. The use of a rapid-scanning detector offers the possibility to monitor even more closely the changes that occur in the

brightener components. At present, we are investigating further the fate of the brightener in acidic copper baths and their effect on the quality of the plated copper.

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REFERENCES

1 D. Tench and J. White, *J. Electrochem. Soc.*, 132 (1985) 831.
2 *Dionex's Application Update, AU111*, Sunnyvale, CA, October, 1986.
3 *LeaRonal's TechSpecs, 30019-HPLC*, June, 1987.
4 J. Reid, *PC Fab.*, November (1987) 5.