Determination of Pyridinium-1-Propane-2-Hydroxide-3-Sulfonate and Saccharin in a Bright Nickel Electroplating Bath

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A new method, using an ultraviolet absorption spectrophotometer, was developed for the simultaneous determination of pyridinium-1-propane-2-hydroxide-3-sulfonate (PPSOH) and saccharin in a bright nickel electroplating bath. The effect of pH, inorganic salt concentration and 1,4-butynediol concentration on the absorbance of PPSOH and saccharin, was reported. This method is rapid and simple. It can be applied to the on-site determination of the concentration of PPSOH and saccharin in the bright nickel electroplating bath.

Keywords: Bright nickel electroplating, additives, PPSOH, saccharin

Introduction

The rapid and accurate detection of organic additives in electroplating baths is the key point in improving the quality of electroplated products. Further, it is a useful and important research field. Up to now, there is still a lack of rapid and accurate analytical methods for qualitative analysis of organic additives in industrial applications. This limitation arises from the following:

- 1. Organic additives are complicated and are generally used at low concentrations, requiring microanalytical techniques.
- 2. The high concentration of inorganic salt in the electroplating bath strongly interferes with the detection of organic additives.
- Most commercial formulas are secret. Their chemical compositions are generally not disclosed.
- Some organic additives take part in the electrode reaction and form oxidized or reduced products, adding to the complexity of the organic components.
- 5. Powerful instruments, such as IR, NMR and MS are difficult to apply to the analysis of organic additives.

Carano¹ determined the concentration of pyridine-based leveling compounds in nickel plating baths by differential pulse polarography. Chang² measured of concentrations of subcomponents of plating solution additive mixtures by cyclic voltammety. Crotty³ analyzed zinc plating brighteners by high performance liquid chromatography (HPLC). Sonnenberg⁴ analyzed brighteners and levelers used in metal electroplating baths by the differential adsorption of these additives on a working electrode during a sequence of steps prior to and during metal plating.

As new electroplating processes have emerged, some of the organic intermediates have become more widely used, providing a good opportunity for applying additive analysis. Ultraviolet absorption spectrophotometry has been used to determine Ni⁺², Fe⁺² and additives in electroplating baths.⁵⁻⁹ The analyses of saccharin¹⁰ or PPSOH¹¹ have also been reported. Saccharin and PPSOH are important in nickel plating and are often used together in many processes to obtain good deposits. In this report, we studied possible factors affecting the absorbance of saccharin and PPSOH in order to provide a simple, rapid and accurate method for the simultaneous determination of saccharin and PPSOH. This method can be applied to online monitoring of these organic additives during the electroplating process.

Reagents and instruments

Instruments

The instrumentation used in this work consisted of a UV-2450 spectrometer (Daojin, Japan), a one-cm quartz cell and a pH meter (Leici, Shanghai, China).

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Reagents

Analytical reagent grade NiSO₄·6H₂O (270 g/L), NiCl₂·6H₂O (50 g/L), H₃BO₃ (35 g/L) and H₂SO₄ were used to prepare the Watts nickel bath. Saccharin (food-grade reagent), PPSOH, sodium dodecyl sulfate (SDS) and 1,4-butynediol were used as plating additives.

Results and discussion

UV absorption analysis of a Watts nickel electroplating bath

A Watts nickel plating bath containing 0.3 g/L 1,4-butynediol and 0.1 g/L SDS was scanned in the wavelength range of 225 to 350 nm (versus distilled water). Experimental results showed that nickel sulfate, nickel chloride, boric acid, 1,4-butynediol and SDS exhibited no absorption in this range (Fig. 1).

UV absorption spectrum of saccharin

0.1 g/l saccharin in the Watts bath was added to the above bath and scanned from 200 to 350 nm. The UV results are shown in Fig. 2. It can be seen that the maximum absorption of saccharin was localized at 261 nm, and was not influenced by the other components in the plating bath.



Figure 1-Absorption spectrum of a Watts nickel bath.



Figure 2—Absorption spectrum of saccharin.

The Lam-Beer law shows that an absorbance value between 0.3 and 0.8 will provide high accuracy and low error. In order to keep the absorbance of saccharin in this range, we selected a saccharin concentration in the range of 0.06 to 0.12 g/L for the experiments.

UV absorption spectrum of PPSOH

PPSOH absorption spectra at a concentration of 0.021 g/L in the Watts bath containing 0.3 g/L saccharin and 0.1 g/L SDS are shown in Fig. 3. It can be seen that there are three absorption peaks in the range of 200 to 350 nm, at 203.3 nm, 220.0 nm and 261.0 nm.

The experimental results show that the appropriate concentration for PPSOH detection is between 0.007 and 0.035 g/L. In industrial plating applications, the concentration of PPSOH is 0.1 to 0.03 g/L. In order to guarantee accuracy, we diluted the original electroplating baths by a factor of 20 and then measured the diluted concentration of PPSOH.

Effect of pH on the absorbance of PPSOH and saccharin

Experimental results showed that changing pH had no effect on the absorbance of PPSOH and saccharin.¹⁰⁻¹¹

UV absorption spectrum for the mixture of PPSOH and saccharin

To the Watts bath containing 0.3 g/L 1,4-butynediol and 0.1 g/L SDS, we added 0.021 g/L PPSOH and 0.1 g/L saccharin, then scanned the absorption spectrum in the range of 200 to 350 nm. The absorption spectrum for the mixture is shown in Fig. 4. The figure shows that, saccharin had a relatively strong absorption at 285 nm, while PPSOH had no absorbance at that wavelength. Therefore, the absorbance at 285 nm can be used for the determination of saccharin concentration.

From the absorption of the PPSOH and saccharin mixture, we can detect the concentration of saccharin, but the absorption spectrum of PPSOH interferes somewhat. Within the absorption band from 210 to 335 nm, the absorbance of PPSOH and saccharin interfere to a large extent, and it is not appropriate for PPSOH detection.



Figure 3-Absorption spectrum of PPSOH.

In the mixture mentioned above, we can measure the absorbance of saccharin at 285 nm (A_2) and calculate its concentration (C_1) and absorption coefficient (K_{12}). From the absorption spectrum of saccharin without PPSOH, we can obtain the absorption coefficient of saccharin at 285 nm (K_{12}). Using the same method, we can obtain the absorption coefficient of PPSOH at 261 nm (K_{21}). Therefore, we can obtain the following equation:

$$A_1 = A_{11} + A_{12} = K_{11}C_1 + K_{21}C_2$$
(1)

$$A_2 = A_{21} + A_{22} = K_{12}C_1$$
(2)

From equation (1) and (2),

$$C_{2} = (K_{12}A_{1} - K_{11}A_{2}) / K_{12}K_{21}$$
(3)

$$C_1 = A_2/K_{12}$$
 (4)

After measuring the absorbance at 285 nm and 261 nm, we can monitor the concentration of PPSOH (C_2) using equation (3).

Working curve

At a pH of 6.6 and containing 2.0 mL of Watts solution diluted to 50 mL, we measured the 261.0 nm (A_1) and 285.0 nm (A_2) absorbances of saccharin at concentrations of 0.008, 0.016, 0.024, 0.032, 0.040 and 0.048 g/L. The results are shown in Table 1.

4.45% 4.60% 3.60% 2.60% 2.60% 5.



Under the same conditions we measured the absorbance of PPSOH at 261 nm (A_{21}) at concentrations of 0.007, 0.011, 0.015, 0.020, 0.026, 0.033 and 0.040 g/L. The results are also shown in Table 1. The working curves of saccharin and PPSOH are shown in Figs. 5, 6 and 7.



Figure 5-The work curve of saccharin at 261 nm.



Figure 6-The work curve of saccharin at 285 nm.

Table 1	
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The relationship between the absorbance and the concentration of saccharin or PPSOH

C _{Saccharin} (g/L)	0.008	0.016	0.024	0.032	0.040	0.048	0.060
Absorbance A_{11} (261 nm)	0.053	0.115	0.175	0.236	0.302	0.366	0.453
A ₁₂ (285 nm)	0.036	0.082	0.115	0.155	0.193	0.244	0.308
C _{PPSOH} (g/L)	0.007	0.011	0.015	0.020	0.026	0.033	0.040
A ₂₁ (261 nm)	0.096	0.152	0.201	0.265	0.342	0.421	0.518



Figure 7-The work curve of PPSOH at 261 nm.



Figure 8-Variation of saccharin during the electroplating process.



It should be stressed that all the experiments deriving the working curves are at the same plating solution composition. Hence:

$K_{11} =$	7.517
$K_{12} =$	5.012
$K_{21}^{12} =$	13.020

Figure 8 shows that with increasing electroplating time, the saccharin is consumed and its concentration decreases. This also indicates that the saccharin consumed has little relationship to its concentration, but is connected with the electroplating time. From the curve shown in Fig. 8, we can calculate the consumed rate to be 70 g/KAH.

As plating proceeds, the concentration of PPSOH decreases, and the PPSOH consumed has a close relationship with its concentration. When the concentration of PPSOH is 0.196 g/L, the consumed amount is 47.5 g/kA-hr. At a PPSOH concentration of 0.076 g/L, the corresponding amount consumed is 15.0 g/kA-hr and at 0.035 g/L PPSOH, 5.0 g/kA-hr is consumed. At the lower concentration of PPSOH, the smaller consumption is obvious.

Conclusions

We have shown that the use of UV absorption to detect the concentration of saccharin and PPSOH in nickel plating solutions is convenient, accurate and has a high tolerance with respect to 1, 4butynediol and SDS. The absorbance of saccharin or PPSOH is not influenced by solution pH. The consumption of saccharin is related to electroplating time. The longer the electroplating time, the lower the concentration. The consumption of PPSOH is different, even at the same electroplating time. It is related to the electroplating time and the concentration of PPSOH. The higher the concentration of PPSOH, the more PPSOH is consumed. This method can be applied to the on site determination the concentration of PPSOH and saccharin in the industrial electroplating bath itself.

Figure 9-Variation of PPSOH concentration during the electroplating process.

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