Determination of Pyridinium-1-Propane-2-Hydroxide-3-Sulfonate and Saccharine in Brighten Nickel Electroplating Bath

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Abstract:

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

Key words: Bright nickel electroplating; additives; PPSOH; saccharine

1. Introduction

The rapid and accurate detection of the organic additives in electroplating bath is the key-point to improve the quality of electroplating products. Meantime it is still the useful and important research field. Up to now, there is still lack of the rapid and accurate analytical methods for organic additives in industrial application. This limitation comes from the points listed below. (1) The Organic additives are complicated and with low concentration. It belonged to the microanalysis. (2) The detection of organic additives is strongly interferenced by the high concentration of inorganic salt in the electroplating bath. (3) Most of the formula of trade product is secrecy. Their chemical composition is undeclared. (4) Some organic additives take part in the electrode reaction and form oxidized or reduced product, to further the complexity of the organic component. (5) The powerful instrument such as, IR, NMR, MS etc. is difficult to be applied to the analysis of organic additives in the electroplating baths. Carano[1] determined of Pyridine-based leveling Compounds in Nickel

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Electroplating Baths by differential Pulse Polarography. Chang[2] measured of concentrations of subcomponents of plating solution additive mixtures by cyclic voltammetric method. Crotty[3] analyzed Zinc Plating Brighteners by HPLC. Sonnenberg[4] 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.

With the development of electroplating technique, some of the organic intermediate became more and more publicity, which provide a good opportunity for the additive analysis. The method of ultraviolet absorption spectrophotometer was developed for the determination of Ni^{+2}, Fe^{+2} and additives in electroplating bath[5-9]. The analysis of saccharine or PPSOH have been reported, respectively[10-11]. The saccharine and PPSOH are important in the electroplating process. To get good plating product they often exist in the same electroplating baths. In this report, we studied the possibly effective factors on the absorbance of Saccharine and PPSOH and provide a simple, rapid and accurate method on the simultaneous determination of Saccharine and PPSOH. This method can be applied to the online monitor the concentration change of these organic additives during the electroplating process.

2. Reagents and Instruments

2.1 Instruments

UV-2450 spectrometer (Daojin Japan); 1 cm quartz cell; pH meter (Leici, Shanghai, China).

2.2 Reagents

$NiSO_4 \cdot 6H_2O$, $NiCI \cdot 6H_2O$, H_3BO_3, H_2SO_4 are analytical reagents, Saccharine is food reagent, PPSOH, SDS (sodium dodecyl sulfate) and 1,4-butynediol are electroplating reagents.

Composition of Watt Nickel: $NiSO_4 \cdot 6H_2O$ (270 g/l), $NiCI_2 \cdot 6H_2O$ (50g/l), H_3BO_3 (35g/l).

3. Results and discussion

3.1 UV absorption of Watts nickel electroplating bath

Watts nickel plating baths contained 0.3 g/l 1,4-butynediol and 0.1 g/l SDS are scaned in the wavelength range of 225-350 (versus distilled water). Experimental results proved that nickel sulfate, nickel chloride, boric acid, 1,4-butinediol and SDS have no absorption in this range (Fig. 1).

3.2 UV absorption spectrum of saccharine

0.1 g/l saccharine in the Watts bath in addition with 0.3 g/l 1,4-butinediol and 0.1 g/l SDS was scanned in 200-350 nm. The UV results were shown in Fig. 2. From Fig. 2, it can be seen that the maximum absorption of Saccharine localized at 261 nm, which has no influence from other components in the electroplating baths.

Lam-Beer law showed that the absorbance between 0.3 and 0.8 will provide high accuracy and low error. To keep the absorbance of Saccharine at this range we selected the saccharine concentration at the range of 0.06-0.12 g/l by experiment.

3.3 UV absorption spectrum of PPSOH

PPSOH absorption spectra at 0.021 g/l in the watts bath contained 0.3 g/l saccharine and 0.1 g/l SDS are shown in Fig. 3. From Fig. 3, it can be seen that there are 3 absorption peaks in the range of 200-350 nm, with the absorption peaks at 203.3nm, 220.0 nm and 261.0 nm, respectively.

Experimental results proved that the appropriate concentration for PPSOH detection is 0.007-0.035 g/l. During the industrial application, the concentration of PPSOH is 0.1-0.03 g/l. To guarantee the accuracy, we dilute the original electroplating baths for 20 times then detect the concentration of PPSOH.

3.4 Effect of pH on the absorbance of PPSOH and saccharine

Experiment results proved that the change of pH has no effect on the absorbance of PPSOH and saccharine[10-11].

3.5 The absorption spectrum for the mixture of PPSOH and saccharine

In the Watts baths containing 0.3g/l 1,4-butinediol and 0.1 g/l SDS, we added 0.021 g/l PPSOH and 0.1 g/l saccharine, then scan the absorption spectrum in the range of 200-350 nm. The absorption spectrum for the mixture is shown in Fig. 4.

By comparing the spectrum mentioned above, we can see that, saccharine has relative strong absorption of at 285 nm, while PPSOH has no absorbance at that wavelength. So the absorbance at 285 nm can be used for the detection of saccharine concentration.

From the absorption of the PPSOH and saccharine mixture, we can detect the concentration of Saccharine, but the absorption spectrum of PPSOH is somewhat superposition. At the absorption band of 210-335 nm, the absorbance of PPSOH and saccharine interferenced greatly, it is not appropriate for PPSOH detection.

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

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

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

From equation (1) and (2), we can get $C_2=(K_{12}A_1-K_{11}A_2)/K_{12}K_{21}$ (3)

$$C_1=A_2/K_{12}$$

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

3.6 Working Curve

Under the pH of 6.6 and contained 2.0 ml Watts solution in 50 ml, we detect the 261.0 nm (A_1) and 285.0 nm (A_2) absorbance of saccharine of 0.008, 0.016, 0.024, 0.032, 0.04 and 0.048 g/.l, respectively. The results are shown in Table 1.

Under the same conditions detect the absorbance of PPSOH at 261 nm (A_{21}) under 0.007, 0.010, 0.014, 0.021, 0.028, 0.032, 0.035 and 0.042 g/l. The results are shown in Table1. The work curves of Saccharine and PPSOH are showed in fig. 5, fig. 6 and fig. 7.

Please note that all the experiment on working curve is versus the same concentration of electroplating solution.

Hence we can get: K_{11}=7.517; K_{12}=5.012; K_{21}=13.020

Fig. 8 showed that with the increasing of electroplating time, the saccharin in electroplating baths being consumed and its concentration decreased. This also indicated that the consumed amount of saccharin has little relationship with its concentration, but connected with the electroplating time. From the curve showed in Fig. 8, we can calculate the consumed rate is 70 g/KAH.

With the electroplating going on, the concentration of PPSOH decreased, meantime the consumed amount of PPSOH has close relationship with its concentration. Such as when the concentration of PPSOH is 0.196 g/l, the consumed amount is 47.5 g/kAh; while the PPSOH concentration is 0.076 g/l, the corresponding consumed amount is 15.0 g/kAh and 0.035 g/l of PPSOH corresponding to 5.0 g/kAh consumption. The lower concentration of PPSOH, the smaller consumption is obvious.

4. Conclusions

Experiment proved that the method of UV absorption to detect the concentration of saccharin and PPSOH is convenient, accurate and has high tolerance with l, 4-butinediol and SDS. The absorbance of saccharin or PPSOH is still not influenced by pH. The consumption of saccharin is related with electroplating time. The longer electroplating time, the lower concentration is. The consumption of PPSOH is different, even under the same electroplating time. It is related with bath the electroplating time and the concentration of PPSOH. The higher concentration of PPSOH, the more PPSOH is consumed.

It can be applied to the on site determination the concentration of PPSOH and saccharine in the industrial electroplating bath.

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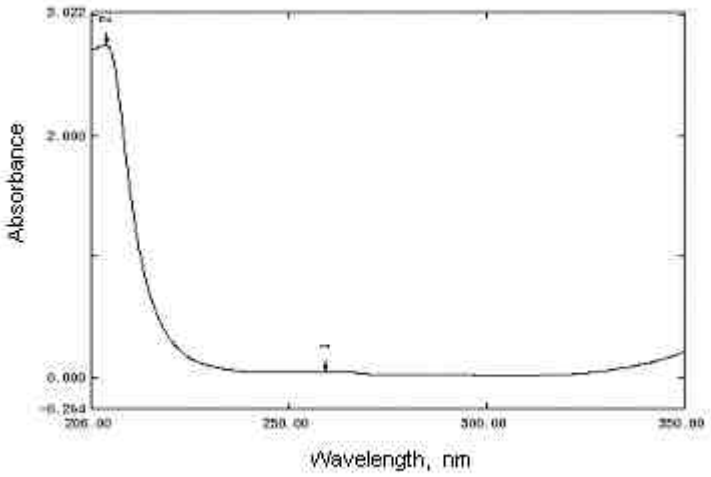

Fig. 1 Absorption spectrum of Watts nickel baths

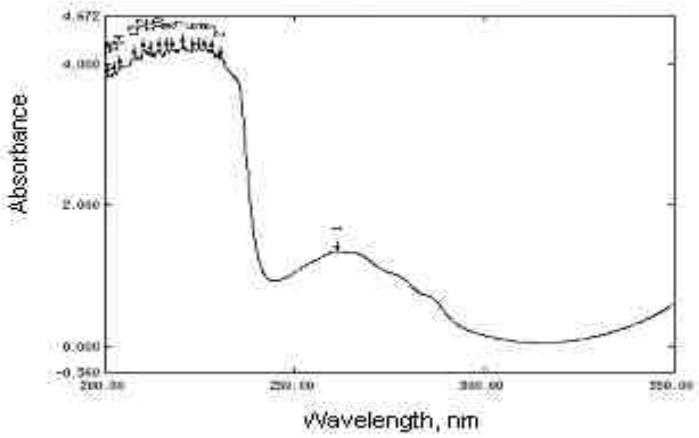

Fig.2 Absorption spectrum of Saccharine

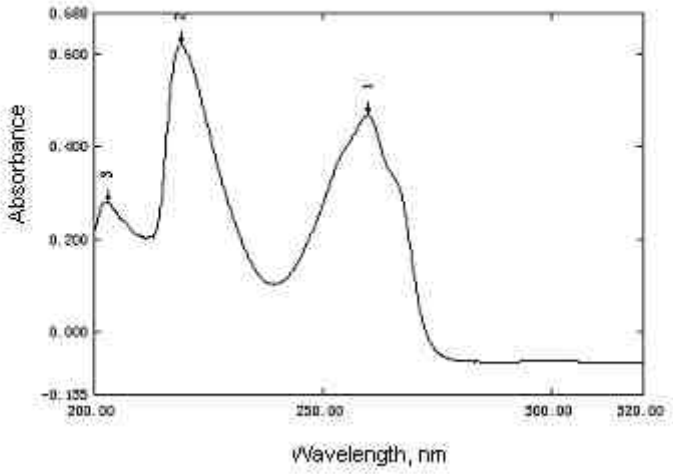

Fig.3 Absorption spectrum of PPSOH

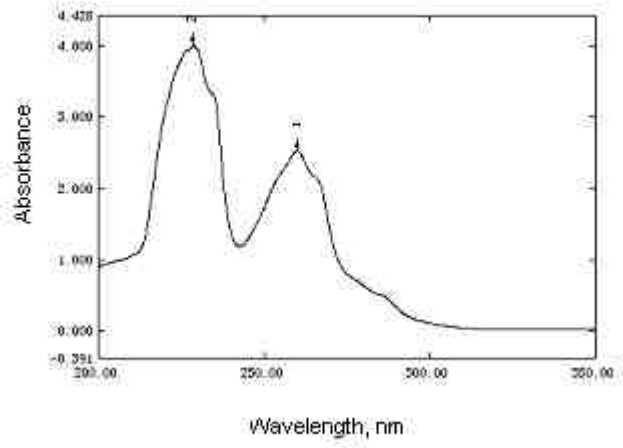

Fig.4 Absorption spectrum for the mixture of PPSOH and saccharine

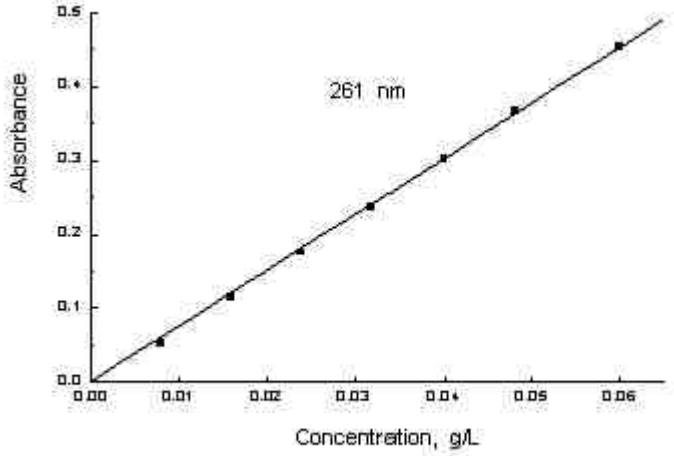

Fig.5 The work curve of Saccharine at 261 nm

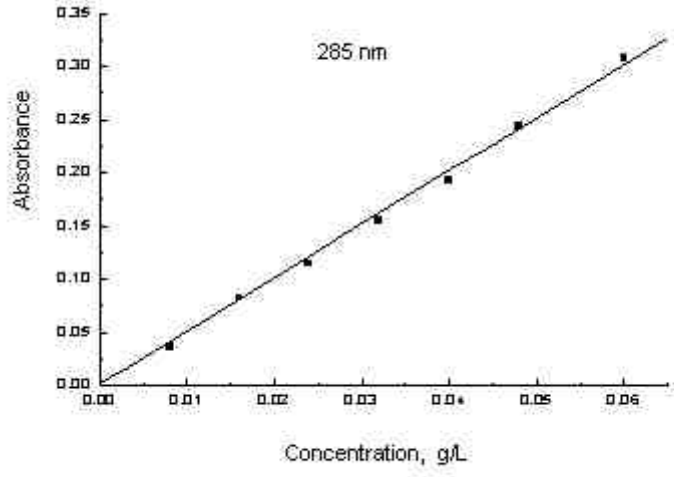

Fig. 6 The work curve of Saccharine at 285 nm

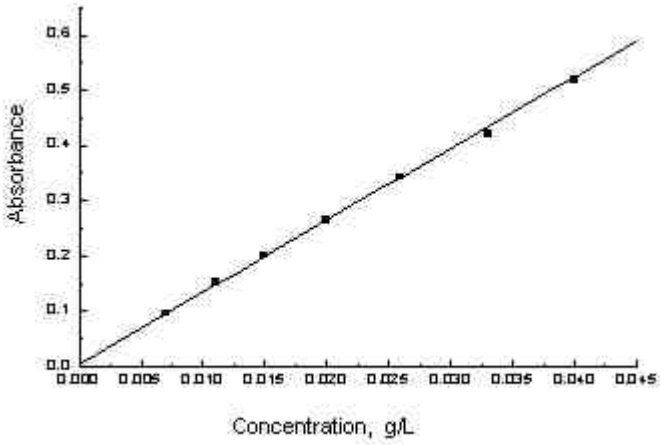

Fig.7 The work curve of PPSOH at 261 nm

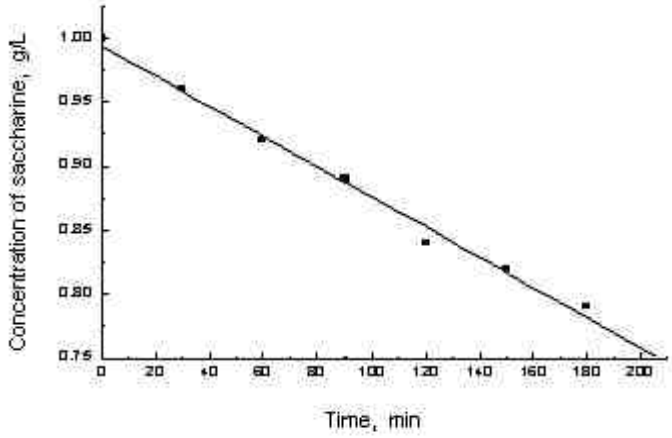

Fig. 8, Variation of saccharin during the electroplating process

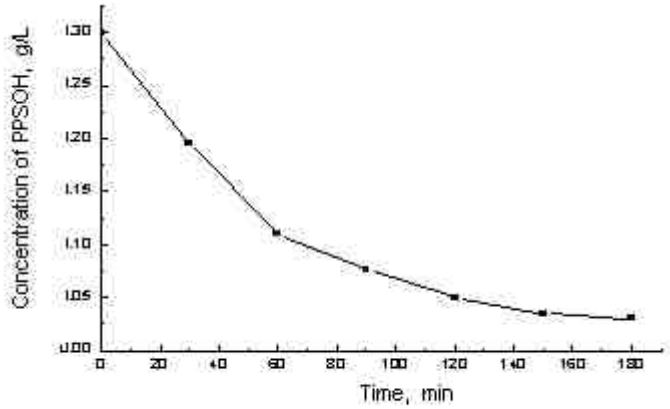

Fig. 9 Variation of PPSOH concentration during the electroplating process

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

$C_{Saccharine}$ (g/l)	0.008	0.016	0.024	0.032	0.040	0.048	0.060
Absorbance A_{11}(261nm)	0.053	0.115	0.175	0.236	0.302	0.366	0.453
A_{12}(285)	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}(261nm)	0.096	0.152	0.201	0.265	0.342	0.421	0.518

