

Effects of Phenolsulfonate on the Electrolyte, Plating Efficiency and the Deposit

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In phenolsulfonic acid-based bath for electroplating, extended use of electrolyte makes the desirable plating current density range narrower. It was assumed that the aging of electrolyte was caused by the contamination of metal impurities and the accumulation of phenolsulfonate. In this study, the effects of the accumulation of phenolsulfonate, added as sodium phenolsulfonate, on the characteristics of electrolyte, plating efficiency and the deposit were investigated. The rise of phenolsulfonate concentration decreases the desirable plating current density range.

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Introduction

Among the commercial acidic electro-tinning processes, the Ferrostan process, in which the phenolsulfonic acid-based electrolyte (PSA bath) has been adopted, is the most widely applied for continuous strip electroplating line. About 80% of tinplate produced in the world is deposited from the electrolyte¹⁾.

The PSA bath consists of stannous sulfate, phenolsulfonic acid and a brightener (ethoxylated α -naphthol sulfonic acid). In the bath, the extended use of the electrolyte results in the narrower optimum current density range, which is called as electrolyte aging. It has been known that the aging of the PSA bath could be caused by the accumulation of inorganic ions such as Fe^{2+} , Cl^- , Sn^{4+} and Cr^{6+} , and/or the organic substances such as grease, oil.^{2) - 4)} However those factors have been failed to reveal the full causes of the aging. Even though the concentrations of the above aging-suspected substances were properly low, the aging phenomena were also able to be observed.

In PSA bath the phenolsulfonic acid is added persistently to keep the acidity of the bath and to prevent the oxidation of the stannous ions. During the analysis of the PSA bath using UV-VIS spectrophotometric method, it was founded that the concentration of phenolsulfonate ion was quite different from the concentration of PSA, which had been generally accepted as the converted value of free acidity. It means that the concentration of the phenolsulfonate ion present in the bath has nothing to do with the acidity of the bath. By the UV-VIS analysis, the phenolsulfonate concentrations of fresh and aged electrolytes were 57 g/l and 176 g/l, respectively, even though the concentration of PSA was maintained in the range of 14 to 16 g/l. It implies that the phenolsulfonate ions dissociated from the PSA become accumulated as the operation keeps running, while the dissociated hydrogen ions are consistently consumed by side reaction during electrodeposition of tin

In this paper, it was assumed that the accumulation of phenolsulfonate could have a close relationship with electrolyte aging in the PSA bath, and thereby, the degree of aging could be controlled by the concentration of phenolsulfonate accumulated in the bath. The electroplating and electrochemical behaviors in the electrolytes, in which the phenolsulfonate was artificially accumulated, were investigated in comparison with

the behaviors in the aged electrolyte by long-term operation.

Experimental procedures

Table 1 shows the compositions of the electrolytes. Electrolyte #A and #E are fresh and aged one, respectively. In order to change the concentration of phenolsulfonate artificially, sodium phenolsulfonate (Aldrich Co, 98%) was added to the electrolyte #A in the electrolytes #B, C, and D, while the concentration of other major components (Sn^{2+} , free acid, ENSA) were kept similar. The concentration of the major components and phenolsulfonate were analyzed by the conventional methods and UV-VIS spectrophotometric method, respectively. The physical properties of the electrolytes were measured in terms of conductivity and surface tension.

Table 1 Chemical composition of electrolyte

Sample	Concentration (g/l)			
	Sn^{2+}	Free acid	ENSA *	Phenol-sulfonate
A (fresh)				57
B	28~	14~16	5~6	120
C	30			180
D				240
E (aged)				176

* Ethoxylated α -naphthol sulfonic acid

For a preliminary investigation, the electroplating behaviors of the electrolytes were examined by a Hull cell test. The electrolyte temperature was 40°C and a plating current of 3A was applied for 30 seconds under repeatable and proper agitation. The Hull cell patterns were determined by naked eyes.

To find out the effect of electrolyte aging on the surface properties of the electrolytic tinplate, a circulation cell, in which the electrolyte was forced to circulate into a plating cell, was utilized. In the plating cell, the anode (99.9% Sn) and the cathode (steel sheet) were mounted 20mm apart, and the electrolyte was passed between the electrodes at 3m/sec. Prior to electroplating, the cold-rolled steel sheet with a average roughness of 0.35 μm was degreased and pickled. Electroplating

was conducted under bath temperature of 40°C with variation of current density from 10 to 70A/dm². Tin coating weights were controlled to 5.6g/m² and 11.2g/m². After electroplating, the cathode was rinsed and dried, and the surface resulted in cloudy appearance, which was called as a matte plate. To produce bright coating layer, the matte plate was reflowed in the reflow simulator. In reflow simulator, the matte plate was heated upto 254• by resistance heating and followed by quenching into the water of 70•. After reflow treatment, the surface of the coating layer exhibited glossy and mirror-like appearance, which was called as a reflowed plate. The surface of matte and reflowed plates were examined in terms of glossiness (Glossmeter), crystal orientation (XRD), and surface morphology (SEM).

For the electrochemical investigation, a circulation cell equipped with 3-electrode system was applied. In the cell, a reference electrode probe was inserted through the anode to reach the position 7mm apart from the cathode. The electrode area of both the anode and the cathode were 40mm by 100mm, and the gap between the electrodes was 12mm. The reference electrode was saturated calomel electrode (SCE), and all the potential values noticed hereafter was read with respect to the SCE. The potentiodynamic cathodic polarization was conducted in the electrolytes shown in Table 1, with variation of the electrolyte temperature from 30°C to 50°C. During the potentiodynamic polarization, the potential was swepted from -0.4V to -2.1V with scan rate of 10 mV/sec.

Results and discussions

Electroplating characteristics

The physical properties of electrolytes with various phenolsulfonate concentrations are shown in Fig. 1. As shown in Fig. 1, the variation of the conductivity and the surface tension of the electrolytes with the concentration of phenol-sulfonate could be regarded as negligible. But the conductivity of the aged electrolyte shows a little higher value compared to the electrolyte with similar concentration of phenolsulfonate, because of the difference in the metallic impurity level.

Fig. 2 shows the Hull cell patterns from various electrolytes. The width of white column indicates the current density range for desirable and bright deposit. As increasing the phenolsulfonate concentration, the desirable current density range

becomes lower and narrower. It should be noticed

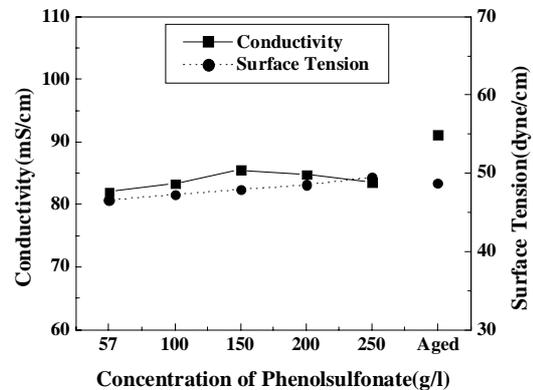


Fig. 1. Effect of phenolsulfonate concentration on physical properties of electrolyte

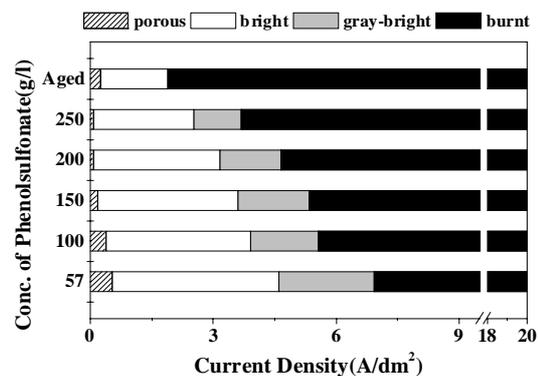


Fig. 2. Hull cell patterns

that a little difference in the width of the bright region could be found between the electrolyte with the highest phenolsulfonate concentration and the aged one, which implies that the accumulation of the phenolsulfonate could have something to do with the electrolyte aging.

Fig. 3 shows the effect of phenolsulfonate concentration on glossiness of matte plates with a coating weight of 5.6g/m². In the fresh electrolyte, the glossiness is gradually decreased with current density, and followed by sudden fall in high current density region. It could be assumed that the current density represents the upper limit of the desirable plating range. As increasing the concentration of phenolsulfonate in the electrolyte, the upper limits of the desirable plating range shift to lower current density region, and the upper limit of the aged electrolyte is close to that of the highest phenolsulfonate concentration, which confirms the

results obtained from Hull cell test.

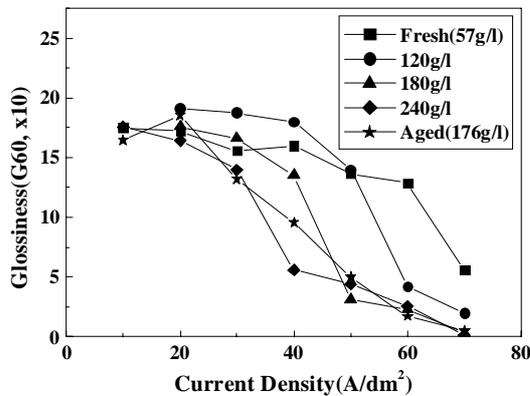


Fig. 3. Effect of phenolsulfonate concentration on glossiness of matte plate (5.6g/m²)

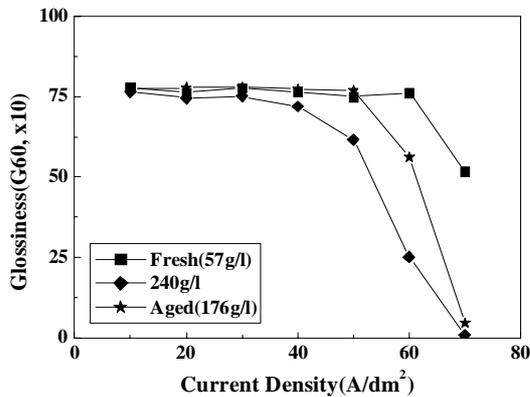


Fig. 4. Effect of phenolsulfonate concentration on glossiness of reflowed plate (11.2g/m²)

Fig. 4 shows the variation of glossiness of reflowed plates with a coating weight of 11.2g/m². Compared to Fig. 3, the variation of glossiness with current density is clear. In high current density region, the improper electrodeposit of the matte plate results in poor glossiness of the reflowed one, which may be attributed to the internal oxidation during heating step⁵⁾. In this figure, it can be deduced that the decreasing point of glossiness from aged electrolyte coincides with the electrolyte with the phenolsulfonate concentration of 120 or 180g/l. A general trend does not quite differ from the previous results.

Fig. 5 shows the variation of relative intensities of β -Sn(101) and β -Sn(112) planes in matte deposits with a coating weight of 5.6g/m². By the relative intensity, which indicates the preferred orientation of the crystallographic planes parallel

to the surface of the plate, it is possible to

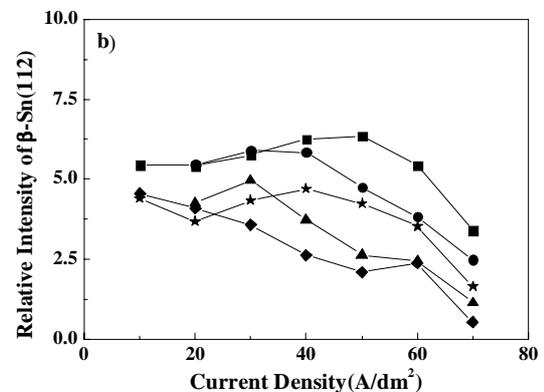
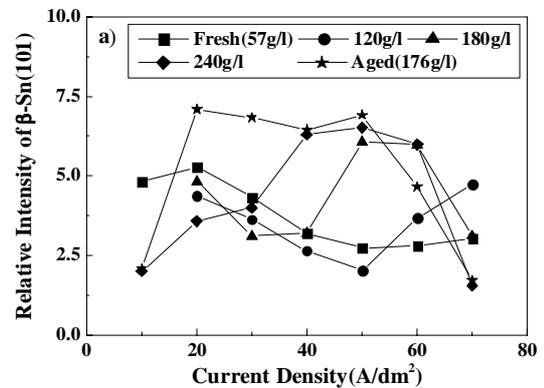


Fig. 5. Effect of phenolsulfonate concentration on relative intensity of matte deposit
a) β -Sn(101) b) β -Sn(112)

characterize the identity of the deposit⁶⁾. The β -Sn(101) and β -Sn(112) planes are the major crystallographic planes obtained from electrodeposits. In Fig. 5a), the variations of the relative intensity of β -Sn(101) plane do not show clear trends with current density. But the relative intensity from high phenolsulfonate concentration (180g/l, 240g/l, and aged) resides in the higher value than those from low phenolsulfonate concentration (fresh and 120g/l). In Fig. 5b), the relative intensity of β -Sn(112) plane decreases with current density and phenolsulfonate concentration. Even though clear trends could not be found in the preferred orientation of the major crystallographic planes, it could be mentioned that a similarity in the variation of relative intensities exists between the aged electrolyte and the electrolyte with phenolsulfonate concentration of 180g/l.

Fig. 6 shows the surface morphology of matte coating layer with a coating weight of

5.6g/m² electroplated at 50A/dm².

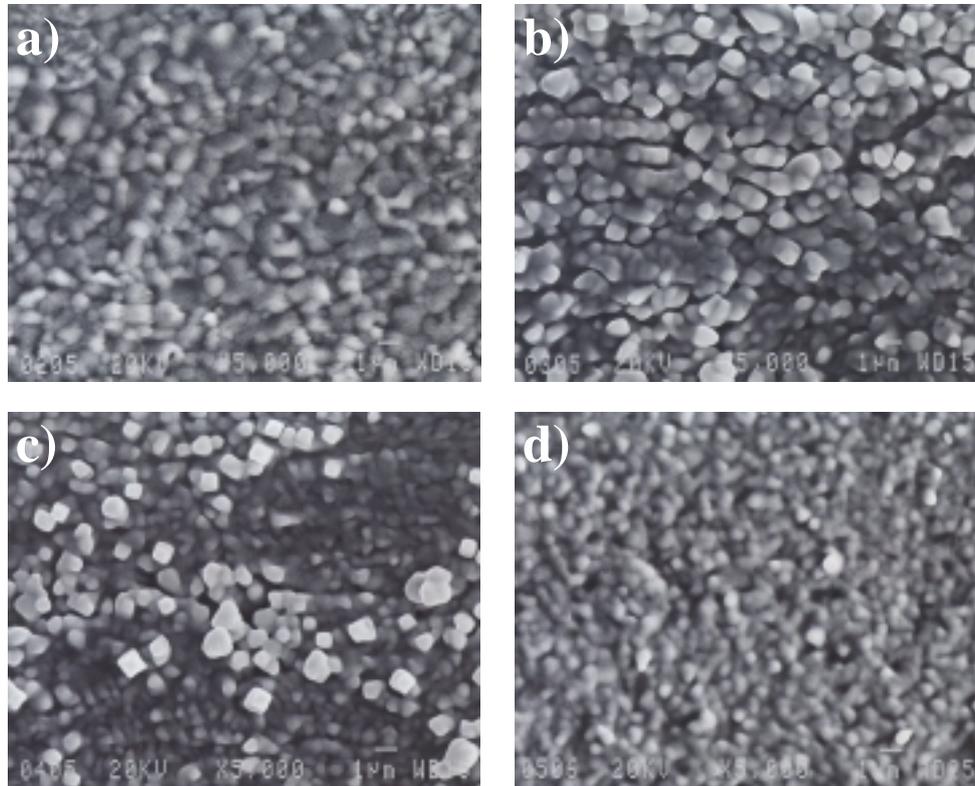


Fig. 6. Effect of phenolsulfonate concentration on morphology of matte coating layer
a) 120 g/l, b) 180 g/l, c) 240 g/l, d) aged (176 g/l)

In Fig. 6(a), compact pyramidal granules are formed in the coating layer. As increasing the concentration of phenolsulfonate, dendrite-like rough granules are found in deposits, which renders non-glossy appearance. In aged electrolyte [Fig. 6(d)], the granule size is smaller than Fig. 6(b) and 6(c), but the granules are not compact as Fig. 6(a).

Summing up the results of electroplating and surface characteristics, the increase in the concentration of phenolsulfonate, which could be identical to the accumulation of phenolsulfonate in the bath, renders the deposit of poor qualities which is similar to the deposits obtained from aged electrolyte. Therefore the long-term accumulation of phenolsulfonate in PSA bath could be counted as a cause for the electrolyte aging. To support these results, it is necessary to investigate the electrochemical behaviors caused by the accumulation of phenolsulfonate.

Potentiodynamic polarization behaviors

Fig. 7 shows the effect of phenolsulfonate concentration on potentiodynamic polarization behavior of tin electrodeposition at a electrolyte temperature of 40°. In fresh electrolyte, the activation polarization region could be found in the potential range of -0.6V ~ -1.4V, followed by mixed polarization in the high overpotential region. Increasing the concentration of phenolsulfonate in the electrolyte to 120 g/l, a limiting current density is found instead of activation polarization in the -0.6V ~ -1.4V range vs. SCE. Further increase in the concentration of phenolsulfonate renders lower limiting current densities in the same potential region.

Fig. 8 shows the effect of temperature on the potentiodynamic polarization behaviors in the fresh electrolyte. At 30°C, a similar limiting current

density as in the aged electrolyte is found, while it

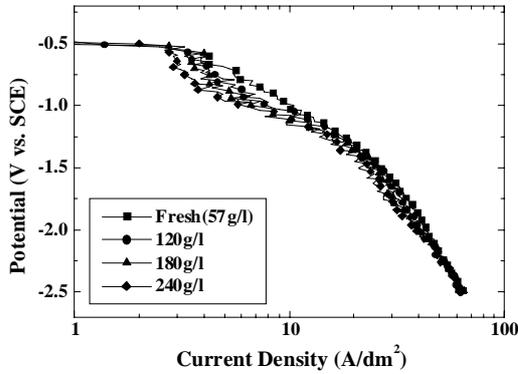


Fig. 7. Effect of phenolsulfonate on potentiodynamic polarization behaviors

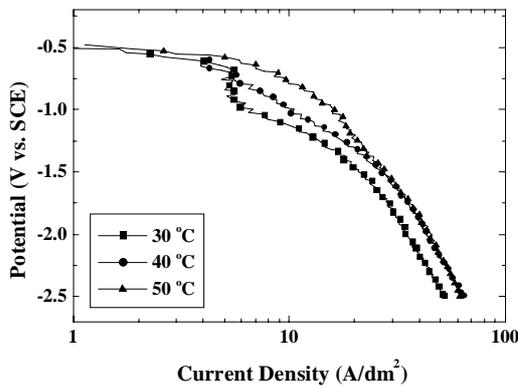


Fig. 8. Effect of electrolyte temperature on potentiodynamic polarization behaviors in fresh electrolyte

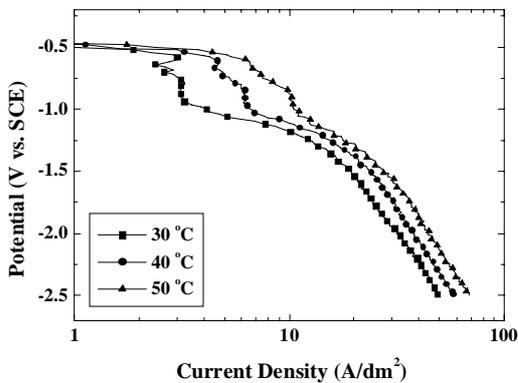


Fig. 9. Effect of electrolyte temperature on potentiodynamic polarization behaviors in aged electrolyte

is diminished at the elevated temperature.

Fig. 9 shows the effect of temperature on the potentiodynamic polarization behavior in the aged electrolyte. As increasing the temperature, the limiting current density shifts to higher current density, and the activation polarization becomes feasible process.

By combining the effects of both the concentration of phenolsulfonate and that of the temperature, the aging caused by the accumulation of phenolsulfonate could be interpreted in terms of the inhibition of thermally-activated process, such as mass transfer of reducing ions. That is, it is possible to state that the electrolyte aging comes from the limitation of the mass transfer of reducing ions in the electrolyte, and the accumulated phenolsulfonate could play the crucial role to hinder the mass transfer.

Conclusions

- 1) Increasing the phenolsulfonate concentration, which could be related to the accumulation of phenolsulfonate, renders the electrodeposit of poor qualities and makes the desirable current density region narrower.
- 2) By the electrochemical interpretations, it is possible to state that the electrolyte aging comes from the limitation of the mass transfer of reducing ions in the electrolyte, and the accumulated phenolsulfonate could play the crucial role to hinder the mass transfer.

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