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Study of Some Surfactants on Tin and Tin-Bismuth Electrodeposition from An Acid Electrolyte Sn(II) Sulphate

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The effects of surfactants on the electrodeposition of tin and its alloy are studied. It appears that they provide several functions in the electrodeposition baths. They reduce the surface tension, strongly inhibit the process of metallic ions electroreduction, ensure the role of dispersants of poorly soluble brightening and improve the chemical stability of the electrolytes. These results have enabled us to choose the Syntanol DS-10 which added in small quantities: 2.5-10.0 g/L ensures a better functioning of the tinning bath. This product has an alkylic hydrocarbon chain, therefore biologically degradable. This is most important on the pollution point of view.

Key Words: Surfactant, Tin, Alloy, Electrodeposition, Biodegradable.

INTRODUCTION

The electrolytic coatings based on Sn-Bi alloys are widely used in the electronics industry, because they provide a weld ability over a long enough period up to 18 months. At present, there is a large number of shining compositions[1-6]. The major disadvantage of these electrolytes is the poor biodegradability of the most of organic additives, mainly, that of used surfactants, such as: OP-7, OP-10, OP-20[7,8]. These surfactants, as a result of their adsorption on the electrodes, significantly change the interfaces properties[9-11]. Thus, they are added to the electrolyte, not only to facilitate the detachment of hydrogen bubbles, but to change the interface properties and hence the deposit obtained. However, little attention is paid to the multiple functions of these agents in the electroplating process. Thus, taking into account that they are indispensable in the tinning electrolytes, in present work, the various roles of some surfactants such as: OS-20, Syntanol DS-10, Tween 20, Triton-X-100…, were studied, the nature of radical hydrocarbon and the oxyacetylene chain length are also discussed.

EXPERIMENTAL

The Sn-Bi alloy deposits are obtained from an acid sulphate electrolyte with a composition of (g/L): $SnSO_4$ 20, $Bi(NO_3)_3 \cdot 5H_2O$ 1, H_2SO_4 100. The cathode is copper plates 200 µm thick. The anodes are pure tin. The content of Bi in the Sn-Bi alloy

obtained is determined using a photocalorimeter. The sharing power is measured in a cell Möhler[9] where the cathode is compound of 5 sections. The polarization curves in potentodynamic mode were obtained from stationary electrode using a potentiostat, in a classic cell of 3 electrodes. The electrolytes are maintained at 25 °C and deoxygenated by paddling with nitrogen.

RESULTS AND DISCUSSION

The cathodic polarization measurements in potentiodynamic mode (Fig. 1) show that the Triton-X-100, Syntanol DS-10, Tween 20, OS-20, polyocol and neonol AF6 inhibit differently the metal electroreduction and practically have no effect on the hydrogen release process.

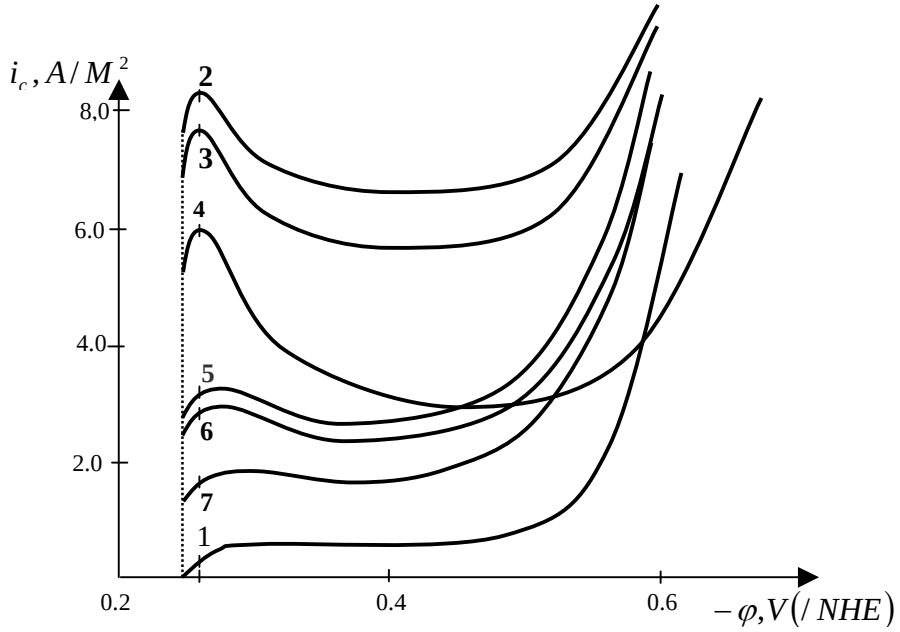

Fig. 1. Cathodic polarization curves electroreduction Sn^{2+} in the presence of non-ionic surfactants: 1) H_2SO_4 (1 M); 2) 1 + $SnSO_4$ (5.10^{-3} M); 3) 2 + Polyocol (25 g/L); 4) 2 + Katamine (25 g/L); 5) 2 + OS-20 (25g/L); 6) 2 + Triton-X-100 (25g/L); 7) 2 + Syntanol DS-10 (25 g/L)

In fact, these substrates have little influence on the performance of cathodic current output as a function of the current density (Table-1).

The best deposits are obtained in the presence of surfactants (OS-20, Triton-X-100 and Syntanol DS-10) which inhibit harder than others (Katamine B, polyocol…) the electrodeposition of Sn-Bi: which prove that surfactants provide not only the function of shining compositions dispersants, often poorly soluble in water, but also to be strong inhibitors (Fig. 1, curves 3-7) of the Sn^{2+} ions electroreduction. It is noted that as the surfactant decreases the surface tension (Fig. 2) and inhibited

the metal electrodeposition (Fig. 1, curves 3-7), the deposits obtained are brighter and without prick, except the Katamine B which differs from others by being a cationic surfactant (Fig. 1, curve 4).

TABLE-1
INFLUENCE OF THE NATURE OF SURFACANT ON THE FIELD OF CATHODIC CURRENT DENSITIES, THE DEPOSITS ASPECT, THE CHEMICAL STABILITY OF ELECTROLYTE AND THE INTERFACIAL GAS-LIQUID TENSION

Surfactant	Concen-tration g/L	Cathodic current density (A/dm^2)	Aspect of the deposit	Chemical stability (d)	Interfacial tension (dyn/cm)
Syntanol Ds-10	2.5-10	200-1500	Very bright	200	32 10
X-100 triton	2.5-10	200-1500	Very bright	60	32 10
Katamine B	5.0-15	200-1000	Mate	60	32 10
OS-20	20-25	200-1000	Bright + Pittings	60	40 10
Tween-20	15-25	200-1000	Brillant + Pittings	60	40 10
Néonol AF6	10-25	200-600	Semi-bright + Pittings	30	60 10
Polyocol	10-25	200-600	Semi-bright + Pittings	15	60 10

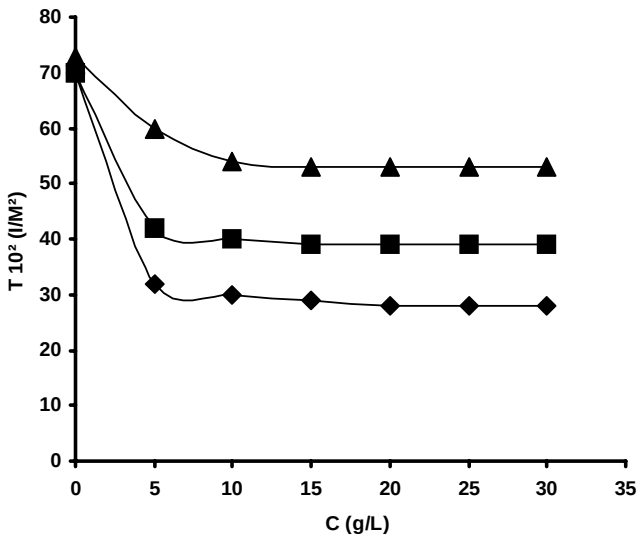

Fig. 2. Influence of surfactant nature on interfacial tension liquid-gas in an acid sulfate electrolite; (▲) Neonol AF6, Polyocol (■) OS-20, Tween-20 (◆) Syntanol DS-10, Triton-X-100, Katamine B

It is important to emphasize that a part from the decrease of surface tension, these substances provide other functions. In fact, a maximum decrease of the interfacial tension is observed from 1 g/L for OS-20, whereas the necessary concentration for obtaining quality deposits is 20-25 g/L. So, it is possible to assume that with concentrations higher than critical concentration of micellaneous (ccm) formation

these substances form at the surface of the electrode an aggregate of miscellaneous, having a favourable effect on the process of brightening. This allows us to conclude that their nature is a significant factor. The surfactants used for the tin electroplating are often substances that contain polyoxyethylenic groupings:

-OCH_2CH_2-OH linked to an hydrocarbonic chain either alkylic: C_XH_{2X+1} - (OS-20, Neonol AF6 and Syntanol DS-10); or an alkylphenylic chain: C_XH_{2X+1} - C_6H_4- (Triton-X-100, OS-20).

It is important to emphasize that alkylphenols are less biodegradable. That is why their use is to be reduced.

Thus special attention has been paid to the role of the two best surfactants (OS-20 and Triton-X-100) in the chemical stability of the electrolyte sulphate. The use of Syntanol DS-10 or Triton-X-100 allows, the first day to obtain very bright deposits. But on the second day and in the case of Triton-X-100, a correction by the ALSOC brightener is necessary to restore the brightness. Such stability is also seen with other brighteners such as benzaldehyde or salicylic aldehyde. This is probably related to the fact that these substances have a benzene ring, with a strong chemical activity with the electrolyte components.

The most convenient surfactant is the Syntanol the DS-10, its high chemical stability in acidic solution (pH < 1), as well as the absence of benzene rings in its molecule makes it a surfactant to be recommended for the galvano-techniques. In addition, the Syntanol DS-10 is added in small quantities: 2.5-10 g/L compared to OS-20: 20-25 g/L. This difference may be explained by the fact that the oxyethylenic chain of OS-20 is twice longer than that of Syntanol DS-10. So, for the same amount input, the Syntanol DS-10 adsorbs more. This is the reason for choosing the essential component in present tinning electrolytic (g/L): $SnSO_4$ 20, $Bi(NO_3)_3 \cdot 5H_2O$: 1, H_2SO_4: 100, Syntanal DS-10: 2.5 and ALSOC: 2 mL/L.

The study of the influence of bismuth salt concentration (Fig. 3) and the cathode current density (Fig. 4) on the composition of the Sn-Bi alloy shows that the content of bismuth increases with the increasing of the concentration of salt in the electrolyte.

Since a content of 0.8 % Bi is sufficient to prevent the passage of the tin from the modification β to α; bismuth salt should be introduced in quantities of 1 g/L. Fig. 4 shows that the density of the cathodic current has a small influence on the Bi content. So, this electrolyte has the advantage to electroplate a bright Sn-Bi alloy pieces of a complex profile provided that the penetrating power is high.

The mathematical treatment of present results allowed obtaining the regression equation describing the performance of the cathodic current output (RC) as a function of the ALSOC brightener concentration (C_{ALSOC}), the cathodic current density (I_c) and the electrolysis time (t):

$$RC = 81.9 - 10C_{ALSOC} - 7.8I_c + 0.3t + 0.8C_{ALSOC}.I_c + 0.21t.I_C$$

The dispersion is 6,351. The coefficients are subjected to the Student criterion.

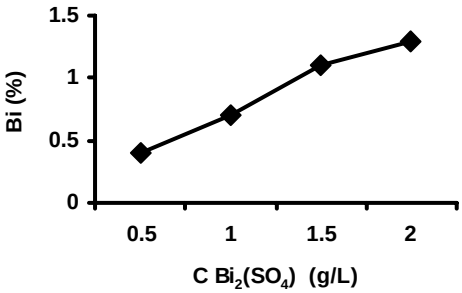

Fig. 3. Bi concentration in Sn-Bi alloy in relation with $Bi(NO_3)_3.5H_2O$ concentration in the electrolyte

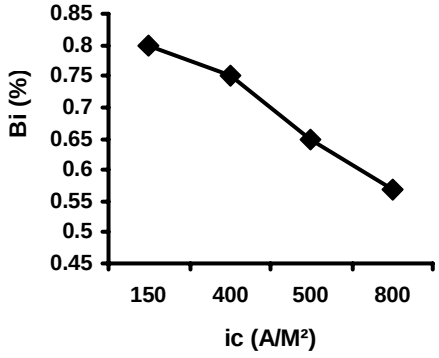

Fig. 4. Bi concentration in Sn-Bi alloy, in relation with cathodic density curent

Conclusion

The cathodic polarization measurements in potentiodynamic mode show that the Triton-X-100, Syntanol DS-10, Tween 20, OS-20, Polyocol and Neonol AF6 inhibit differently the Sn^{2+} ion electroreduction.

The best deposits are obtained in the presence of surfactants (OS-20, Triton-X-100 and Syntanol DS-10) which strongly inhibit the process of metallic ions electro-reduction,

The most convenient surfactant is the Syntanol DS-10, its high chemical stability in acidic solution (pH < 1), as well as the absence of benzene rings in its molecule makes it a surfactant to be recommended for the galvano-technics. In addition, the Syntanol DS-10 is added in small quantities: 2.5-10 g/L compared to OS-20: 20-25 g/L.

The elaborated tinning electrolyte composition (g/L): $SnSO_4$ 20, $Bi(NO_3)_3 \cdot 5H_2O$: 1, H_2SO_4: 100, Syntanal DS-10: 2.5 and ALSOC: 2 mL/L has the advantage to electroplate a bright Sn-Bi alloy pieces of a complex profile with high cathodic current output.

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