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APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Organic Compounds for Preparing Lustrous Tin Coatings

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Abstract—Organic compounds for preparing lustrous tin coatings were selected taking into account their ionization potential. The best electrolyte composition for plating these coatings was determined.

Various organic compounds are added to sulfate electrolytes for tin-plating [1]. To obtain dense finely crystalline dull or lustrous coatings, these electrolytes should contain colloid-forming compounds (glue, gelatin) and wetting agents (e.g., ethylene oxide condensation products) along with other organic compounds. Unsaturated alcohols, ketones, aldehydes, and products of the electrochemical synthesis are used for preparing lustrous tin coatings [1–3]. It should be noted that organic compounds for plating lustrous tin coatings are selected empirically.

Nechaev *et al.* [4–7] showed that the sorption on the surface of tin and other metals is caused by not only electrostatic interactions but also chemical bonding. The chemisorption is maximal when the energy of electronic levels of the metal is similar to that of the molecular orbital of the organic compound, which provides formation of donor–acceptor bonds between the molecules of the additive and the metal surface. Under these conditions the occupied molecular orbitals of the adsorbent and the adsorbate overlap to form a common electronic system. The correlation between the adsorption properties of organic compounds and the energy of the highest occupied molecular orbital (MO) can be quantitatively characterized by the first ionization potential I.

According to [4–7], the range of I of organic compounds optimal for their sorption on tin is 7.74–7.96 eV. The second maximum is observed at I = 9.6 eV. To explain this phenomenon, Nechaev and Volgina suggested [8] that the tin surface consists of pure and oxidized regions. However, the dependence of the adsorption energy on I, measured on cathodically polarized tin whose surface is constantly renewed (oxide formation is thermodynamically forbidden), also has two maxima. It was suggested that not only highest occupied MO characterized by the first I but also other occupied orbitals are involved in the bonding. Dull finely crystalline tin coatings were plated from sulfate electrolyte containing organic compounds with I = 7.8–8.0 eV [4, 5, 10]. Introductions of compounds with I = 9.5–9.7 eV makes the coatings compact, uniform, and semilustrous. Organic compounds with I other than 7.8–8.0 and 9.5–9.7 eV do not inhibit tin-plating. No high-quality coating are formed in their presence.

In this work, taking into account I of organic compounds, we selected such compounds or their mixtures that provide plating of lustrous tin coating from sulfate electrolyte.

For this purpose we mainly used an electrolyte containing 30 g l^{-1} $SnSO_4$ and 100 g l^{-1} H_2SO_4. The coatings were plated at 20–22°C with or without stirring of the electrolyte with a mechanical stirrer.

The tested organic compounds are presented in the table.

Condensation products Syntanol DS-10 (I = 9.4 eV), OP-7, OP-10 (I = 9.3 eV), OS-20 (I = 9.2 eV), VA-20 smoothing agent (I = 9.5 eV), hide glue, and gelatin (I = 7.5 eV) were also studied.

The ionization potentials of the tested organic compounds ranged from 6.88 to 12.2 eV. The concentration of these compounds was varied from 1 to 15 g l^{-1}. Saturated solutions of difficultly soluble compounds were used. The ionization potentials of organic compounds were taken from [6, 7] or calculated by the PM3 method [11].

The most precise experimental procedure for determining ionization potentials of atoms and molecules is PES [12]. In this work, the I values determined by PES were correlated with those calculated quantum-chemically. First, we examined how semiempirical

Organic compounds tested and their first ionization potentials

Compound nos.	Compound	I, eV	Compound nos.	Compound	I, eV
1	Benzidine	6.88	21	Quinoline	8.62
2	*N,N*-Dimethylaniline	7.14	22	Piperidine	8.7
3	Diphenylamine	7.25	23	Benzotriazole	8.72
4	α-Naphthylamine	7.3	24	Imidazole	8.8
5	*m*-Toluidine	7.5	25	Furan	8.88
6	Aniline	7.7	26	Benzyl alcohol*	8.95
7	Indole	7.74	27	Coumarin*	8.97
8	β-Naphthol	7.76	28	2-Butene-1,4-diol*	9.13
9	α-Naphthol	7.78	29	Acetic anhydride	9.5
10	Phloroglucinol	7.87	30	Benzenesulfonic acid	9.6
11	Hydroquinone	7.95	31	2-Butyne-1,4-diol*	9.77
12	Pyrogallol	8.0	32	*p*-Phenolsulfonic acid	9.8
13	Pyrocatechol	8.07	33	Propargyl alcohol	10.41
14	Naphthalene	8.2	34	Butane-1,4-diol*	10.43
15	*p*-Cresol	8.24	35	3,5-Dinitrobenzoic acid	10.7
16	Resorcinol	8.31	36	Formaldehyde	10.88
17	*o*-Cresol	8.34	37	Nitromethane	11.18
18	*m*-Cresol	8.37	38	Trinitrobenzoic acid	11.3
19	Phenol	8.5	39	Valeric acid	12.2
20	Triethylamine	8.6			

* Determined in this work.

methods for calculating the electronic structure (MNDO, AM1, and PM3) and *ab initio* methods with STO-3G and 3-21G basis sets describe PES data.

We found that the PM3 method [11] gives the most satisfactory results. In this case, the ionization potentials of organic molecules can be calculated by the equation

$$I = 1.075I_{\mathrm{PM3}} - 1.1679. \qquad (1)$$

The correlation coefficient is 0.979.

The ionization potentials calculated by Eq. (1) from the PM3 data are given in the table (the corresponding compounds are denoted with asterisks).

The degree of luster of the coatings was measured on an FB-2 photoelectric luster meter. The polarization curves were recorded with a P-5828 potentiostat under the potentiodynamic conditions. In the course of tin-plating, the capacitance of the electrical double layer was measured with a P-5021 ac bridge operating at 30 kHz in the successive substitution mode. Tin coatings 6–9 μm thick were plated on copper supports.

High-quality coatings were obtained in the presence of none of the tested organic compounds whose concentrations were varied in a wide range. The use of the glue and gelatin gave similar results. Dull finely crystalline coatings are formed in the presence of the condensation products in the electrolyte. When both condensation products and the organic compounds given in the table are present in the electrolyte, silvery dull coatings are obtained. Some sulfate electrolytes for plating lustrous tin coatings contain formaldehyde (I = 10.88 eV) along with luster-producing additives [1, 2]. Taking into account this fact, we performed the subsequent studies in electrolyte no. 2 containing 2 g l^{-1} Syntanol and 6 ml l^{-1} Formalin. Dull, semilustrous, and lustrous coatings were plated from these electrolyte in the presence of various organic additives. Depending on the electrolyte composition, lustrous coatings are formed at i_{c} = 1–12 A dm^{-2}.

The dependence of the luster L (%) of the coating plated from electrolyte no. 2 with mechanical stirring on I of organic additives is shown in Fig. 1. Two maxima in this curve correspond to formation of lustrous coating. The first maximum appears at I = 7.25 eV (diphenylamine). The second maximum is observed in a broader range of ionization potentials (I = 8.95– 10.43 V), i.e., lustrous coatings are plated in the presence of benzyl alcohol, coumarin, 2-butene-1,4-diol, acetic anhydride, benzenesulfonic acid, 2-butyne-1,4-diol, *p*-phenolsulfonic acid, propargyl alcohol, or butane-1,4-diol [13, 14]. Lustrous coatings are also formed when these additives are present in combination with smoothing agents and formaldehyde. It should be noted that lustrous coatings are plated from electrolyte containing OP-7, OP-10, and OS-20 condensation products and luster-producing agents without addition of formaldehyde [15]. Formaldehyde addition is not required also when luster-producing agents, gelatin (glue), and cresol are present in the electrolyte [3].

Previously we found [16] that formaldehyde in an electrolyte containing gelatin (glue) and cresol starts to exhibit luster-producing properties itself, but only after plating for a definite time.

It should be noted that high-quality lustrous films are plated only from the stirred electrolyte. Without stirring, dull coatings are formed.

The study of cathodic polarization in the electrolyte for tin-plating (Fig. 2) showed that the condensation products inhibit electrodeposition (curves *1, 2*).

The polarization curves flatten out at the limiting current. The polarization ΔE_c decreases (curves *2–4*) in the presence of the condensation products, formaldehyde, and luster-producing agents in the electrolyte.

The polarization also decreases with stirring of the electrolyte (curves *4, 5*). However, when the electrolyte contains condensation products, formaldehyde, and benzyl alcohol, ΔE_c increases (curves *6, 7*).

Probably, organic compounds present in the electrolyte are adsorbed on the electrode surface, thus inhibiting tin-plating. The measured capacitance of the electrical double layer C confirms this assumption. As seen from Fig. 3, the capacitance of the electrical double layer decreases in the presence of the organic compounds in the electrolyte (curves *1–3*). In this case, the C–E curves pass through a minimum at E from -0.3 to -0.4 V. In this potential range, $C = 6$–10 μF cm^{-2}. At higher potentials, the continuity of the adsorption layer is broken owing to desorption of organic compounds from the cathode surface. As a result, the capacitance of the electrical double layer increases [17].

Thus, to obtain lustrous tin coating, the electrolyte should contain an inhibitor, formaldehyde, and a luster-producing agent or an inhibitor and a luster-producing agent.

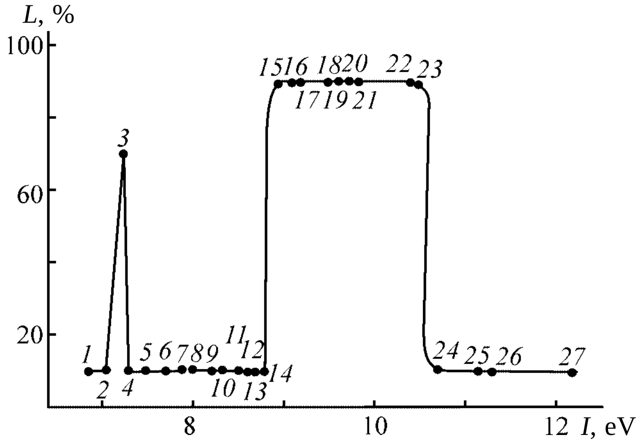

Fig. 1. Luster of tin coatings L as a function of the ionization potential of the organic additives I: (*1*) benzidine; (*2*) *N,N*-dimethylaniline; (*3*) diphenylamine; (*4*) α-naphthylamine; (*5*) *m*-toluidine; (*6*) aniline, indole, and (α- and β-naphthols; (*7*) phloroglucinol and hydroquinone; (*8*) pyrogallol and pyrocatechol; (*9*) naphthalene and *p*-cresol; (*10*) resorcinol, *o*-cresol, and *m*-cresol; (*11*) phenol; (*12*) triethylamine and quinoline; (*13*) piperidine and benzotriazole; (*14*) imidazole and furan; (*15*) benzyl alcohol; (*16*) coumarin; (*17*) 2-butene-1,4-diol; (*18*) acetic anhydride; (*19*) benzenesulfonic acid; (*20*) 2-butyne-1,4-diol; (*21*) *p*-phenolsulfonic acid; (*22*) propargyl alcohol; (*23*) butane-1,4-diol; (*24*) 3,5-dinitrobenzoic acid; (*25*) nitromethane; (*26*) trinitrobenzoic acid; and (*27*) valeric acid.

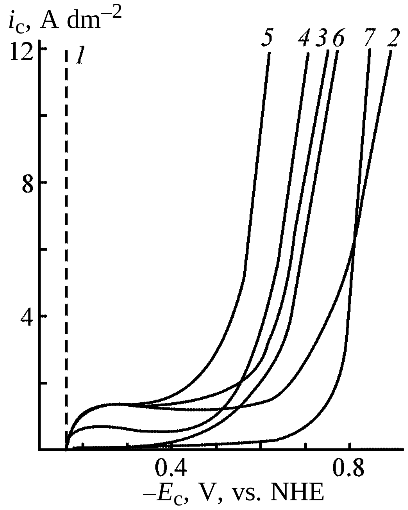

Fig. 2. Cathodic polarization curves recorded in sulfate tin-plating electrolyte no. 1. (i_c) Current density and (E_c) potential. (*1*) Electrolyte no. 1; (*2*) 1 + Syntanol, 2 g l^{-1}; (*3*) *2* + Formalin, 6 ml l^{-1}; (*4*) *3* + propargyl alcohol, 10 ml l^{-1}; (*5*) *4* with stirring; (*6*) *3* + benzyl alcohol, 6 ml l^{-1}; and (*7*) *6* with stirring.

An inhibitor decelerates tin-plating and provides formation of dull finely crystalline deposits. Condensation products (Syntanol DS-10, OP-7, OP-10, OS-20), VA-20 smoothing agent, gelatin, and glue can be used as inhibitors. However, the two latter substances weakly inhibit tin-plating. In this case, cresols ($I = 8.24$–8.31 eV), phenols ($I = 8.5$ eV), and naphthols ($I = 7.76$–7.78 eV) should be added to the elec-

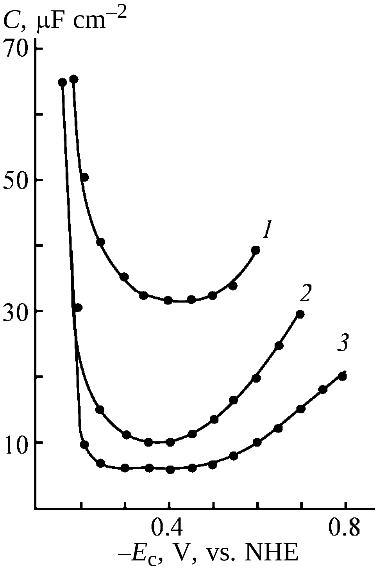

Fig. 3. Capacitance of the electrical double layer C as a function of the cathodic potential E_c: (*1*) electrolyte no. 1; (*2*) *1* + Syntanol, 2 g l^{-1} + Formalin, 6 ml l^{-1} + propargyl alcohol, 10 ml l^{-1}; (*3*) *1* + Syntanol, 2 g l^{-1} + Formalin, 6 ml l^{-1} + benzyl alcohol, 6 ml l^{-1}.

trolyte to obtain high-quality dull coatings [1, 2]. Formaldehyde (I = 10.88 eV) present in the electrolyte is a depolarizer of the process. Organic compounds with I = 7.25 and 8.95–10.43 eV exhibit lister-producing properties.

The fact that lustrous coating are formed only at a definite combination of organic compounds and stirring of the electrolyte suggests that sorption of organic compounds on the cathode surface is necessary but insufficient for obtaining such coatings. In this case, there are other factors affecting the luster of the coatings. Among them are complex physicochemical processes occurring in the catholyte layer [2] and the conditions of diffusion hydrodynamic feeding (or removal) of ions, which change the structure and properties of the absorption layer on the cathode surface [18].

Thus, the proposed approach affords a criterion of selection of organic compounds that, in combination with inhibitors, may provide formation of lustrous tin coatings. However, it does not warrant obtaining such coatings with particular additives *a priori*. Electrolytes for plating lustrous tin coatings are developed on the basis of this principle [13–16, 19, 20].

CONCLUSIONS

(1) Organic compounds promising for plating lustrous tin coatings were selected taking into account their first ionization potential. Lustrous tin coating were plated from the electrolyte containing an inhibitor, formaldehyde, and a luster-producing agent or an inhibitor and a luster-producing agent.

(2) Products of ethylene oxide condensation (Syntanol DS-10, OP-7, OP-10, and OS-20), VA-20 smoothing agent, as well as gelatin and glue in combinations with cresol, phenol, or naphthol can be used as inhibitors.

(3) Diphenylamine (I = 7.25 eV), benzyl alcohol (I = 8.95 eV), coumarin (I = 8.97 eV), 2-butene-1,4-diol (I = 9.13 eV), acetic anhydride (I = 9.5 eV), benzenesulfonic acid (I = 9.8 eV), 2-butyne-1,4-diol (I = 9.77 eV), *p*-phenolsulfonic acid (I = 9.8 eV), propargyl alcohol (I = 10.41 eV), and butane-1,4-diol (I = 10.43 eV) can be used as luster-producing additives to tin-plating electrolyte.

(4) The luster-producing additives allow plating of lustrous coatings from electrolyte containing or not containing formaldehyde, depending on the particular inhibitor. In the presence of gelatin, glue, and cresol, formaldehyde exhibits luster-producing properties.

(5) The proposed approach can be used to select organic compounds that may provide formation of lustrous tin coatings from electrolyte containing inhibitors.

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