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ELECTRODEPOSITION OF ZINC FROM A ZINCATE ELECTROLYTE AT HIGH CURRENT DENSITIES

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The known noncyanide zinc plating electrolytes – pyrophosphate, ammonium chloride, tripolyphosphate, and zincate [1-5] – are inferior in throwing power to cyanide electrolytes. Aratsov et al. [6, 7] have proposed a zincate electrolyte of the following composition (g/liter): ZnO 10, NaOH 100, polyethyleneimine (PEI) with mol. wt. 10,000 1; this has a high throwing power. The latter is due to the enhanced cathodic polarizability and the decrease in the current yield on increase in the current density. Addition of PEI greatly expands the current density range on the cathode in which compact bright deposits are obtained, but below 1 A/dm^2 the deposits obtained from electrolyte prepared from ordinary tap water containing salts of certain metals as impurities are dark. Addition of veratraldehyde (0.03-0.08 g/liter) enhances the luster of the deposits, and incorporation of versene (5-10 g/liter) enables the electrolyte to be prepared from tap water and compact bright deposits to be obtained, beginning at 0.25 A/dm^2 [8].

Our aim is to make a comparative estimate of the properties of cathodic deposits of zinc obtained from zincate, cyanide, and sulfate electrolytes, and to refine certain technological parameters of the process.

The compositions of these electrolytes (g/liter) and the electrolysis conditions are as follows: ZnO 10, NaOH 100, PEI 1, t = 20-50°C, i_c = 1-6 A/dm^2; 2) ZnO 10, NaOH 100, PEI 1, veratraldehyde 0.05; t = 20-50°C; i_c = 1-10 A/dm^2; 3) ZnO 10, NaOH 100, PEI 1, veratraldehyde 0.05, versene 5, t = 20-50°C, i_c = 0.25-10 A/dm^2; 4) $ZnSO_4 \cdot 7H_2O$ 250, $Na_2SO_4 \cdot 10H_2O$ 80, $Al_2(SO_4)_3 \cdot 18H_2O$ 25, dextrin 10, pH = 4.5, t = 20-25°C, i_c = 1-3 A/dm^2 [9]; 5) ZnO 30-40, $NaCN_{tot}$ 80, NaOH 90, Na_2S 0.5, BTSU 8, t = 20-30°C, i_c = 1-4 A/dm^2 [9].

The luster of the deposits, γ, was measured on an FM-58 device by the procedure given in the description of the latter. On steel specimens covered with a zinc layer 10 μ thick, the value γ = 50-100 corresponded to semilustrous deposits.

The microhardness was measured on a PMT-3 microdurometer, the internal stress was determined on an apparatus designed by Solov'eva and Adzhiev [10].

The throwing power (TP) was measured in a slot cell with slot width 2 mm, cathode compartment width 4.25 cm and length 10 cm [11], and it was calculated [12, 13] from the equation

$$TP = \frac{\sum_{n=1}^{n=10} |b_n - a_n|}{\sum_{n=1}^{n=10} |1 - a_n|} \cdot 100.$$

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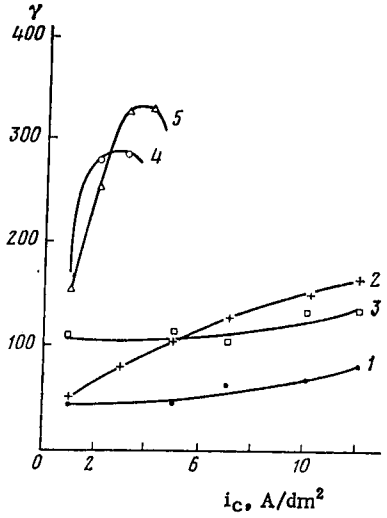

Fig. 1

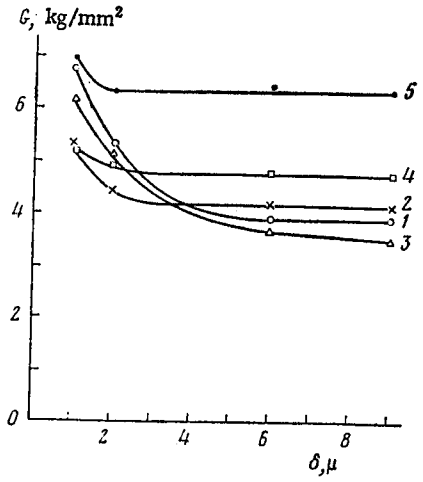

Fig. 2

Fig. 1. Luster of zinc deposits obtained from different zinc plating electrolytes at 20°C. The curve numbers correspond to the electrolyte numbers.

Fig. 2. Internal stresses in electrolytic zinc deposits vs coating thickness at 20°C and current density 2 A/dm². Curve numbers same as in Fig. 1.

TABLE 1. Throwing Power of Certain Zinc Plating Electrolytes

Electrolyte No.	Temperature, °C	Average current density i_{av}, A/dm²					
		0.5	1.0	2.0	3	4	5
		Throwing power TP_m					
1	20	53	50	45	42	40	38
	50	47	43	38	37	36	35
2	20	58	53	48	45	42	40
	50	51	45	41	40	37	36
3	20	60	55	51	47	45	43
	50	54	48	43	41	40	38
4	20	15	—	10	—	—	—
5	20	61	56	63	53	—	—

Here $b_n = \Delta G_n/\Delta G_{av}$ is the distribution of the metal, a_n is the primary current distribution, G is the mass of the cathode deposit on each section of the cathode, n is the serial number of the section, $\Delta G_{av} = \sum_{n=1}^{n=10} \Delta G_n/10$ is the mean mass of the deposit on the section of the dismountable cathode, and $\sum_{n=1}^{n=10} 1-a_n = 6.365$ when $l/h = 2.3$.

The principal components of the electrolytes, ZnO and NaOH, were of analytical reagent grade. The solutions were prepared from distilled water. As we see from the curves (Fig. 1), the luster of deposits from a cyanide electrolyte with BTsU luster-former and sodium sulfide, and from a sulfate electrolyte with dextrin, is greater than from zincate electrolytes, but the working range of permissible current densities in them is much narrower. Incorporation of versene and veratraldehyde into the electrolyte enhances the luster, which remains constant over a wide range of current densities.

The internal stresses in the deposits are small in every case, but smaller in the zincate electrolytes (Fig. 2).

The microhardness of the coatings from zincate electrolytes retains fairly high constant values for zinc: ~120 kgf/mm² up to a current density of 12-14 A/dm². In sulfate and cyanide electrolytes the microhardness decreases on increase in the current density above 2 A/dm². As indicated in a previous communication [8], on increase in i_c from 0.5 to 10 A/dm² the current yield in zincate electrolytes decreases from 74 to 35% at

t = 20°C and from 82 to 55% at t = 50°C. However, despite this, the real deposition rate of the metal remains high. Thus at i_c = 5 A/dm^2 and 20°C (current efficiency = 40%) it is 0.6 μ/min, and at 50°C (current efficiency 64%), ~1 μ/min.

The throwing power (TP_m) of a zincate electrolyte with added organic surfactants greatly exceeds that of an acid electrolyte and differs little from that of a cyanide electrolyte with respect to All-Union State Standard (GOST) (Table 1).

Thus, we can recommend for commercial use a zincate electrolyte of the following composition (g/liter) in place of a cyanide electrolyte: ZnO 10, NaOH 100, $PEI_{mol.\ wt.\ 2000\text{-}100,000}$ 1-2, veratraldehyde 0.05, and versene 5; t = 20-50°C and i_c = 0.25-10 A/dm^2. The following can be used instead of veratraldehyde: hydroxycoumarin, o-vaniline, polyvinyl alcohol, salicylaldehyde, 4,4-diaminostilbene-2,2-disulfonic acid, and dimethylaminobenzaldehyde, in amounts ranging from 0.05 to 0.1 g/liter.

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