TABLE 1

Coating layer, μm				Coating porosity, cm^{-2}	Time to appearance of corrosion, h
copper	nickel	chromium p	chromium b		
0	0	20	1	0,36	130
0	0	12	1	0,45	91
0	0	8	1	0,48	52
0	0	6	1	0,52	40
0	0	0	12	0,78	27
6	6	0	1*	0,65	31
0	0	0	0	–	1,5

* Coating according to GOST 538-72.

pyrophosphate, ethylene- and polyethylenediamine) and tinning electrolytes (acid and alkaline), and in a nickel plating electrolyte, TsAM 4-1 strongly dissolves. For this reason, coatings with good adhesion were not obtained in these electrolytes.

In a standard chrome plating electrolyte, solution of TsAM 4-1 is slower. The rate of solution in a polychromate chrome plating electrolyte is zero. Chromium (chromium p) deposited on TsAM 4-1 from this electrolyte has good adhesion. However, polychromate chrome plating gives a dark gray coating. To bestow a decorative appearance on artifacts, polychromate chromium was polished and bright chromium (chromium b) was deposited onto it from a standard electrolyte. Table 1 lists the results of corrosion tests of an alloy with this type of combined coating.

It will be seen from Table 1 that the combined chromium coating is superior in corrosion resistance to an M6N6Khb standard coating. A direct relation between the corrosion resistance and the porosity of the coating is observed.

Since the coatings are porous, it appears that corrosion of the alloy is due to operation of an alloy-coating galvanic couple. The steady potentials of the alloy, copper, nickel, and chromium are −0.73, 0.10, 0.15, and −0.19 V, respectively. Hence the emf of the alloy–copper couple is 0.83 V, that of the alloy–nickel couple is 0.88, and that of the TsAM-chromium couple is 0.54 V. The corrosion rate is directly proportional to the emf of the corrosion galvanic couple. Therefore, the standard potentials and the emf of the corrosion galvanic couples also indicate the better anticorrosion properties of the proposed combined chromium coating.

Thus, for protective-decorative treatment of zinc–aluminum alloys we can recommend a coating consisting of 6 μm of polychromate chromium + 1 μm of bright chromium instead of M6N6Khb. The deposition procedure for this coating is very simple, because polychromate and standard chrome plating electrolytes are simple to make and operate. The use of cyanide electrolytes is completely eliminated and the output of the plant is increased by a factor of 5-6.

ELECTRODEPOSITION OF BRASS FROM ALKALI-TARTRATE ELECTROLYTES

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Cyanide electrolytes are usually employed to obtain an electrolytic coating with copper–zinc alloy. Oxalic [1], alkali-tartrate [2-7], pyrophosphate [8], and glycerate [9] electrolytes have been suggested by way of substitutes for them.

Most investigations have been performed in alkali electrolytes, in which copper is present as a complex of type $Cu(OH)_2Tart$ ($K = 7.3 \cdot 10^{-20}$) and zinc as $Zn(OH)Tart$ ($K = 2.4 \cdot 10^{-8}$) [10].

* Deceased.

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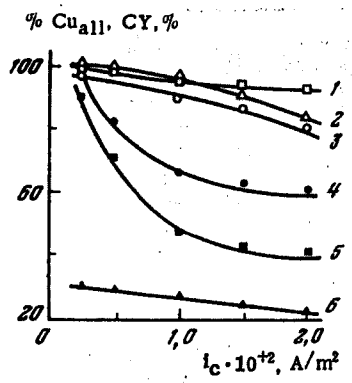

Fig. 1

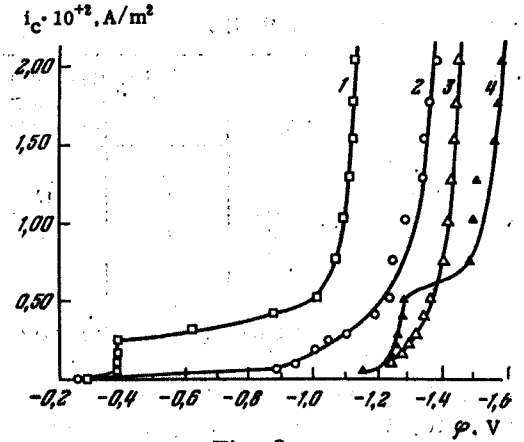

Fig. 2

Fig. 1. Current density vs current yield (1-3) and copper content of deposit (4-6) from an alkali-tartrate electrolyte containing $CuSO_4 \cdot 5H_2O$ (g/liter): 1, 3, 4, 5) 32; 2, 6) 3.2; Cu: Zn ratio in electrolyte: 1, 3-5) 1:1; 2, 6) 1:10; 3, 5) without PEI; others – with PEI.

Fig. 2. Polarization curves during deposition of Cu–Zn alloy from electrolyte containing $CuSO_4 \cdot 5H_2O$ (g/liter): 1, 2) 32; 3, 4) 3.2; Cu: Zn ratio in electrolyte: 1, 2) 1:1; 3, 4) 1:10; 1, 3) with PEI; 1, 4) without PEI.

It has been shown [11-13] that addition of 0.5-10 g/liter of polyethylenimine (PEI) to an alkali zincate solution greatly improves the quality of the deposits and permits attainment of a cathodic current density of up to 10 A/dm² or more.

Our aim is to investigate the effect of PEI on electrodeposition of brass from alkali–tartrate electrolytes.

The electrolyzer capacity was 0.5 liter, the cathodes were 0.8 KP steel plates with surface area 0.1 dm². We used an L-68 brass anode with a doubled surface. The electrolyte temperature was 20 ±1°C. The copper content of the deposit and electrolyte was determined by electroanalysis [14], the zinc content of the deposit was found from the difference in the masses. The potentials were measured with a high-ohmic cathode voltmeter with respect to a silver chloride half-cell. The electrolyte was prepared as follows: To obtain copper tartrate we dissolved Rochelle salt and copper sulfate separately in distilled water, after which the solutions were poured together with continuous mixing. Zinc oxide was dissolved in alkali of given concentration with mixing and poured into a copper tartrate solution.

The composition of the initial solution was as follows: 10 g/liter zinc oxide, 150 g/liter Rochelle salt, and 100 g/liter NaOH. The concentration of copper in the form of $CuSO_4 \cdot 5H_2O$ was varied from 3.1 to 64 g/liter. The thickness of the deposit, calculated from the mass, was 10 μm.

We investigated the influence of the current density at different ratios of copper to zinc (from 0.1 to 2) on the alloy composition, the current yield (CY), and cathodic polarization (Figs. 1, 2).

Preliminary investigations showed that alloy deposits with the most stable composition are obtained when the ratio of copper to zinc in the electrolyte is 0.1 or 1.0. However, in absence of PEI the deposits were brittle and rough. In the electrolyte containing from 1 to 6 g/liter PEI, however, the deposits were uniformly dense and plastic.

It will be seen from Fig. 1 (curves 1-3) that with an increase in the current density from 0.25 to 2 A/dm² the current yield in the electrolyte decreases from 100 to 80-85%; in the PEI-containing electrolyte, at Cu: Zn = 1 it is more constant than in the electrolyte without PEI.

With a ratio Cu: Zn = 1, the percentage of copper in the deposit for the PEI-containing electrolyte (Fig. 1, curves 4-6) is higher than in the PEI-free electrolyte, and in the current density range 1-2 A/dm² it is 61-66%, corresponding in composition to "yellow" brass. However, in external appearance the deposits had a color ranging from pale pink to brown.

In the electrolyte with Cu:Zn = 0.1 and a PEI content within the above range, the copper content of the deposit remained constant over a wide current density range and was 22-30% (Fig. 1, curve 6).

It will be seen from Fig. 2 that in the presence of PEI the deposition of copper–zinc alloy takes place at more positive potentials than in its absence. However, with Cu:Zn = 0.1 the depolarizing effect of PEI is less pronounced.

Thus, our investigations have shown that addition of 1-6 g/liter PEI to an alkali-tartrate electrolyte improves the quality of the cathodic deposits at specific ratios of copper to zinc in the solution and promotes formation of deposits of stable composition over a wide current density range.

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ROLE OF ADDITIVES IN FORMATION OF BRIGHT NONTARNISHING COMPOSITE SILVER COATINGS

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Composites $Ag-Be(OH)_2$ and $Ag-Al(OH)_3$ with enhanced darkening resistance are obtainable from a cyanide electrolyte [1]. We have obtained similar composite electrochemical coatings (CEC) from a noncyanide (cyanide–ferrate) electrolyte of the following composition (g/liter): AgCl 40, $K_4Fe(CN)_6 \cdot 3H_2O$ 200, K_2CO_3 20, pH = 9-10. We investigated the role of substances promoting coprecipitation with silver of dispersed $Al(OH)_3$ particles formed with addition of soluble aluminum compounds (10 g/liter $Al_2(SO_4)_3 \cdot 18\ H_2O$) to the electrolyte. During this process the electrolyte was mixed by a magnetic stirrer. The brightness of the coatings was determined on a brightness meter with a selenium photocell, the degree of darkening was determined by the method in [2].

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