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ELECTRODEPOSITION OF BRASS FROM ALKALINE TARTRATE—CITRATE SOLUTIONS

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As shown in [1, 2], deposits containing 74-51% Cu are formed on the cathode from alkaline glycerate brass-plating solutions at $t = 18$-$20°C$ and $i_c = 0.3$-0.2 A/dm^2. However, they were not like brass deposits and had a steel-gray color at a thickness of 1-5 μm. Fedot'ev et al. [3] obtained from alkaline tartrate electrolytes copper—zinc deposits of the tombac type with a copper content of 88-91%. Vyacheslavov [4] recommends a tartrate electrolyte for deposition of brass with a Zn content of 30%. However, none of these authors indicates the quality of the deposits obtained.

We have ascertained the feasibility of obtaining yellow brass with a constant copper content of 50-70% within the current density range 0.25-2 A/dm^2 from alkaline tartrate—glycerate electrolytes.

We investigated the influence of the electrolyte composition and electrolysis conditions on cathodic polarization, the current yield (CY), and the composition and quality of the deposits.

TABLE 1. Dependence of Current Yield, Composition, and Quality of Deposits on Additions of Glycerin and Rochelle Salt (separately) to the Following Solution (mole/liter): $CuSO_4 \cdot 5H_2O$ 0.13, ZnO 0.12, NaOH 2.5 (coating thickness — 10 μm)

Concn., mole liter		t, °C	i_c, A/dm^2	Copper content of deposit	Current yield	Quality of deposits
Rochelle salt	Glycerin					
–	0,3	20	0,25	95	100	Gray pink, no adhesion
			0,5–1	79–73	100	
			1,5	57	95	Greenish gray, no adhesion
			2	49	95	
–	0,6	20	0,5	64	96	Gray green, peels off
			1	46	86	
0,5	–	20	0,25	85	100	Orange
			0,5	72	98	Poor adhesion
			1–2	47–42	95–80	The same
1,0	–	50	0,5–1	95–83	99–97	Pink, lustrous
			1,5	75	96	Brown
			2,0	52	82	Bright green, lustrous
1,5	–	20	0,25	59	95	Gray green
			0,5–1	40	90–88	Gray
			1,5–2	40	80	
1,5	–	50	0,25	98	95	Pink, lustrous
			0,5–0,75	74	91	Pink violet
			1–2	36	86	Green

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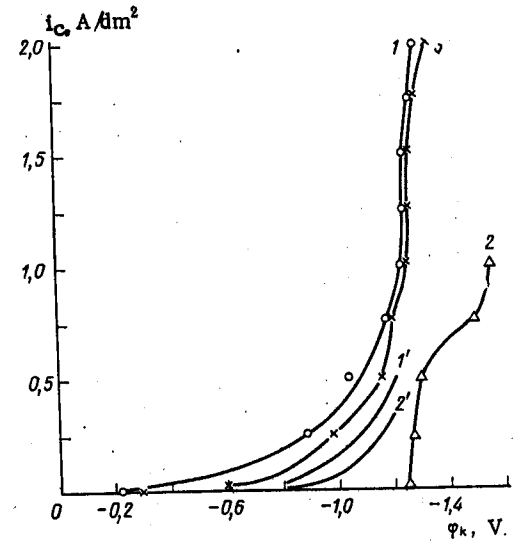

Fig. 1. Polarization curves of electrodeposition of metal from tartrate–glycerate electrolyte (mole/liter): 0.5 $KNaC_4H_4O_6 \cdot 4H_2O$; 2.5 NaOH; t = 20°C; 1) deposition of copper from electrolyte with addition of 0.13 M $CuSO_4 \cdot 5H_2O$; 2) deposition of zinc from electrolyte with addition of 0.12 M ZnO; 3) deposition of copper–zinc alloy from electrolyte containing 0.13 M $CuSO_4 \cdot 5H_2O$ and 0.12 M $CuSO_4 \cdot 5H_2O$ and 0.12 M ZnO; 1', 2') partial polarization curves for copper and zinc.

The experiments were performed in a 0.5-liter electrolyzer. The anodes were of L-68 brass, the cathodes of 0.8 kp steel sheet. Experiments with mixing were performed with the cathode oscillating at 112-115 oscillations per minute. The potentials (depending on the current density) were measured with a high-resistance cathodic voltmeter with respect to a silver chloride reference electrode.

The data obtained are given in Tables 1 and 2 and Fig. 1.

TABLE 2. Dependence of Current Yield, Composition, and Quality of Deposits on Additions of Glycerin and Rochelle Salt (present simultaneously) to a Solution Containing (mole/liter) $CuSO_4 \cdot 5H_2O$ 0.13, ZnO 0.12, and NaOH 2.5; t = 20°C; i_C = 0.25-2.0 A/dm^2, Coating Thickness 10 μm

Concn., mole/liter		Copper content of deposit, %	Current yield	Quality of deposits
Rochelle salt	Glycerin			
0,5	0,15	70–43	99–81	Greenish pink, brittle
0,5	0,30	63–42	99–72	Pink gray, brittle
0.5 with mixing	0,30	58–54	99–84	Orange, brittle
1,0	0,30	60–40	90–72	From green to dark brown velvet, platy
1,5	0,30	44–40	90–65	The same

It will be seen from Tables 1 and 2 that with an increase in temperature to 50° the copper content of the deposit and the current yield increase. In every case the deposits are nonuniform and do not have the usual color of brass. In alkaline tartrate, alkaline glycerate, and mixed electrolytes, with $i_c = 0.25\text{-}2$ A/dm^2, deposits formed on the cathode have a color ranging from pink to dark brown. In a glycerate electrolyte (without Rochelle salt), the deposits, 10 μm thick, were brittle and had poor adhesion. An increase in the NaOH concentration to 4.1 had practically no effect on the quality and composition of the deposits or on the current yield. Deposits with a copper content of 50-70%, corresponding to the composition of yellow brass, were obtained from a tartrate electrolyte (1 mole/liter $KNaC_4H_4O_6 \cdot 4H_2O$) at 50° within a very narrow current density range (1.5-2 A/dm^2). An increase in the Rochelle salt concentration to 1.5 mole/liter (Table 1) at 20° reduces the copper content of the deposit.

An analysis of the polarization curves (Fig. 1) shows that with simultaneous deposition of copper and zinc from alkaline tartrate—glycerate electrolyte (0.5 M $KNaC_4H_4O_6 \cdot 4H_2O$ and 0.3 M $C_3H_5(OH)_3$) the discharge rate of the zinc ions increases, and that of the copper ions decreases, in comparison with their deposition from the corresponding solutions. The overall polarization curves of codeposition of copper and zinc from a tartrate—glycerate electrolyte lies near the partial curve of copper deposition; with $i_c = 0.75\text{-}0.5$ A/dm^2, it is shifted toward more negative potentials (to −1.3 V when $i_c = 1.75$ A/dm^2). Similar results were obtained in an alkaline tartrate electrolyte.

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ELECTRODEPOSITION OF COPPER FROM CITRATE SOLUTIONS

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We have investigated the effect of a number of inorganic anions in citrate electrolytes containing heteronuclear copper—aluminum complexes on the adhesion of copper coatings to steel, and on the throwing power. The first was monitored by repeated bending of a steel plate over an angle of 180°, the second by the Field method and form. The polarization curves were recorded at a rate of 1 V/min.

Previously [1], we showed that aluminum forms two types of heteronuclear complexes with copper: $[CuAl(C_6H_5O_7)_2]^{-1}$ and $[CuAl_2(C_6H_5O_7)_4]^{-7}$. Formation of these complexes is maximal at pH 3.5 and 8.0, respectively. The throwing power strongly depends on the pH as a result of the change in the nature of the predominant complexes, but it is maximal in the presence of aluminum sulfate (Fig. 1b). Bearing in mind that contact deposition of copper on steel is not suppressed during formation of heterocomplexes in acid solutions, the effect of the anions on electrodeposition of copper was investigated at pH 8.0 in a basic solution containing (mole/liter) 0.1 $CuSO_4$ + 0.4 Na_2Citr + 0.1 $Al_2(SO_4)_3$. This addition of aluminum enhances the adhesion of the copper deposit to the steel substrate, but when 5-7 μm of nickel is deposited on it the coatings peel off during repeated flexure. We checked the additional influence of NO_2^- and NO_3^- ions [2, 3], and that of buffering ions (CO_3^{-2} and PO_4^{-3}) which reduce alkalization of the layer adjoining the electrode and prevent precipitation of copper hydroxide in it.

Addition of $NaNO_2$ and $NaNO_3$ (Fig. 1a) increases the limiting current by a considerable factor and shifts the polarization curves toward positive potentials. The simultaneous sharp

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