INFLUENCE OF INDIFFERENT SALTS ON THE QUALITY OF ELECTROLYTIC SILVER COATINGS FROM CYANIDE ELECTROLYTES

E. A. Nechaev, R. Yu. Bek,
G. S. Solov'ev, and N. T. Kudryavtsev

UDC 621.357.7

The influence of the nature of indifferent salts on the physical properties of electrolytic deposits of silver, produced from cyanide electrolytes, has been noted in the literature by a number of authors [1].

It has been established that cyanide baths, prepared on the basis of potassium salts, permit the production of high-quality coatings at higher current densities than baths containing sodium cyanide. It has also been noted repeatedly [2] that in the presence of a large excess of extraneous salts (KCN, KCl, K_2CO_3, etc.), in certain cases the permissible current density can be substantially increased.

New data [3, 4] on the kinetics of the process of electrodeposition of silver and the structure of the electrical double layer in cyanide solutions have prompted a more detailed investigation of the influence of the nature of indifferent salts on the structure of silver deposits.

The investigations were conducted in electrolytes containing 0.2 N Ag and 0.7 N $NaCN_{total}$.

In a study of the influence of cations (Li^+, Na^+, K^+, Rb^+, Cs^+) the corresponding chlorides were added to the initial solution in a 1 N concentration. Polarization measurements were conducted by a compensation method. The structure of the deposits was investigated by optical and electron microscopy. In all cases the thickness of the investigated deposit was 10 μ.

As we established earlier [5], in the electrodeposition of silver from cyanide electrolytes at potentials (φ) equal to −0.45 and −0.7 V, there are sharp changes in the structure of the deposits. In our previous work, it was hypothesized that in the first region ($\varphi > -0.45$ V) there is a substantial specific adsorption of CN^- ions, determining the high quality of the deposits. For this reason, the nature and concentration of extraneous salts have no appreciable effect upon the structure of electrolytic deposits. When alkali metal salts are added to the electrolyte, in this case only a slight increase in the permissible current density, from the standpoint of quality of deposits, increasing in the series Li^+, Na^+, K^+, Rb^+, Cs^+, is observed. This result is evidently due to the decrease in the cathodic polarization in the same sequence (Fig. 1), as a result of which the potential at which the quality of the deposits deteriorates is reached at higher current densities.

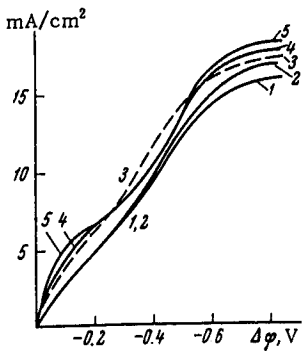

Fig. 1. Polarization curves obtained in electrolytes containing 0.2 N Ag, 0.7 N $NaCN_{total}$, and 1 N chlorides of alkali metals: 1) Li; 2) Na; 3) K; 4) Rb; 5) Cs.

At more negative potentials (< 0.5 V), the bond between silver and the CN^- anions is probably weakened [3], and their desorption from individual portions becomes possible. Naturally under these conditions, various random impurities in the electrolyte may influence the quality of the silver deposits. Their effect is expressed in the fact that spherical growths (Fig. 2), described in [5], are formed on the cathode surface. The number of growths increases when the potential is shifted in the negative direction and reaches a maximum close to the potential −0.7 V, which may be due to the maximum adsorbability of impurities close to the point

D. I. Mendeleev Moscow Chemicotechnological Institute. Translated from Zashchita Metallov, Vol. 3, No. 4, pp. 512-514, July-August, 1967. Original article submitted June 14, 1966.

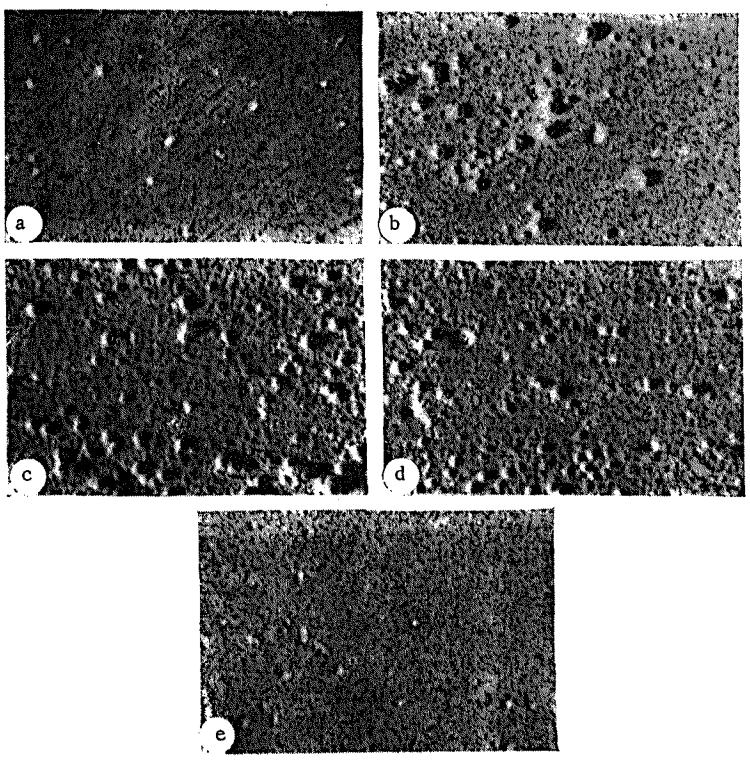

Fig. 2. Microstructure (× 250) of electrolytic deposits of silver, obtained in an electrolyte with the composition: 0.2 N Ag, 0.7 N $NaCN_{total}$, and 1 N LiCl. Potentials: a) −0.5; b) −0.6; c) −0.7; d) −0.8; e) −0.9 V.

of zero charge. The appearance of these growths on the cathode can be practically eliminated by thorough purification of the electrolyte by filtration through activated charcoal, or by preparation of the electrolyte from salts calcined and recrystallized twice in double-distilled water. The addition of alkali metal salts in this potential region ($-0.7 < \varphi < -0.5$) leads to a reduction of the growths and an improvement of the external appearance of the coatings.

At potentials more negative than −0.7 V, instead of shining hemispherical growths on the cathode surface (Fig. 2b), loose knobby formations are produced, and the external appearance of the deposits deteriorates sharply (Fig. 2c). In the absence of any special purification, this phenomenon is observed in cyanide electrolytes independent of the nature of the alkali cation. In electrolytes purified by the indicated method, prepared on the basis of potassium salts, no deterioration of the quality of the deposits is observed at $\varphi = -0.7$ V; the deposits obtained are dense all the way up to the limiting current density (Fig. 3a). In the presence of Li, Na, Rb, and Cs salts, on the other hand, purification of the solutions leads only to a disappearance of the growths, but has no appreciable positive effect upon the quality of the coating: the deposits at potentials more negative than −0.7 V deteriorate both in contaminated and in specially purified electrolytes (Fig. 3b).

The mechanism of such an effect of potassium ions on the structure of electrolytic silver deposits is not entirely clear. In a study of the electrical double-layer capacitance in the presence of various alkali cations, we did not detect any peculiarities in the behavior of electrolytes based on potassium [3]. The influence of potassium ions upon the kinetics of the process proved more appreciable: in their presence, there was noticeably less cathodic polarization than in electrolytes containing other cations (Fig. 1). However, the relationship between this phenomenon and the structure of the deposit cannot yet be explained.

In our previous works we noted a positive effect of NO_3^- anions on the cathodic process and scattering power of the electrolyte in the electrodeposition of silver [6]. The NO_3^- anion also exerts the same influence in electrolytes prepared on the basis of potassium salts.

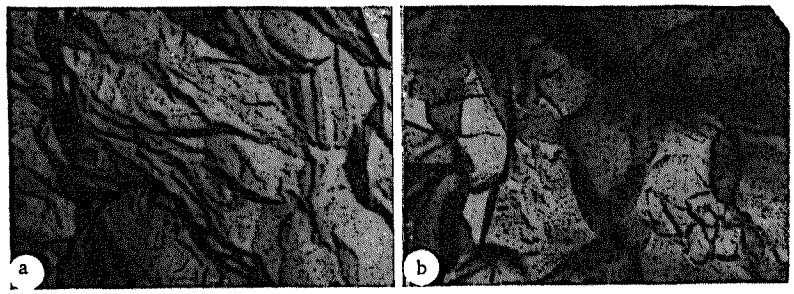

Fig. 3. Electron micrographs (×10,000) of galvanic deposits of silver produced in purified electrolytes: a) 0.2 N Ag; 0.7 N $NaCN_{total}$; 1 N KCl; $\varphi = -0.80$ V; b) 0.2 N Ag; 0.7 $NaCN_{total}$; 1 N NaCl; $\varphi = -0.80$ V.

In electrolytes prepared on the basis of potassium salts, the presence of 70-120 g/liter KNO_3 proved especially useful. In this case the silver deposits obtained are of high quality, all the way up to the limiting current, even without special purification of the electrolyte, which, as was mentioned above, is essential for the production of good deposits in electrolytes that do not contain NO_3^- anions. It may be that NO_3^- anions are well adsorbed by the silver surface and prevent the adsorption of impurities.

Thus, to improve the work of galvanic silver-plating baths, they should be prepared on the basis of potassium cyanide, with supplementary introduction of 100-150 g/liter KNO_3 into the electrolyte. In this case, the operation of producing silver chloride from $AgNO_3$, followed by washing of the precipitate to remove KNO_3, usually practiced, is entirely superfluous and even harmful. Silver-plating electrolytes should be prepared directly from silver nitrate, by pouring an aqueous solution of it into a solution of KCN in suitable amounts.

Hence, a study of the influence of additions of alkali metal salts on the quality of the deposits and cathodic polarization in the electrodeposition of silver from cyanide electrolytes has shown that at potentials more positive than −0.5 V, additions of alkali metal salts have no appreciable effect upon the structure of the deposit, but increase the maximum permissible current densities; moreover, their effect is intensified in the series Li, Na, K, Rb, Cs.

At potentials more negative than 0.5 V, extraneous impurities in the electrolyte have a substantial influence on the structure of the deposits.

The addition of potassium nitrate to the electrolyte substantially improves the external appearance of the coating and permits the production of high-quality deposits of silver at high current densities (all the way up to the limiting diffusion current).

On the basis of our investigations, it is recommended that silver-plating electrolytes be prepared directly from silver nitrate, introducing $AgNO_3$ into a solution of KCN and adding an additional 100-150 g/liter KNO_3.

LITERATURE CITED

1. S. Glasstone and E. B. Sanigar, Trans. Faraday Soc., 25, 590 (1929); F. Elser, Metalloberfläche, 13, 379 (1959).
2. F. Mason, Trans. Faraday Soc., 16, 534 (1921); W. R. Barclay, Trans. Faraday Soc., 16, 515 (1921); A. M. Molchadskii, B. I. Lebednikas, and Yu. Yu. Matulis, In: Theory and Practice of Shining Electroplating [in Russian], p, 271, Vil'nyus (1963).
3. E. A. Nechaev, R. Yu. Bek, and N. T. Kudryavtsev, Élektrokhimiya, 1, 1443 (1965).
4. E. A. Nechaev and R. Yu. Bek, Élektrokhimiya, 2, 150 (1966).
5. R. Yu. Bek, N. T. Kudryavtsev, and E. A. Nechaev, In: Theory and Practice of Shining Electroplating [in Russian], p. 297, Vil'nyus (1963).
6. N. T. Kudryavtsev and R. Yu. Bek, Zh. Prikl. Khimii, 35, 1030 (1962).