In the electrolytic deposition of metals and alloys one of the important factors influencing the process itself and the character and properties of the deposit is the nature of the anion of the salt used in the electrolyte. With many metals the degree of cathode polarization can change on passing from one anion to another, and either coarse- or fine-crystalline deposits can thus be formed [1, 2].

The electrodeposition of the iron-group metals is usually performed from aqueous solutions of salts such as sulfates or chlorides. The influence exerted by the nature of the anion on the metal electrodeposition process is linked with changes in the activity of the cations being reduced, the capacity of the cathode for passivation, the formation of a variety of complex compounds, the specific adsorption of individual anions, etc. [3-7]. In the electrodeposition of the iron-group metals from aqueous electrolytes metal and hydrogen cations are as a rule discharged simultaneously, the rates of discharge of metal and hydrogen ions varying depending on the electrode potential, which in turn is also affected by a number of factors (e.g., the nature of the anion of the salt). At a certain electrode potential hydrogen ions are discharged at an appreciable rate, and the metal current efficiency is low.

From what has been said above it follows that, by varying the anionic composition of an electrolyte, it is possible to control within certain limits the electrodeposition process and hence the structure and properties of the cathode deposit. This is of particular importance in the manufacture of fine iron and ferrous alloy powders intended for use in the production of permanent magnets and magnetic memory elements. In this connection, in the present work a study was made of the effects of the salt anions on the electrodeposition of iron powder from a two-layer electrolytic bath [8] containing chloride, sulfate, and perchlorate electrolytes and on the properties of the resultant powder.

Electrodeposition of finely divided iron was performed, by Natanson's method [8], in an apparatus with a 120-mm-diameter nickel disk cathode revolving in a vertical plane and a soluble iron (Armco) anode. The cathode revolved at a speed of 60 rpm. The lower layer of the bath was an aqueous solution of the divalent iron salt being investigated, and the upper layer a 0.5% solution of oleic acid in toluene. The temperature in the electrolytic bath was maintained constant by means of a device incorporating a cooling unit [9]. Polarization (cathode potential vs cathode current density) curves were constructed by a compensation technique, using a chlorine-silver reference electrode, after a constant value of cathode potential was established. Current efficiency was determined coulometrically. The particle size and shape of the powder were studied by the transmission method in an EMV-100L electron microscope.

In a two-layer electrolytic bath fine metal and alloy powders form at the comparatively high cathode potential due to two characteristic features of such a bath, namely the presence of a solution of surface active agents in an organic medium, which passivate the cathode surface, and of a revolving cathode [10]. Other electrochemical factors, such as the concentrations of ions of the metal being deposited and hydrogen, temperature, cathode current density, and the nature of the anion of the salt, can appreciably shift the cathode potential in either direction.

To determine the effects of the nature of the anion of the salt on the magnitude of cathode polarization, \( \varphi \) vs \( i \) polarization curves were plotted for electrolytes of various anionic compositions. The di-
valent iron ion concentration was varied from 2.5 to 20 g/liter at pH 3 and an electrolyte temperature of 20 ± 1°C. From Fig. 1 it can be seen that, at any given divalent iron ion concentration, the polarization curves shift toward more electronegative values on passing from one anion to another in the order \( \text{ClO}_4^- - \text{Cl}^- - \text{SO}_4^{2-} \). A similar shift of the potential is observed when the divalent iron ion concentration is lowered for each of the electrolyte compositions investigated.

A change in cathode potential affects the powder current efficiency. Thus, when the cathode potential shifts toward more negative values on passing from one anion to another in the order given above, the current efficiency drops at any given divalent iron ion concentration in the electrolyte (Fig. 2), and hydrogen evolution becomes more intense. The maximum current efficiency is observed at \( C_{\text{Fe}} = 5 \) g/liter for the perchlorate and chloride electrolytes and at 10 g/liter for the sulfate electrolyte. For all the electrolytes investigated the maximum current efficiency is reached in the cathode current density range 15-30 A/dm². Further increase in current density leads to more intense hydrogen evolution, as a result of which the yield of metal falls.

The nature of the anion of the salt, together with some other parameters of the electrodeposition process, strongly affects also the particle size and shape of the fine iron powder obtained as a result of this process. Our electron microscopical examinations have shown (Fig. 3) that particles produced from the electrolytes investigated are imperfectly developed dendrites whose length and degree of ramification vary depending on the nature and concentration of the electrolyte. Thus, at a divalent iron ion concentration of 20 g/liter and low current densities fairly coarse particles with thick central cores are obtained from all the electrolytes investigated (a and b). At lower iron ion concentrations in the electrolyte the dendrites forming at low current densities are somewhat smaller in size, and their central cores and branches are thinner (c and d).