

**THE EFFECTS OF ORGANIC AND
INORGANIC "ADDITION-AGENTS"
UPON THE ELECTRO-DEPOSITION
OF COPPER FROM ELECTROLYTES
CONTAINING ARSENIC**

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BY

CHING YU WEN

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
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INTRODUCTION.

In the production of good and pure copper by electrolysis, the composition of the electrolyte is one of the important factors. The causes of poor copper deposits are chiefly due to the impurities which accumulate in the electrolyte, and which, under usual conditions, are precipitated along with the copper. Of those impurities, the most harmful and troublesome ones are arsenic and antimony, the presence of which in the deposited copper makes it brittle and nodular. It has been a known fact that during electrolysis, part of the arsenic and antimony contained in the anode dissolves and remains in solution. These two elements, especially the arsenic, are allowed to accumulate in the electrolyte till a critical point is reached, which has not yet been definitely determined. When this point is passed, they begin to be deposited with the copper on the cathode and render the deposit bad and brittle. To prevent this, it is therefore of utmost importance to maintain the electrolyte within a certain degree of purity, in other words, to keep the amount of arsenic and antimony in the electrolyte below the critical point. This is usually accomplished in practice by withdrawing a certain portion of the electrolyte and replacing it with an equal quantity of fresh solution, and the copper in the impure electrolyte recovered either by crystallization or by electrolysis with insoluble lead anodes. This not only complicates the process of electrolytic refining of copper, but also entails an extra item of expenditure in the production of electrolytically refined copper.

Another thing that is observed during the electrolysis is that "sprouts" or dendritic "trees" often form, especially along the edges of the cathode. The formation of such "trees" interferes with the work, renders it more difficult to operate, and prevents the electrodes from being placed close together; as there is danger that the electric current would be short-circuited. In conducting the electrolysis in a commercial way, the removal of these "trees" becomes absolutely necessary and is usually done by the tank inspectors, thus increasing the cost of refining.

The object of the present investigation is, therefore, twofold: first, to prevent the deposition of arsenic and antimony on the cathode, and second, to prevent the formation of dendritic "trees." This problem was worked out, having in mind the production of solid and smooth deposits, from copper electrolytes containing high percentages of arsenic, by means of organic and inorganic "addition-agents."

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ABSTRACTS OF LITERATURE.

In reviewing the literature regarding both organic and inorganic addition-agents little was found.

Kiliani¹ was, perhaps, the first man, who had conducted systematic experiments to investigate the behavior of impurities present in the copper anode, and to study the effect of inorganic salts on the character of the copper deposit. For the latter case he used an electrolyte containing 15 grams of copper sulphate and 5 grams of sulphuric acid, in 100 c.c. solution with a current density of 20 amperes per square meter. He observed the fact that, with a small amount of tin salt in the electrolyte, good smooth, malleable copper was produced while, in the case when the electrolyte contained no tin salt, the deposit was extremely bad and brittle. He noted also the fact that the presence of a small amount of tin in the anode caused the potential difference between electrodes to be greatly reduced.

W. Borchers² performed experiments with the object of preventing the crystalline growth of copper on the deposit, by adding to the electrolyte a sufficient amount of sodium chloride, or magnesium chloride. He found, however, by the addition of these reagents, only a diminution of the evil could be effected.

H. O. Hoffman³ has pointed out that hydrochloric acid is used in practice to precipitate the antimony in the electrolyte. This is accomplished by the addition of a sufficient quantity of crude hydrochloric acid to the head tank to maintain 0.04 gram of chlorine per liter in solution. The hydrochloric acid reacts with the antimony and precipitates it as oxychloride. When there is deficiency of hydrochloric acid the sample-plate becomes streaked, tarnished, black and brittle.

It is said that ammonium sulphate⁴ has been used in the

¹ *Berg und Hüttenmännisches Zeitung*, 1885, p. 249.

² W. Borchers, "Electrolytic Smelting and Refining," p. 206 (translated by McMillan).

³ *T. A. I. M. E.*, 1904, Vol. 34, p. 312.

⁴ T. Ulke, "Modern Electrolytic Copper Refining," 1st ed., p. 18.

electrolyte to hinder the precipitation of arsenic on the cathode, and the amount usually added was from 0.5 to 20 per cent. The addition of this salt decreases the conductivity of the electrolyte.

L. W. Wickes⁸ investigated the percentage of arsenic which the deposited copper would contain for a given potential between electrodes, and the relation between variations in the potential and the amount of arsenic in the copper deposited. For his experiments he used anodes containing 1 per cent., 2 per cent., and 4 per cent. arsenic, and an electrolyte containing 75 parts of water, 19 parts of copper sulphate, and 6 parts sulphuric acid, by weight, and also an electrolyte of the same composition, but containing 0.101 per cent. arsenic in the form of arsenic acid. The experiments were conducted with 0.4 volt, 0.6 volt, and 0.8 volt. He found that with different voltages and the same percentage of arsenic in the anode, the percentage of arsenic in the cathode copper was practically the same in all cases, and that the greater the percentage of arsenic in the anode, the more erratic were the results. The conclusion which he drew of his experimental data is that the percentage of arsenic in the deposited copper is not a function of the potential between electrodes, but of the degree of hydrolyzation of the sulphate of arsenic in the electrolyte.

Of the work on organic addition-agents, that of Edward F. Kern and Royal P. Jarves⁹ should be mentioned. They conducted experiments to investigate the effect of the presence of tannin, pyrogallol, gelatine, and resorcinol upon the density and coherence of electrolytically deposited copper, lead, and silver. For their experiments on copper they used two kinds of electrolyte, the cupric sulphate and the cupric fluo-silicate. With the former electrolyte which contained 16 grams of cupric sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 4 grams of sulphuric acid (H_2SO_4) per 100 c.c., they found that the presence of tannin, resorcinol or gelatine equally caused the copper to deposit more smoothly. The deposited copper formed at 30° C. was better than that at 20° C. With the fluo-silicate electrolyte, which contained 6.34 grams of copper, and 3.60 grams of free hydro-fluo-silicic acid (H_2SiF_6)

⁸ E.M. thesis, Metallurgical Library, School of Mines, Columbia University.

⁹ *School of Mines Quarterly*, 1909, Vol. 30, p. 119.