

DISCUSSION

THE PAPER BY E. A. UKSHE AND A. I. LEVIN "ON THE COMPOSITION AND PROPERTIES OF THE COMPLEX ELECTROLYTE OF THE COPPER-PYROPHOSPHATE BATH" [1]

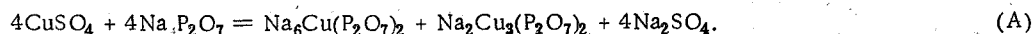
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The paper contains the statement: "... ratios of concentrations of $\text{Na}_4\text{P}_2\text{O}_7$: $\text{CuSO}_4 \leq 2$, should be aimed at since then the nature of the discharging ions will scarcely change, and the lowering of the concentration of free pyrophosphate offers better prospects since in this case crystallization of $\text{Na}_4\text{P}_2\text{O}_7$ on the surface of the cathode becomes improbable [2]. And later: "We have realized in practice such a ratio of concentrations of CuSO_4 and $\text{Na}_4\text{P}_2\text{O}_7$ with simultaneous introduction of extraneous complex formers, and this led to fully satisfactory results".

We agreed with the statement of the authors that the nature of the discharging ions when $[\text{Na}_4\text{P}_2\text{O}_7]: [\text{CuSO}_4] < 2$ does not change, but at this ratio of concentrations a precipitate of $\text{Na}_2\text{Cu}_3(\text{P}_2\text{O}_7)_2$ or CuP_2O_7 is formed and lowers the concentration of discharging complex ions. Consequently a fall in the ratio of $[\text{Na}_4\text{P}_2\text{O}_7]: [\text{CuSO}_4]$ is here equivalent to simple dilution of the solution. In the absence of a change in the nature of the discharging ions, it is impossible to obtain in the solution the ratio of concentrations envisaged by the authors. By introducing "extraneous complex formers" the authors actually introduce new complex ions of copper in order to compensate for the loss of copper in solution - naturally at the cost of solution of the precipitate.

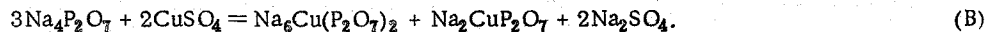
The word "precipitate" is not mentioned a single time by the authors, while a precipitate ought to have come down at the ratios of concentrations of $\text{Na}_4\text{P}_2\text{O}_7$ and CuSO_4 indicated by them. The precipitate substantially changes the concentration of ions in solution and somewhat complicates the theoretical consideration of the problem of the ionic composition of the solution.

In Table 1, for example, is the remark: "Assumed predominating form: $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ " (for the first five lines of the table). Actually at the concentrations employed in electroplating, such an ion will not be present in solution since in the main the reaction goes according to the equation [3]:

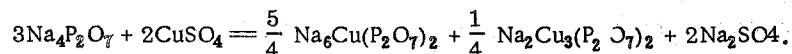


The concentration of copper is thus reduced by a factor of 4, which could certainly lead (although at concentrations very much lower than those cited by the authors in the tables) to the appearance of $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ ions, in appreciable, even if not predominating, amount.

The summary contains the statement: "an inflexion of the curves is observed which corresponds to substantially complete transition of copper into a complex ion". In the text of the paper appears an indication that this situation corresponds to a ratio of $[\text{Na}_4\text{P}_2\text{O}_7]: [\text{CuSO}_4] = 3:2$. Evidently (assuming the validity of the authors' statement that the solution will then only contain complex ions of $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ and $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$), this ratio will correspond to the equation:



This ratio thus corresponds not to substantially complete transition of copper to the complex ion but to a 1:1 ratio of the concentrations of hexavalent and bivalent complex ions. This ratio is also confirmed by the data of the authors' themselves; indeed they point out that in Fig. 1 the ratio of 3:2 for the concentrations of $[\text{Na}_4\text{P}_2\text{O}_7]$ and $[\text{CuSO}_4]$ corresponds to point *a* for which the relative concentrations of the hexa- and bivalent ions are approximately equal to 50% (the curves of relative concentrations of ions of $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ and $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ intersect at this point). Moreover, it must be noted that equation (B) is only valid at very low concentrations of electrolytes (10^{-4} molar and less), when precipitate ceases to form and formation of $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ ions becomes possible [3]. At the concentrations considered by the authors, $\text{Na}_2\text{Cu}_3(\text{P}_2\text{O}_7)_2$ is precipitated according to the equation:



As we see, the concentrations of the compounds formed bear a fortuitous, or more correctly, an intermediate, character, and do not correspond, contrary to the authors' statement, to "nearly complete transition of copper to the

$[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ ion", because here a break on the curve of $x=f(C)$, cannot occur. The break obtained by the authors on a curve with only four experimental points is very likely the result of an error of measurements, since some difficulty must arise in measurement of the electrical conductivity in presence of the precipitate formed, so that the operation calls for considerable skill. (Strictly constant conditions must be maintained during formation of the precipitate and its distribution throughout the solution at the instant of measurement, for the conductivity of such a system depends on the form of the particles and on their distribution in the solution. In particular a gross error results from measurement of electrical conductivity without preliminary stirring of the solution, especially when the electrodes are partly immersed in precipitate.)

We did not observe the appearance of any breaks on the isotherms of specific electrical conductivity corresponding to a 3:2 ratio of $[\text{Na}_4\text{P}_2\text{O}_7]$ to $[\text{CuSO}_4]$, and in particular at the concentrations cited by the authors: 0.06 M $\text{Na}_4\text{P}_2\text{O}_7$ and 0.04 M CuSO_4 [3].

In the light of the foregoing considerations, the authors' statement that the nature of the discharging ions, and consequently also the ionic composition, do not change with decrease in the ratio of $[\text{Na}_4\text{P}_2\text{O}_7]$ to $[\text{CuSO}_4]$, although valid, does not follow from the results of the investigation, since at the concentrations required in electroplating the ionic concentration of the solution is governed not so much by the excess of $\text{P}_2\text{O}_7^{-4}$ ions (the influence of whose concentration on the ionic composition of the solution was considered by the authors) as by the dilution of the solution or the formation of a precipitate when there is a deficiency of these ions (i.e. when $[\text{Na}_4\text{P}_2\text{O}_7]:[\text{CuSO}_4]$ is less than 2). In the latter case the concentration of $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ ions and the total concentration of copper in the solution are lowered due to separation of the precipitate of $\text{Na}_2\text{Cu}_3(\text{P}_2\text{O}_7)_2$. Thus, the authors' suggested fall in the $[\text{Na}_4\text{P}_2\text{O}_7]:[\text{CuSO}_4]$ ratio scarcely possesses practical significance, although it would also appear to be required from the condition of prevention of crystallization of $\text{Na}_4\text{P}_2\text{O}_7$ at the cathode, which is detrimental to the electrolytic deposition of copper. By adding sodium citrate (see end of the paper [1]) the authors nevertheless prevented the precipitation but obviously at the cost of partial change of the composition of the discharging ions.

There is another possible method of preventing crystallization of $\text{Na}_4\text{P}_2\text{O}_7$ at the cathode which hinders the increase in cathodic current density during prolonged passage of current due to deterioration of the quality of the copper deposit and lowering of the current yield [2]. This method is the reduction of the pH of the solution, which may be permissible in absence from the solution of SO_4^{-2} ions which lower the practical limit of cementation. This is achieved by using the electrolyte proposed by I. G. Shcherbakov [4] which enables working at lower pH and higher current densities without cementation (absence of the latter is reflected in good adhesion of the deposit) and the other harmful effects mentioned above.

The paper also contains a number of minor errors. The value of $K_H = 2 \cdot 10^{-11}$ cited by the authors as appearing in [5] is actually not mentioned in this source. It is incomprehensible why the author has already given this erroneous reference in three papers (see also [2, 6]). Again, in equation for $E - E_{\text{Cu}}^0(2)$ [1] the concentration of $\text{P}_2\text{O}_7^{-4}$ is calculated as the difference $C_{\text{P}_2\text{O}_7}^0 - C_{\text{Cu}}^0$, which is not true at the usual concentrations, again due to separation of a precipitate in accordance with equation (A). Equation (2)[1] (as also the results of the calculation given in Fig. 1 [1]) are evidently only valid at very low concentrations of electrolyte at which a precipitate ceases to come down (about 10^{-4} and less g-ions/liter Cu^{+2}).

LITERATURE CITED

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