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ON PASSIVATION OF SILVER DURING ELECTRODEPOSITING

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In a number of recently published papers it has been demonstrated, that the form of polarization curves and, likewise, the structure of electrodeposited metals are closely connected with the velocity of passivation of a freshly-deposited metallic surface.

At the same time, the question of what the passivation phenomenon itself depends on, had not been definitively ascertained till the present day. Various hypotheses have been advanced on the problem. According to some of them, the passivation of the cathode surface is a result of oxidation with oxygen dissolved in the electrolyte. At the same time an oxide film is formed on the electrode surface, which interferes with a direct contact between metal and electrolyte. According to other hypotheses, the passivation is caused by insufficient purification of the electrolyte from traces of organic impurities. Other hypotheses have been ventured besides: thus, Kohlschütter and Torricelli suppose that a silver cathode immersed into the electrolyte prior to the beginning of electrolysis is passivated in consequence of the following reaction taking place on its surface:

$$Ag + Ag^+ \rightleftarrows Ag_2^+.$$

As a result of this reaction the surface of the electrode is smoothed out, which leads to its passivation. The electrode passivation at an intermission in the electrolysis has been explained by Kohlschütter and Torricelli as a result of potential differences, rising between separate parts of the cathode surface in consequence of some differences in their structure, these potential differences leading to a rise of local currents.

In studying the passivation phenomenon with an aim of quantitative determination of its value, it is necessary to have as a criterion an electrolyte which causes no passivation. What would seem to be the most natural way towards obtaining such an electrolyte, is to make good use of the dependence between current intensity and the increasing cathode surface, first observed by Aten and Boerlage (1). According to their data, the active electrode surface adapts itself to current intensity, the density of the current (d_2) being preserved constant. This dependence is the result of two mutually opposed processes: the growth of active surface of the deposit and the process of its passivation.

When the velocities of these processes are equal, the active surface of the cathode remains constant, which accounts for the phenomena observed by Aten and Boerlage.

In a case when at the cathode surface there is growing only one crystal, the latter attains the form of a filament with constant cross-section.

This dependence between active cathode surface and current intensity cannot take place in the case when the electrolyte stimulates no passivation of the electrode surface. Therefore, the electrolyte requisite as a criterion, i. e. one that causes no passivation, should be an electrolyte, during the electrolysis of which the above-mentioned phenomenon is not observed. However, this regularity was sometimes found by the author to fail even in such cases when the impurities present in the electrolyte brought about a passivation of cathode, as it was evident from the form of polarization curves. Therefore, this method could not be employed.

In 1910 Leblanc noticed that there is a temporary increase of polarization in the beginning of electrolysis. Next the polarization decreases to a certain constant value. It has been shown by the author (²) that increase in polarization, observed at the beginning of electrolysis, is due to the smallness of the original size of the active cathode surface. In the course of electrolysis the active surface increases attaining a constant value under given experimental conditions, which is reflected in the form of the polarization curves. Likewise, part of the active surface of an electrode immersed in electrolyte (with broken circuit) ceases with time to conduct electric current, which leads to an increase of current density and of polarization in the moment when the current is being switched on. It is obvious, that there should be no alteration in cathodic polarization after an intermission in electrolysis for various intervals of time, if the electrolyte causes no passivation of the cathode surface*.

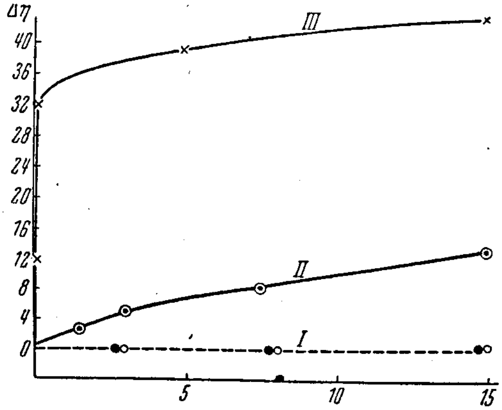

Fig. 1.

What we ask to consider here as a normal curve is one, corresponding to such a run of polarization. This curve shows the polarization value not to vary with the length of the intermission interval in the electrolysis (Fig. 1, dotted line *I*).

Such a form of polarization curve is therefore evidence of the electrolyte purity**; the author has taken advantage of this fact in a search for an electrolyte that causes no passivation and may be applied as a criterion in studying this phenomenon.

In the present communication evidence is given, which to our mind must contribute to the disclosure of the causes of passivation.

The method used by the author in the present study had been described in detail in our previous communication (²). It should, however, be mentio-

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* That on switching off the current the crystals of silver present in the cathode immersed in the electrolyte are subject to passivation and the more so, the longer was the period when electrolysis was suspended, has been first experimentally demonstrated by Kohlschütter and Torricelli (³). Gorbunova and Vahramian (⁴) have found that in the case of a freshly formed cathode surface during its contact with electrolyte, while the circuit was broken, the rate of passivation was high at first, but diminished gradually afterwards.

** By pure electrolyte is meant one causing no passivation.

ned that in contrast with the experiments previously described, the polarization value has not been determined by compensation method, but by means of a short-period galvanometer—a Cambridge electrocardiograph with a sensibility 10^{-9} A. This method made it possible to determine the polarization value directly after the current had been switched on.

In the beginning the electrolyte was prepared from chemically pure silver nitrate, previously twice recrystallized from bidistillate. However, the polarization curve obtained during the electrolysis of this salt did not coincide with a normal one (Fig. 1, curve *II*), thus pointing at a presence of impurities in the salt. Therefore, subsequently the twice recrystallized preparate of salt was purified from organic impurities by means of their oxidation in the presence of platinized platinum in the atmosphere of oxygen during 24 hours or more. In electrolysis of a solution of the salt purified in this way, a polarization curve was obtained with no deviations from the normal one, even when electrolysis was stopped for 30 minutes.

As has already been mentioned above, the following factors have been put forward in literature to account for passivation during depositing of silver: presence of oxygen in the electrolyte; change in the amount of semivalent silver present in the electrolyte; effect of local current and presence of traces of organic material.

The following three series of experiments have been made with an aim of establishing the effect of each of these factors.

1. If passivation is due to the formation of an oxide film on the cathode surface at the expense of the oxygen dissolved in the electrolyte, no passivation should be observed if the electrolyte has been freed from oxygen thoroughly. Therefore, the first series of tests were made with an electrolyte thoroughly freed from the traces of oxygen. To eliminate the dissolved oxygen, before taking the curve there was blown a stream of nitrogen through the electrolyte. This nitrogen contained no traces of oxygen or other impurities, because it had been passed over red-hot copper and then through a trap with liquid air.

Under the same conditions were made the tests with preliminary saturation with oxygen of the same electrolyte. The latter was prepared electrolytically and freed from traces of hydrogen by passing over palladium asbestos at 300°C.

In both cases the curves $\Delta\eta/t$ have been found to be identical and demonstrated that there was a complete absence of passivation within the limits of sensitivity of the experiments.

Thus, the passivation cannot be explained by formation of an oxide film upon the cathode. Even if such a film should form there, it would not prevent further depositing of the metal.

2. Two series of experiments were intended to verify the second of the above-mentioned hypotheses. The first was run with electrolyte enriched with Ag_2^+ ions of semivalent silver; the second with electrolyte made low in these ions. All other conditions were equal. Enriching and impoverishing the electrolyte with Ag_2^+ ions of semivalent silver was accomplished by the method described by A. D. Obrucheva (⁵). In both cases identical curves $\Delta\eta/t$ have been obtained, thus showing an absence of passivation.

It will be obvious that the presence of semivalent silver in the electrolyte is not responsible for passivation either, contrary to the opinion of Kohlschütter and Torricelli. Nor is the author inclined to share another opinion of Kohlschütter and Torricelli, according to which the passivation of silver is caused by local currents. If that were the case, the passivation should be observed during the tests with perfectly pure electrolytes; however, in the tests described above there was observed no passivation.

3. In the third series of experiments the effect of organic impurities has been studied. As it has been indicated above, the electrolyte was freed from organic impurities by oxidizing them in a stream of oxygen in the presence of platinized platinum.

A series of experiments has demonstrated that there was almost no passivation during electrolysis of electrolytes purified in this way. There was no passivation whatever when the purification of electrolyte by oxidation of organic impurities and the subsequent electrolysis had been performed at a comparatively high temperature (60° C). This effect of temperature may be explained by a more complete oxidation of organic impurities at a higher oxidation temperature, the electrolyte being, therefore, obtained in a state of higher purity. On the other hand, if the passivation were caused by adsorption of organic impurities on cathode surface, their passivating effect should decrease at higher temperatures in consequence of an increase of desorption.

In another series of experiments performed under the same conditions, but with some small amounts of certain organic substances, as for instance 0.2% of dextrine (from Kahlbaum), being added, a very strong passivation was observed (Fig. 1, curve *III*).

The passivating effect of organic impurities should be explained by their adsorption on the active surface of the cathode. At present a study of the rate of poisoning of cathode surface by various organic materials is in progress.

The experiments described above demonstrate in this way that a curve which exhibits independence of polarization value of the length of the intermission in electrolysis, may serve as a criterion of purity of the electrolyte, i. e. the absence in it of the impurities capable of poisoning the cathode surface. In case of a change in the polarization value, the incline of the curve will be a quantitative expression of the rate of passivation of the electrolytically deposited metal.

The presence of oxygen in the electrolyte as well as the presence of semivalent silver are not the factors causing the passivation of silver during electrodepositing. Neither is passivation caused by the local currents; it is effected by casual organic impurities present in the electrolyte.

In conclusion the author desires to express his appreciation to A. N. Frumkin for many helpful suggestions.

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