THE COMPOSITION, PROPERTIES, AND ROLE OF THE ANODE LAYER OF ELECTROLYTE IN THE ELECTROLYTIC POLISHING OF COPPER IN PHOSPHORIC ACID

G.S. Vozdvizhensky, V.A. Dmitriev, A.G. Mozhanova, and E.V. Rzhevskaya

Since the time of Jaquet [1] the mechanism of the electrolytic polishing of copper in phosphoric acid has been related to the formation of a viscous liquid film at the surface of the dissolving anode. It must be admitted that although, according to results obtained in our laboratory [2], a viscous liquid film obviously cannot play the decisive role in the mechanism of electrolytic polishing, its auxiliary role in the process is evident.

Unfortunately, the literature still contains little information on the composition and properties of these films. The data obtained by Jaquet himself and by his co-workers are well known from monographs [3].

Batashev and Nikitin [4] studied the chemical changes in the films at various stages of the process. They attribute the smoothing of the rough surface to formation of trisubstituted copper phosphate in the cavities, while at the projections the process continues by formation of the disubstituted phosphate.

In another paper [5], Batashev put forward the view that the process which determines electrolytic polishing is the discharge of the corresponding anions at the anode projections, simultaneously with dissolution of the projections.

TABLE 1

Changes on Electrolyte Properties During Electropolishing

$\frac{\text{Anode area}}{\text{Cathode area}} = 1/25$, $D_a = 50$ A/dm^2

Amp-hours per liter of electrolyte	Copper content (in g/liter)	Specific gravity	Viscosity (in centipoises)	Electrical conductivity (in ohms^{-1})	Luster* in arbitrary units
0	0	1.549	19.19	0.1357	—
3.8	0.76	1.549	19.31	0.1354	—
16.9	2.44	1.552	19.74	0.1291	92
48.3	3.30	1.558	20.45	0.1272	84
132.0	3.96	1.564	21.14	0.1230	—
272.7	4.24	1.570	22.48	0.1197	87
335.3	4.24	1.571	22.80	0.1195	87

*Separate specimens, polished at $D_a = 50$ A/dm^2 for 10 minutes, were taken for luster measurements.

Anion discharge results in destruction of the anode layer at the projections and changes in the surface conditions of the projections themselves. Unfortunately Batashev did not indicate the nature of the destruction of the anode layer or the methods by which it may be demonstrated.

Laforgue-Kantzer [6] studied the composition of the viscous anode film by different methods and showed it to be $PO_4(OH)CuH_2$. The film is in equilibrium with the electrolyte on the one hand, and with the oxide on the electrode surface, on the other.

Evidently there is no doubt concerning the formation of an anode layer, of a composition different from the main bulk of the electrolyte, during the electrolytic polishing of copper in phosphoric acid. However, the role of this layer is still not clear, as its properties have not been studied sufficiently.

The aim of the present investigation was to study certain physicochemical properties of the electrochemical bath during its operation, and to relate them to the properties and structure of the anode layer of electrolyte

EXPERIMENTAL

Specimens of sheet copper of M-1 grade, as supplied from the factory, were used for the experiments. The electrolyte was orthophosphoric acid (density 1.55). The direct current was supplied from an alkaline storage battery.

TABLE 2

Variation of the Copper Concentration with Changes in the Ratio of the Anode and Cathode Areas

Anode area / Cathode area	Maximum copper content (in g/liter)	Luster in arbitrary units
1/25	0	86
1/25	4.24	87
1/10	5.54	90
2/1	10.68	98

The copper content of the electrolyte, its viscosity, electrical conductivity, phosphate content, and polishing power were determined during the electropolishing process.

Phosphates were isolated from the electrolyte with the aid of anhydrous acetone. Acetone dissolves water and mineral acids, while the dissolved phosphates are precipitated. The phosphate content in the isolated phosphates was determined by the molybdate method, and the copper in the electrolyte and the phosphates was determined electrolytically; the electrical conductivity and viscosity of the electrolyte were determined by the usual methods. The polishing power of the electrolyte was determined from the luster of the specimens. The luster was measured by means of a reflectometer with a selenium photocell.

TABLE 3

Composition of Phosphates in the Electrolytes

Sampling conditions	Content in sample (in g/liter)		$\frac{Cu \cdot 95}{PO_4 \cdot 63.6}$
	Cu	PO_4	
Anode electrolyte layer 120 seconds after connection of current	0.0052	0.01045	0.74
Anode electrolyte layer 200 seconds after jump of potential	0.0120	0.0223	0.80
Bath electrolyte (copper content 4.24 g/liter)	0.034	0.0071	0.71
Bath electrolyte (copper content 1.76 g/liter)	0.0050	0.01213	0.61

Changes in the electrolyte during use. Copper compounds gradually accumulate in the electrolyte during electropolishing. The properties of the electrolyte change simultaneously, as can be seen from Table 1.

These results show that the content of copper compounds increases, the viscosity and specific gravity increase, and the conductivity of the electrolyte decreases with increasing quantity of electricity passed through it. The polishing power, determined from the luster of the surfaces, remains practically constant during these changes. It should be noted that the maximum content of copper compounds in the electrolyte depends on the ratio between the anode and cathode areas, which is also related to the anode and cathode efficiencies.

By variations of the ratio of the anode and cathode areas, it is possible to vary the maximum concentration of copper compounds in the electrolyte, as can be seen from the data in Table 2.

It is seen that an increase of the copper content of the electrolyte up to 10.68 g/liter has no appreciable

effect on the luster of the electropolished surface.

Composition of the anode layer of electrolyte. For the determination of the composition of the phosphates formed at different stages of the process and under different conditions, electrolyte samples were taken from the anode layers by the method described by Batashev [4].

TABLE 4

Results of Experiments on Regulation of the Process by Variation of Potential

Potential (in V)	Contents (in g/liter)		$\frac{Cu \cdot 95}{PO_4 \cdot 63.6}$
	Cu	PO_4	
0.5	0.0048	0.0102	0.70
1.2	0.0199	0.0354	0.82
1.6	0.0224	0.0400	0.84

The samples were taken at a current density of 1.5 A/dm^2 120 seconds after the current was switched on and 200 seconds after the jump of potential. The copper and phosphorus contents of the samples were determined. The phosphate content of electrolytes containing 1.76 and 4.24 g of copper per liter was determined as a comparison. The results are shown in Table 3.

In all cases, both in the anode electrolyte layer (Experiments 1 and 2) and in the bulk of the electrolyte (Experiments 3 and 4) the ratio $\frac{Cu \cdot 95}{PO_4 \cdot 63.6}$ is less than unity, indicating the formation of a mixture of phosphates.

TABLE 5

Results of Anolyte Analyses

Determinations and analyses	Anolyte			
	Initial (H_3PO_4, s.g. 1.55)	After use	Incompletely saturated with copper	Saturated with copper
Copper content (in g/liter)	0	4.24	43.42	71.20
Specific gravity	1.549	1.571	1.634	1.698
Viscosity (in centipoises)	19.2	22.8	36.87	61.48
Electrical conductivity (in ohm^{-1})	0.1357	0.1197	0.0718	0.0555
$\frac{Cu \cdot 95}{PO_4 \cdot 63.6}$	0	0.71	0.85	0.86

Similar results were obtained in experiments in which the process was regulated by the voltage. This method of regulating the conditions is more convenient for sampling the anode zone at various stages of the process, as a given degree of polarization may be maintained for a long time by maintenance of the required potential.

The samples were taken 10 minutes after the start of electrolysis at 0.5, 1.2, and 1.6 V.

At 0.5 V the anode polarization is low, and the anode is attacked. At 1.2 V electropolishing without gas evolution takes place. At 1.6 V evolution of gaseous oxygen begins at the anode. The results are shown in Table 4.

These results show that a mixture of mono- and disubstituted copper phosphate is formed in the anode layer irrespective of the conditions.

Changes in the electrolyte as the result of partitioning of the anode space. When the anode and cathode spaces are separated by a porous partition, the anolyte as a whole may become saturated with products of anode dissolution until they are precipitated. It may probably be assumed that in such conditions the properties of the anolyte as a whole will be analogous to the properties of the anode film formed under the usual conditions of copper electropolishing.

Therefore studies of the properties of such an anolyte may be of definite value for the determination of the properties of the anode film.

The anode space was partitioned off in the same electrolytic cell which was used for the experiments

described above, by means of a porous diaphragm made of unglazed lightly fired clay.

The anolyte volume was about 100 ml. The catholyte volume was about 200 ml.

After varying amounts of phosphates had accumulated in the anolyte, it was analyzed for copper and phosphorus. The electrical conductivity, viscosity, and specific gravity were also determined. The results are shown in Table 5.

These results show that in all the instances studied of the anodic dissolution of copper in phosphoric acid a mixture of phosphates is formed with a predominant content of the monosubstituted copper phosphate. As the copper concentration in the electrolyte increases, the phosphate composition in the anode layer changes in the direction of an increase in the disubstituted phosphate content. However, the ratio $\frac{Cu \cdot 95}{PO_4 \cdot 63.6}$ is in no instance unity, which would correspond to formation of the disubstituted phosphate. This ratio was less than unity under all experimental conditions.

The anolyte differs substantially in its properties from the general mass of electrolyte. The viscosity of the anolyte becomes more than 3 times that of the original acid. The electrical conductivity of the anolyte is halved. When the copper content of the anolyte reaches 71-72 g/liter, phosphates begin to be precipitated. This is evidently the maximum concentration (in the given conditions) of copper compounds in the original acid (s.g. 1.55).

It must be pointed out that phosphates may be precipitated from the electrolyte without partitioning of the anode space. For this it is sufficient to arrange the anode horizontally in a small depression [7].

Thus it is evident that the anolyte separated off by a porous partition is very similar in composition to the anode liquid film.

It should also be similar to it in its electrochemical properties. This view is supported by the values of the potential of copper both in the saturated anolyte, and in the anode liquid film during electrolysis. The static potential of copper in the saturated anolyte, determined by a compensation method, was found to be 0.408 V.

The static potential of a copper probe in the anode layer saturated with phosphates was found to be 0.410 V [7].

In both cases the value of the static potential remained constant with time.

DISCUSSION

During electropolishing of copper in phosphoric acid, products of anode dissolution accumulate near the anode, and the properties of these products differ from those of the original electrolyte.

The properties of the anode film change gradually as the concentration of the solution products in it increases. It must be pointed out that, in contrast to the results obtained by Batashev and Nikitin, we did not find an abrupt change in the composition of the phosphates formed in relation to the jump of the anode potential, although the electropolishing process was carried out in a variety of conditions. In all cases, both before and after the jump of the anode potential, the $\frac{Cu}{PO_4}$ ratio in the phosphates formed was less than unity, which indicates that a mixture of phosphates is formed in the anode film of electrolyte.

According to Laforgue-Kantzer, the anode film corresponds to the compound $PO_4(OH)CuH_2$. This compound may obviously be written as $CuHPO_4 \cdot H_2O$, or the hydrated disubstituted copper phosphate.

Since phosphates accumulate gradually in the anode film and the properties (viscosity, specific gravity, electrical conductivity) of this film also change gradually, the jump of potential cannot depend only on the composition of the phosphates formed. Their formation is undoubtedly reflected in the value of the electrode potential of the dissolving anode, which changes in the positive direction. Accumulation of the anode dissolution products results in further considerable anode polarization and its further dissolution by the electropolishing mechanism.

It is possible that in cases when the anode potential is sufficient for discharge of hydroxyl ions or of solvent molecules to begin, the jump of potential is associated with the formation of an oxide film on the anode surface [8].

The formation of an anode film is evidently not the determining cause of the electropolishing process, but only an accompanying, although very important, effect.

The treated surface is always inhomogeneous in the electrochemical sense, and contact with the electrolyte results in the commencement of selective dissolution of the most active regions of the surface. This process continues upon application of a potential, but this also results in a substantial redistribution of the active and passive regions, leading to increased electrochemical homogeneity of the surface and therefore to its more regular electrochemical dissolution. Accumulation of the dissolution products favors further polarization and a further increase of the electrochemical homogeneity, which is the basis of the surface leveling during anodic dissolution.

SUMMARY

1. It is shown that during electropolishing of copper in phosphoric acid copper compounds gradually accumulate in the electrolyte up to a constant value for a given ratio of the anode and cathode areas

2. It is shown that the jump of potential is not associated with the formation of trisubstituted phosphate, as a mixture of phosphates is formed at all stages in the electropolishing of copper in phosphoric acid.

3. It is shown that the anolyte isolated by means of a partition and the anode layer of electrolyte have similar physicochemical properties.

4. The suggestion is put forward that the anode film of metal dissolution products plays an auxiliary role in the electropolishing process, by favoring increased electrochemical homogeneity and therefore regularity of the electrochemical dissolution.

LITERATURE CITED

[1] P. Jaquet, Comptes rend. 202, 204 (1936); Nature, 135, 1076 (1935); Trans. Electrochem. Soc., 69, 629-655 (1936).

[2] G.S. Vozdvizhensky, Trans. S.M. Kirov Inst. Chem. Tech., Kazan, 13, 28 (1948); 14, 26 (1949); Proc. Acad. Sci. USSR, 59, 9 (1948); J. Tech. Phys., 18, 3, 403 (1948); Trans. 2nd All-Union Conf. Theoret. Appl. Electrochem., Kiev (1949); G.S. Vozdvizhensky, G.P. Dezideryev, and V.A. Dmitriev, J. Phys. Chem., 25, 5, 547 (1951); G.S. Vozdvizhensky, A.Sh. Valeev, and V.A. Dmitriev, Trans. Conf. Electrochem., Moscow (1953).

[3] P.A. Jaquet, Le polissage électrolitique des surfaces métalliques et ses applications, Paris (1948); L.Ya. Popilov, Electropolishing of Metals, State Machinery Press (1947); V.I. Layner, Electrolytic Polishing and Etching of Metals, State Machinery Press (1947); L.Ya. Popilov, Technology of Metal Electropolishing, State Machinery Press (1953).

[4] K.P. Batashev and E.N. Nikitin, J. Appl. Chem., 23, 3, 263 (1950). (T.p. 273)*

[5] K.P. Batashev, Trans. Conf. Electrochem., Moscow, p 414 (1953).

[6] D. Laforgue-Kantzer, Comptes rend., 233, 8, 547 (1951).

[7] V.A. Dmitriev, J. Appl. Chem., 27,6,37 (1954). (T.p. 833)**

[8] A.V. Fortunatov and A.V. Finkelshteyn, Proc. Acad. Sci. USSR, 90,5,823 (1953).

Received May 20, 1954.

* T.p. = C.B. Translation pagination.

** The only article by this author in Volume 27 appears in No. 8, page 891 – Publisher