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On the Mechanism of the Electrolytic Polishing of Aluminum Part 1. : On the behaviour of perchloric acid-acetic anhydride mixture

メタデータ	言語: eng 出版者: 室蘭工業大学 公開日: 2014-05-16 キーワード (Ja): キーワード (En): 作成者: 西田, 恵三 メールアドレス: 所属:
URL	http://hdl.handle.net/10258/2973

**On the Mechanism of the Electrolytic Polishing
of Aluminum Part I.
On the behaviour of perchloric acid-acetic anhydride mixture**

Keizo Nishida

Abstract

The author measured the electric conductivities, the decomposition voltages, and other properties of HClO_4 - $(\text{CH}_3\text{CO})_2\text{O}$ -electrolyte of many kinds of composition which was used for electrolytic polishing; and discussed the results and the mechanism of the phenomena.

§ 1 Introduction

In recent years, electrolytic polishing has been applied very usefully to the surface-treatment and the preliminary treatment for the disclosure of the structure of metals. Many metals (alloys) and electrolytes available are found to be useful.

Moreover, the mechanism of electrolytic polishing is partially explained on the base of the solubility of metal, the concentration-polarization of solution, and the anodic oxidation of metal.¹⁾ But the behaviour is not fully understood.

For the purpose to discuss the mechanism in detail, the author measured the anodic single potential during the current-density-bath-voltage measurement.

Dr. P. A. JACQUET says in his report as follows, "J'ai mesuré par la méthode classique le potentiel anodique, les courbes obtenues sont beaucoup plus régulières, mais elles ne présentent aucun avantage pour l'étude du phénomène et son utilisation pratique." But the details of their results are not mentioned.

For the author, however, the current-density-bath-voltage curve alone could not reveal the behaviour of anode, especially of its surface, and of the viscous substance on the anode; but of the whole both on polishing only.

Next, there are many theories that acetic anhydride is an inhibitor,

1) P. A. JACQUET: Trans. Electrochem. Soc., 69, (1936) 629.

S. TAJIMA: J. Electrochem. Assn. Japan, 13, (1945) 64; 14, (1946), 4; 41; 129; 164.

N. TAKAHASHI: Bull. Inst. Phy. Chem. Res. Japan, 22, (1943) 1; 10.

but by the author, there are also some respects which prove such a reagent to be not merely an inhibitor, and Dr. P. A. JACQUET used the solution contained as much anhydride as possible.

As to the evolution of gas in the treatment, it is very important to suggest the mechanism, which is to be reported in the next paper.

All the results obtained here are measured at 18°C.

§ 2 On the electrolyte

(a) The consideration in preparation of the electrolyte mixtures.

The reagents used are perchloric acid HClO_4 , 60% aqueous solution and pure acetic anhydride. These are mixed and named as follows:

Name of Soln.	Vol. of HClO_4 (60% aq. soln.)	Vol. of $(\text{CH}_3\text{CO})_2\text{O}$
Soln. (y)	2.5 (cc)	97.5 (cc)
Soln. (x)	5.0	95.0
Soln. (a)	10.0	90.0
Soln. (b)	20.0	80.0
Soln. (c)	30.0	70.0
Soln. (d)	40.0	60.0
Soln. (d-e)	45.0	55.0
Soln. (e)	50.0	50.0
Soln. (f)	60.0	40.0
Soln. (g)	80.0	20.0
Soln. (Q)	100.0	0.

When acetic anhydride is poured into the aqueous solution of HClO_4 , cooled, the evolution of heat and the contraction of the volume of the solution are observed. The states and the colour of the solutions in preparation and after the uses for many measurements, are summed up in Table I.

TABLE I

Name of Soln.	On mixing	Colour after mixing	After the use for many measurements, and after a long time
Soln. (y)	On mixing, it boiled partly to a certain quantity of $(\text{CH}_3\text{CO})_2\text{O}$ liquid, but more $(\text{CH}_3\text{CO})_2\text{O}$ did not, and was warmed merely. This range is between Soln.(y) and Soln. (b).	Orange	At first, the colour became deeper, and after a long time it changed dark red.
Soln. (x)		Reddish orange	At first, deeper than Soln. (y) but after a long time, it equaled to Soln. (y).
Soln. (a)		Orange, but paler than Soln. (x).	Suddenly became reddish orange, and after a long time equaled to Soln. (y).
Soln. (b)		Orange, but paler than Soln. (a).	Became more reddish, but even after a long time the colour did not change.

Name of Soln.	On mixing	Colour after mixing	After the use for many measurements, and after a long time
Soln. (c)	From Soln. (c) to Soln. (g), boiling on mixing was found partly to the last.	More paleorange of colour than the previous soln.	The colour became a little deeper than the solution before use.
Soln. (d) ~ Soln.(g)		Nearer the composition to Soln. (g), paler the colour.	

(b) The measurement of electric conductivity.

By the method of the Kohlrausch bridge, with platinum electrodes (platinized) and H type vessel, the following results are obtained. (Fig 1.)

From these results it is found that if we increase the quantity of $(CH_3CO)_2O$ the electric conductivity is decreased. Moreover, a gap is found

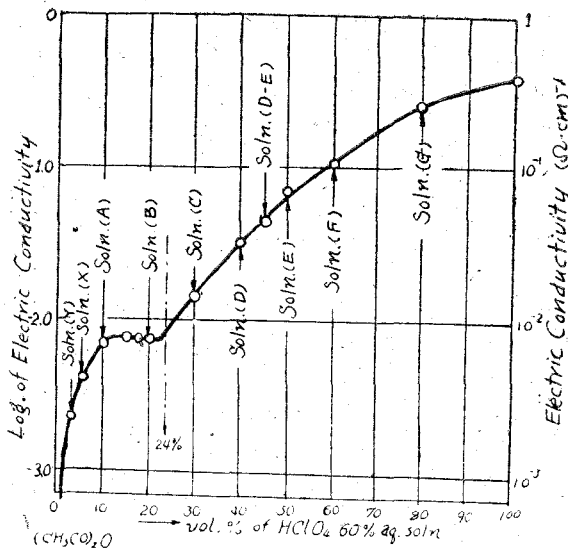


Fig. 1. Composition-Electric Conductivity Curve.

between the compositions of HClO₄ aqueous solution (10% and 20%). So the properties of the solutions of these compositions are considered to be different from other normal ones.

These phenomena are probably explained as follows: when $(CH_3CO)_2O$ is mixed with aqueous solution of HClO₄, the hydration of acetic anhydride will occur,



So the concentration of HClO₄ against free water will increase. If such a change is calculated in each solution, the composition of its constituents is indicated in Fig. 2.

This figure shows that the aqueous solution of 60% HClO₄ is perfectly

dehydrated with 76 cc. of $(\text{CH}_3\text{CO})_2\text{O}$, when the total volume of solution is 100 cc.

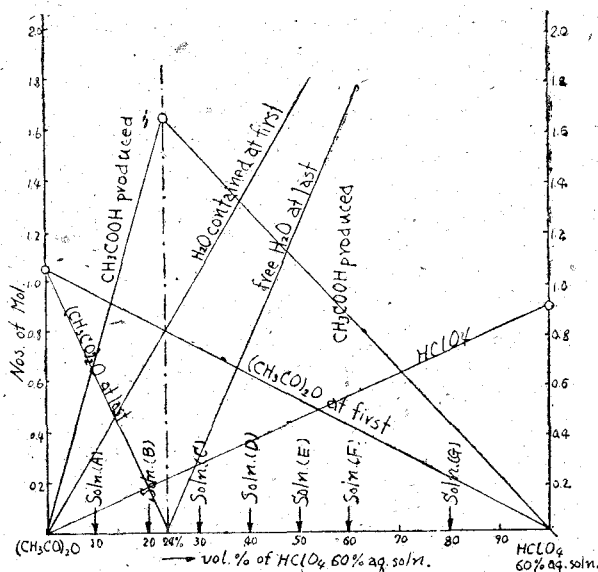
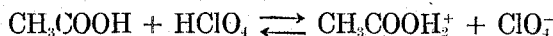
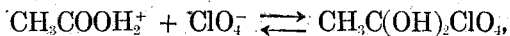


Fig. 2. Numbers of Mol of Each Constituent in 100 cc of the different Solutions at 18°C.

As shown in Table I, when the solution has less HClO_4 than that composition, it is coloured different from the other solutions when mixed. Thus the phenomenon that shows the constant value of electric conductivity between 10% and 20% of HClO_4 aqueous solution, will be understood by the following reactions:¹⁾

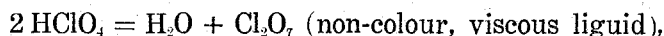


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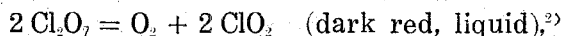


these $\text{CH}_3\text{COOH}_2^+$ and ClO_4^- ions are partly in the form of "ionpair"; then the equilibrium of the latter reaction will be maintained between Soln. (a) and Soln. (b), so the concentration of these ions will be constant and the electric conductivity will be also constant.

Moreover, with the coloration of the so-called anhydride solution HClO_4 , will be partly decomposed:



and this Cl_2O_7 will be decomposed, too,



1) I. M. KOLTOFF and A. WILLMAN: J. Am. Chem. Soc., 56, (1934) 1007.

2) G. F. GOODEVE and F. D. RICHARDSON: J. Chem. Soc. (London).

or



and these will dissolve in acetic acid.

(c) The measurement of the decomposition voltage and of the single potential of anode.

i) The measurement of the decomposition voltage of solutions.

The apparatus used is shown in Fig. 3, schematically. Anode is platinum (planed): 1cm x 1cm x 2 in area, and cathode is aluminum plate (99.8% Al): 3cm x 3cm x 2 in area. The distance between these parallel electrodes is 3.5cm.

In Fig. 3, V is voltmeter, A is ammeter, C is electrolytic bath, and E is applied electromotive force. The reason why aluminum should be used as cathode is that it is very convenient to compare the behaviour of anode at this measurement with that of the following electrolytic polishing of aluminum when the same cathode is used.

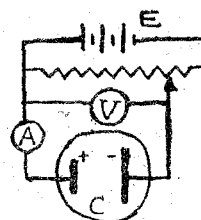


Fig. 3. The Apparatus for Measurement of Decomposition Voltage.

These results obtained are given in Fig 4. From these curves the decomposition voltage of Soln. (y) and Soln. (x) is not ascertained, but in Soln. (a) it is about 5 volts, and others are almost 4 volts.

ii) The measurement of the single electrode potential of anode.

At the same time of the measurement of i) the single electrode potential of platinum (planed) anode is obtained. By this method the values are measured immediately after the current is cut off. The time required to measure after cutting off the current is 3 to 5 seconds.

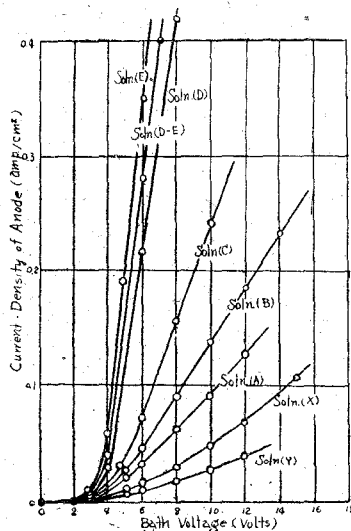
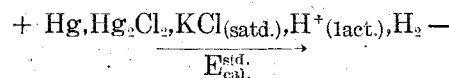


Fig. 4. Current-Density—Bath Voltage Curves.

The apparatus for the measurement is shown abbreviately in Fig.5. Anode is contacted to the end of the salt bridge which is combined to calomel cell (saturated). Then the value (E) of the single potential is for Pt; soln. The value ($E_{\text{cal.}}^{\text{std.}}$) of calomel cell is

E
 - 0.25203 volt, which is also the value of the cell:



Thus, when E is plus, this electrode corresponds to the metal which is baser than H_2 in

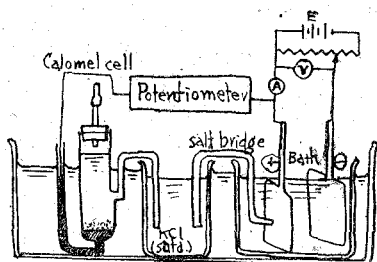


Fig. 5. The Apparatus for Measurement of Anodic Single Potential.

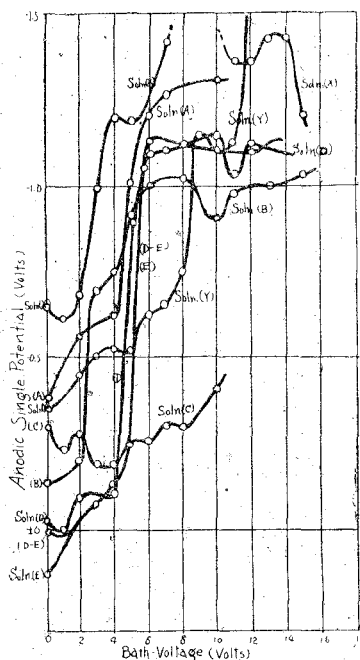


Fig. 6. Bath-Voltage-Anodic Single Potential Curves.

Near the concentration of Soln. (f) its value is maximum, and the less HClO_4 , the less the irregularity. While increasing HClO_4 than Soln. (f), this property decreases and disappears (this is the case of 60% HClO_4 aqueous solution especially).

The horizontal part of the curve of current-density is not found in Soln. (y) to Soln. (b). With Soln. (c) it appears, and as the concentration of HClO_4 increases, the range of this part increases, and reaches maximum in Soln. (f), which shows the constant value even at the voltage of 40 volts.

The value of the constant current-density increases with more of HClO_4 ,

the standard single electrode potential; and when E is minus, the electrode corresponds to the metal nobler than H_2 .

These results are shown in Fig. 6. Apparently they will ascertain the results obtained from the decomposition voltage.

From the change of curve the value (E) becomes nobler as the current increased. Moreover in Soln. (d-e) to Soln. (e) the value of the potential is constant even if the current increases. It is likely the value of the gas evolved. But the property of the gas is not determined.

§ 3 On the case of electrolytic polishing of aluminum

a) The measurement of current-density-bath-voltage in each solution.

The anode used in aluminum plate (99.8% Al). $1\text{cm} \times 1\text{cm} \times$ in area exposed, and cathode is also aluminum plate (in the same state as anode), $3\text{cm} \times 3\text{cm} \times 2$ in area exposed, and they are dipped vertically and aperted 3.5cm.

The results are summed up in Fig. 7.

The behaviour of the solution is explained as follow:

i) On the irregular change of current-density

If the concentration of HClO_4 is increased, the irregularity becomes larger,

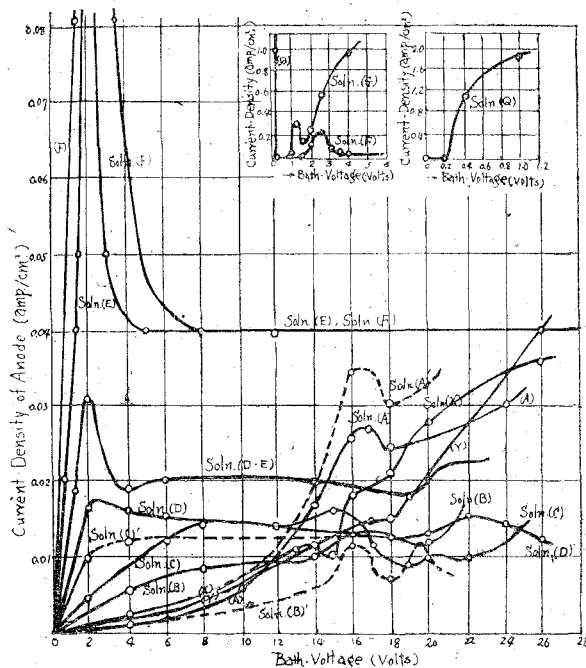


Fig. 7. Current-Density of Anode-Bath-Voltage Curves

and is 0.04 amp./cm^2 in Soln. (e) and Soln. (f). The fact that the current-density at the constant part is equal in these two solutions of different composition will show that it is likely controlled by the behaviour of anode and anolyte in these solutions, and the mechanism of the anodic phenomena is the same in each other.

With Soln. (g) and the solutions of more HClO_4 , this part is shortened, and is not found with pure 60% HClO_4 aqueous solution.

ii) The relation of the gas-evolution to the current-density.

If we increase the current-density with soln. (c) to Soln. (f), the gas is evolved more violently at first, but before the beginning of its irregularity, the gas diminishes abruptly. In the part where the current-density is constant, the gas is hardly found. These phenomena are more clearly observed in Soln. (f).

Beyond the part the current increases suddenly as the bath-voltage increases, and the gas is evolved again, which has been already seen and common in the solution of such mixtures.

In Soln. (y) to Soln. (b) the initial evolution of gas is not found.

iii) On the phenomenon of the oscillation of voltage and current.

This phenomenon has been reported by others. At the time the evolution of gas diminishes the needles of both ammeter and voltmeter begin to

oscillate. This oscillation is maximum with Soln. (e) to Soln. (f), and the current drops sooner than it rises. This change is maximum on the top of the irregularity of current-density and it becomes slowly small with voltage. Sometimes it stops awhile. These behaviours are shown in Fig. 8, which is the relation between current-density and bath-voltage. At first, when the voltage increases, current-density increase along the curve AB and at B it falls suddenly to the value C, then it oscillates between C and D. The values in the curves in Fig. 7 during the oscillation are mean values of these two limits.

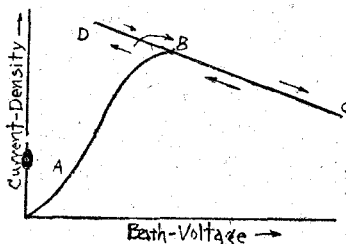


Fig. 8. The phenomenon of the Oscillation of voltage and current.

However, this phenomenon is not only confined with aluminium anode, but also it has been seen in such a case where the formic acid is oxidized anodically with platinum electrode,¹⁾

b) The measurement of bath-voltage-single potential of anode in each solution.

As shown in Fig. 9 the values are obtained with the aid of potentiometer by the same way as ii) in b) of §2, which is given in Fig. 9. The behaviour of the solution is explained as follows:

With the increase of HClO, the initial potential tends to baser state and the potential at the case of constant current-density has the same tendency as the initial one. However it must be noticed that these values are not absolute, considering from the way of measurement, and that the initial value of the potential is much affected by the condition of the surface of metal. Nevertheless these data will indicate some of the behaviour of anode. For comparison's sake, two curves of Soln. (a) and Soln. (b) are given in the figure respectively. It is most important how the potential of anode changes relatively in each solution.

From Soln. (y) to Soln. (a) the anodic potential goes to the noble state till the bath-voltage of 12 volts and then it falls suddenly to the baser state. From Soln. (b) to Soln. (c) the potential falls at first and with higher voltage it does not change greatly, but is unstable. From Soln. (d) to Soln. (f), different from Soln. (b) and Soln. (c), there is given a smooth curve, which is attributed to the stable potential of anode, after the initial change (the shiftness towards the baser state) even by this method. In Soln. (g) and pure 60% HClO, aqueous solution, such a constant part of potential is not observed.

1) E. MÜLLER and S. TANAKA: Zeit. für Electrochem., 24, (1928), 256.

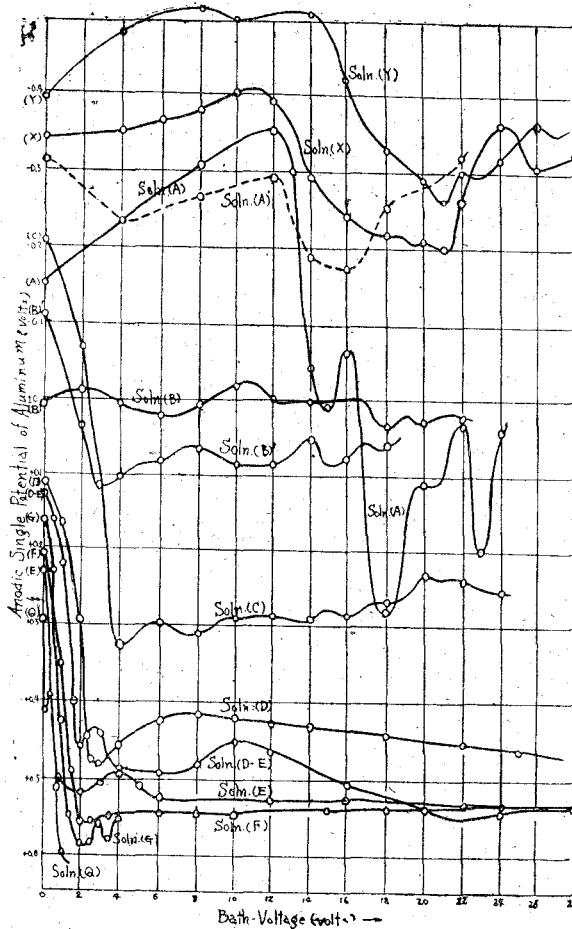


Fig. 9. Bath-Voltage -Anodic Single Potential of Aluminum Curves.

c) The consideration of the above stated phenomena.

The single potential (E) of anode for Al; soln is obtained in cutting

$$\xrightarrow{E}$$

off the current, which indicates the stable potential. So, if there is only the concentration-polarization, as seen with platinum anode, it must be $(\Delta E/\Delta V) < 0$ — where ΔE ; ΔV is the increment of the potential of anode and of bath-voltage respectively-, or the potential will tend nobler with bath-voltage in the curve. This corresponds to the primary part of the curves of Soln. (y), Soln. (x) and Soln. (a).

But if $(\Delta E/\Delta V) > 0$, probably it must be the state which indicates that the anode becomes more soluble into the solution. Strictly speaking, the surface of anode as a test-piece will become active with higher bath-

voltage and come to the different state, then the potential will be stable, which is the case of the solutions with more HClO_4 . However, it must be noticed that the value of the stable potential is baser as the concentration of HClO_4 increases.

Moreover, these behaviours of anode may be attributed to the growth of something on the surface, on the other hand, these may correspond to its flatening as seen from the brightening even in this measurement.

With Soln. (e) and Soln. (f) the stable potential of anode is remarkably constant, so the relation between anode and solution will be always constant with increasing bath-voltage. For Soln. (b) and Soln. (c) this relation will be more unstable.

JACQUEST¹⁾ and UHLIG²⁾ suggested the surface of the metal polished anodically to be the metal itself, and MOOR³⁾, TAKAHASHI⁴⁾, and TAJIMA⁵⁾ have concluded it to be covered with oxide film. But by the author the surface during the treatment may be different from that picked up. Whether the metal itself may be exposed in the solution during the process, it may be very possible that the metal itself of the surface may be covered with oxide film when picked up, and it may be determined to be oxide by the next experiments. For example, it has been found by the author that there occurs the removal of the surface film during a second process in Soln. (b) from the once polished metal.

There is another case where the oxide film will be produced on the metal and dissolved in the solution time to time. In this case the reaction of the oxide with the solution may take place partly or on the whole surface. So, even if the surface of metal may not dissolve into the solution, it may be done by the so-called scale-off.

Mr. TAJIMA concluded the existance of the oxide film by the experimental result the surface polished anodically is nobler in some solutions (for example water, NaCl aqueous solution, and etc.) than the surface of the same metal which is treated by HCl .

But, by the author, there may be oxide film on the aluminum anode even with other treatments. Especially the surface treated by other methods must have more irregularity than that of electrolytic polishing, so the potential of metal may behave as concluded above⁶⁾.

Nowadays these popular solutions of this type are in the state of "anhydride," or near the composition of Soln. (b) in this experiment. From

1) JACQUEST: loc. cit.,

2) H. H. UHLIG: Trans. Electrochem. Soc., 78, (1940), 265.

3) H. H. MOOR: Ann. der Physik. 33, (1938), 133.

4) N. TAKAHASHI: loc. cit.,

5) S. TAJIMA: loc. cit.,

6) T. TAKEI: "The Experimental Electrochemistry," (1939) Kyōritsu-Sha, Tokyo Vol. 1 p. 237.

the result of electric conductivity the favourable concentration will be always maintained in these solutions. But the results from the stable potential and the constant current-density lead to the conclusion that the solution range useful to the process will be between Soln. (b) and Soln. (f).

The reason why the solutions of higher concentration of HClO_4 have not been used, may be by the other factor, or "pitting action", which is not discussed in this paper. On this problem, it will be taken up in the next paper.

Summary

(1) The acetic acid which comes from the hydration of acetic anhydride plays a reservoir of ClO_4^- ion in the solution, so-called "non-aqueous", which corresponds to the composition of Soln. (b), and is most favorite in the process of the electrolytic polishing.

(2) But from the anodic potential and current-density as above mentioned, the composition of the electrolyte for use is between Soln. (b) and Soln. (f).

(3) And the theories of electrolytic polishing which have been reported are discussed partly.

Finally it must be mentioned that this study of mine is entirely thanks to the Grants in Aid of Scientific Research (donated by the Ministry of Education).

(Received November 1, 1945)