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Electrodeposition of Water-soluble Resin by a Constant Voltage or by Pulses[*1]

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The mechanism of deposition was investigated using maleic-linseed oil as a sample. The deposition was made by a constant voltage or by continuous pulses with high voltages, and the initial current-time relations were observed by means of a synchroscope. When we applied pulses with α/β values which were smaller than a value, the current decreased gradually after some time and a deposited film was found on the anode, but the decreases in the current was not found for a long time when the value of β was much larger than the value of α. The induction time was found from the current-time curve observed during a constant voltage deposition. These results were discussed from the standpoint that the deposited film is formed by coagulation resulted from ionic combination with hydrogen ions.

Detailed knowledge of the mechanism of the electrodeposition of water-soluble resin would be useful in enabling the coating method to be satisfactorily applied in varying circumstances.

Finn and Mell[1)] pointed out that local ionic precipitation or coagulation may be important factor in the film formation. From the results of the analyses of the deposited film, it has been made clear that the role of metal ions in deposition is minor,[2-4)] this is clear from the fact that we can obtain the deposited film on platinum plates. Tawn and Berry[5)] suggested a mechanism in which the coagulation of organic anions results from an increase in the concentration of hydrogen ions generated at the anode, but they could not support the mechanism with specific experimental results. Maeda *et al.*[3)] found that $I\cdot\tau^{1/2}$ is nearly constant and explained $I\cdot\tau^{1/2}$ as a parameter which gives a critical concentration of hydrogen ions at the anode, where I=current density and τ is the induction time on the anode potential *vs.* the time curve which is observed during a constant current deposition. Moreover, they found that the period of the induction time increases with an increase in the acid value of the sample.

From the results of many analyses of the gases given off at the anode,[6-9)] it has been clarified that the Kolbe reaction of organic anions in deposition is minor and that the principal electrode reaction during deposition is the oxygen evolution reaction.

Up to the present, many fundamental investigation related to the mechanism of the deposition have been performed at a constant current. In the case of the deposition of water-soluble resin, the current density is low, so that the anode potential for the period of induction time is of the order 1 to 2 V (*vs.* SCE). On the other hand, the practical application of the deposition of water-soluble resin to painting has been performed at a constant voltage, the values of the applied voltages ranging 50 to 200 V. It is questionable whether or not there is any essential difference in the electrode reaction between the cases of a constant current deposition and those of a constant voltage deposition.

In this report, we will describe the results observed by the use of a synchroscope in observing the electrode phenomena at a constant voltage deposition or at a continuous pulse deposition.

Experimental

Samples. The maleic-linseed oil used as the water-soluble resin was obtained by the additive reaction of maleic anhydride to linseed-oil. The reaction was performed for three hours at 200°C and for an hour at

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[*1] Electrodeposition of Water-soluble Resin. V.

1) S. R. Finn and C. C. Mell, *J. O. C. C. A.*, **41**, 219 (1964).

2) M. R. Sullivan, *J. Paint Tech.*, **38**, 424 (1966).

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4) T. Nakamura, M. Nagasawa and I. Kagawa, *J. Ind. Chem. Japan,* **70**, 2(1967).

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6) L. R. L. Brass, *J. Paint Tech.*, **38**, 493 (1966).

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230°C. During the reaction, the mixed solution was stirred mildly and kept in a nitrogen atmosphere. The mole ratio of maleic anhydride to linseed oil was 2.4 : 1. The crude maleic-linseed oil was neutralized by a potassium hydroxide solution in order to make it soluble in water after which the solution was kept in a separating funnel for a few days. After removing the unsoluble substances, we added sulfuric acid to the solution in order to coagulate the maleic-linseed oil. Then the coagulated maleic-linseed oil was dissolved in an ethylcellosolve-water solution and stirred for about ten hours.

A small quantity of carbon tetrachloride was then added to the solution. The solution was shaken for about an hour and then kept in a separating funnel for a day. The maleic-linseed oil was recovered in the carbon tetrachloride layer and the carbon tetrachloride was removed by vaporization. Finnally, maleic-linseed oil was kept for several hours at 50°C and 5 mmHg. The purification procedure after the coagulation by sulfuric acid was performed two times. The purified maleic-linseed oil was then dissolved into a potassium hydroxide solution and the solution used as a sample. The pH of the solution was adjusted only by a potassium hydroxide solution and by the maleic-linseed oil.

Apparatus. The cell was of a beaker type with two platinum plates as the cathodes. The distance between the cathodes was 5 cm, and the surface area of each cathode was 6 cm^2. The platinum anode was placed at the center of the cathodes. A bright platinum plate and wire were used as the anodes; the apparent surface areas of the platinum plate and wire were 2 and 0.31 cm^2 respectively. The platinum plate and wire were rinsed with a concentrated potassium hydroxide solution and dipped in a nitric acid solution for several minutes before each run.

A Takasago Regulated DC Power Supply GPO-50-2 was used as the potentiostat. The pulse generator used in this experiment was an Iwasaki Power Supply PS-201. The potential-time or current-time curves were observed by means of a National Synchroscope SS-5302 B.

The deposition (electrolysis) circuit is shown in Fig. 1. The bath solution was kept at 25±0.5°C.

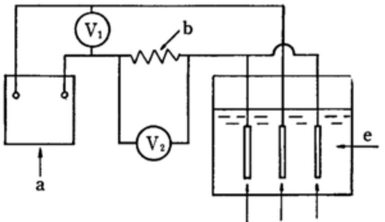

Fig. 1. Deposition circuit.

a: D.C. source, b: resistance, c: anode, d: cathode, e: bath solution, V$_1$, V$_2$ are observed by synchroscope.

Results

Deposition by Continuous Pulses. When we applied continuous pulses to the deposition cirucit, the figure shown in Fig. 2 was obtaind.

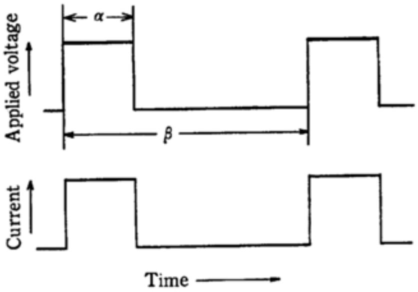

Fig. 2. Applied voltage and current curves against to time before deposited film is formed.

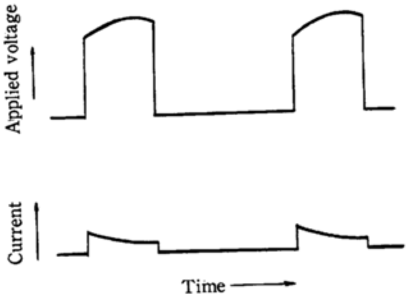

Fig. 3. Applied voltage and current curves against to time after deposited film was formed.

On the other hand, when we decreased only the value of β (see Fig. 2) while keeping the pulse width, α (see Fig. 2), constant, the figure gradually changed to the figure shown in Fig. 3.

The current decreased and the applied voltage increased. These phenomena were caused by the resistance of the deposited film on the anode. Actually, the film was found to have been deposited on the anode after the current decreased.

On the other hand, when the value of β was much larger than the value of α, the current has never been observed to decrease over a long period. These phenomena show that the film formation is not made by the direct discharge of organic anions. If the film formation is made by the direct discharge of organic anions, the current will decrease in spite of the value of β.

In order to make these phenomena clear, we investigated the effects of the current density, the pH of the bath solution, and the rate of the rotation of the electrode on the value of α/β_0, where β_0 is a value of β such that the current begins to decrease one minute after the value of β has been set at a constant value of α. The relation α and α/β_0 are shown in Table 1 at several applied potentials. The values of the applied potential and the current in Table 1. were measured before the deposited film was formed, that is, before the current decreased. The resin concentration was 5% in weight and the pH of the bath solution was 7.6. As may be seen in Table 1, the value of

α/β_0 is nearly constant in spite of the value of α at a constant applied voltage.

Using a platinum wire as the anode, we measured the relation between I and α/β_0 at various applied voltages at pH 7.5 and 8.6, where I is the current density. The results at pH 7.5 are shown in Table 2.

TABLE 1. RELATION BETWEEN α AND α/β_0

Applied voltage (V)	Current density (mA/cm²)	α (μsec)	β_0 (μsec)	α/β_0
5	33	5	19	0.26
		20	76	0.26
		50	185	0.27
		100	390	0.26
		500	1900	0.26
		2000	7600	0.26
8.5	55	1.2	8.2	0.12
		10	80	0.13
		50	400	0.13
		200	1600	0.13

Resin concentration 5% in weight, pH 7.7

TABLE 2. RELATION BETWEEN CURRENT DENSITIES AND α/β_0

Applied voltage (V)	Current density (mA/cm²)	α (μsec)	β_0 (μsec)	α/β_0
10	68	35	420	0.073
8	50	25	210	0.11
5	32	25	90	0.22
2.8	18	25	50	0.34

Resin concentration 5% in weight, pH 7.5

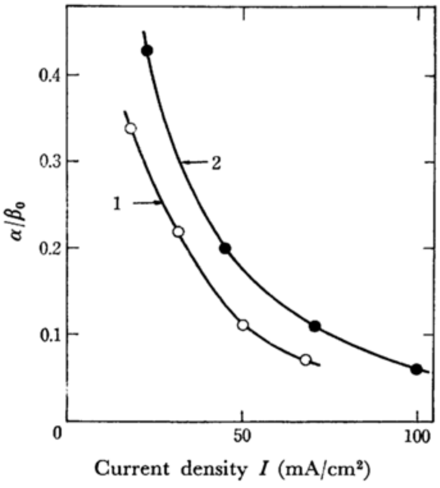

Fig. 4. α/β_0 against to current density.
pH, 1: 7.5, 2: 8.6
Resin concentration 5% in weight

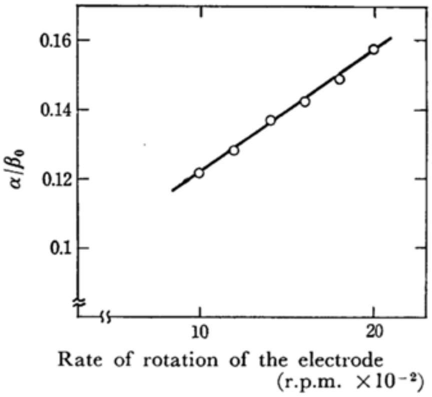

Fig. 5. Relation between α/β_0 and rate of rotation of the electrode. Resin concentration 5% in weight, pH 8.8.

Figure 4 shows the relation between I and α/β_0. α/β_0 decreases with an increase in the current densities.

Using a rotative electrode, we established the effects of the rate of the rotation of the electrode on the α/β_0 value at a constant applied voltage. The results are shown in Fig. 5. The resin concentration was 5% in weight, and the pH of the bath solution was 8.8. The observed current density was not affected by the rate of the rotation.

Constant Voltage Deposition. An induction time has been observed on the potential-time curve when the deposition was performed by a constant current density. It has been found that the values of $I\cdot\tau^{1/2}$ are nearly constant.[3,10] On the other hand, when the deposition was performed by a constant voltage with a high applied voltage, we found no induction time on the current-time curve recorded by means of an XY recorder. These findings show that the direct discharge of organic anions may occur at a constant voltage deposition. However, when the deposition is performed by a constant voltage, the initial current density is much higher than a current density at a constant current deposition. Therefore, the induction time may be considered to be very short at the constant-voltage deposition according to the relation that $I\cdot\tau^{1/2}$=constant.

Then we observed an initial current-time relation by means of a synchroscope during a constant voltage deposition.

When the bath solution was a buffer solution composed of a 1/15 M Na_2HPO_4 solution (160 cc) and a 1/15 M KH_2PO_4 solution (10 cc), we obtained the current-time curve shown in Fig. 6. When the bath solution was a buffer solution including 5% (by weight) of maleic-linseed oil, the results shown in Fig. 6 were obtained. Curve 2 decreases with time more rapidly than Curve 1 and has some

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10) Y. Nakamura, H. Kaneko, N. Higashiyama and H. Nozaki, *Denki-Kagaku,* **36,** 217 (1968).

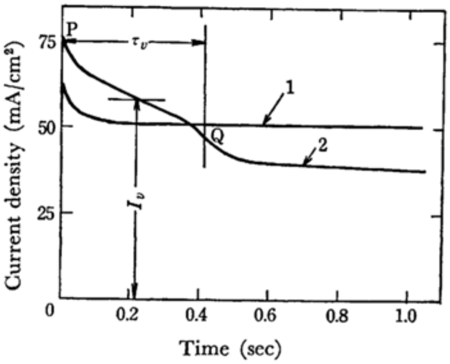

Fig. 6. Current density-time curves.
1: buffer solution (1/15 M Na_2HPO_4 solution 160 cc and 1/15 M KH_2PO_4 solution 10 cc)
2: buffer solution including 5% in weight of maleic-linseed oil.

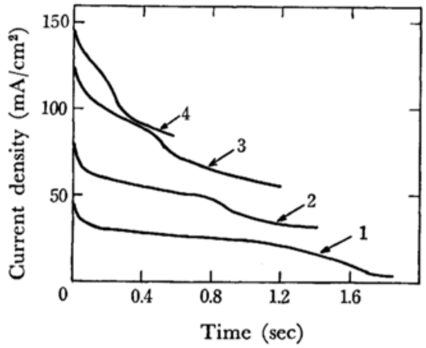

Fig. 7. Current density-time curves at various applied voltages.
Applied voltage, 1 : 5, 2 : 8, 3 : 12 4 : 15 (v)
Resin concentration 5% in weight, pH 7.7.

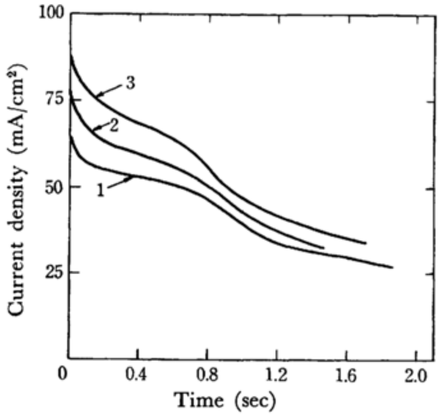

Fig. 8. Current density-time curves at various pHs.
pH, 1: 7.7, 2: 8.4, 3: 8.8
Resin concentration 5% in weight
Applied voltage 8 (V)

induction time. The period of time from P to Q is the induction time; we named that time τ_v. τ_v corresponds to the induction time τ (see Fig. 10) in the constant-current deposition.

Current-time curves observed at various applied voltages are shown in Fig. 7, where the resin concentration was 5% (by weight) and where the pH of the solution was kept at 7.7. The current densities for the induction time increase weight an increase in the applied voltages, but the length of the induction time decreases with an increase in the applied voltages.

The current-time curves observed at various pHs of the solution are shown in Fig. 8. The applied voltage was kept at 8 V, and the resin concentration was kept at 5% (by weight). The current densities for the induction time increase with an increase in the pHs of the solution.

Discussion

Deposition by Continuous Pulses. We consider that the decrease in the current, *i. e.*, the deposition of organic anions, was affected by only the value of β when α was constant. The anode reaction during the current flow must be the electrolysis of water as follows:

$$4H_2O = 4H^+ + 2O_2 + 4e \tag{1}$$

$$4OH^- = 2H_2O + O_2 + 4e \tag{2}$$

Hydroxide ions are in equilibrium as follows:

$$H^+ + OH^- = H_2O \tag{3}$$

Thus, the concentration of hydrogen ions will increase near the anode surface. However, hydrogen ions will decrease upon diffusion and the chemical reaction shown in Eq (4):

$$R(COO^-)_n + H^+ = R(COO^-)_{n-1}COOH \tag{4}$$

This reaction leads to the coagulation of organic anions, *i.e.*, deposition.

The schematic representation of the change in the concentration of hydrogen ions against the time at the anode is given in Fig. 9 (a) and (b). Figure 9(a) shows current *vs.* time curves, while Fig. 9(b) shows a speculative representation of the concentration of hydrogen ions *vs.* time curves at the anode surface. If the current is like Curve 1, that is to say, if β is sufficiently long in comparison

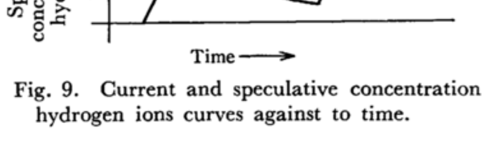

Fig. 9. Current and speculative concentration of hydrogen ions curves against to time.

with α, the diffusion time of the hydrogen ions is so long compared with the generation time of hydrogen ions that the increase in hydrogen ions at the anode surface remains very small.

However, if the β value is decreased while the value of α is kept constant, the decrease in the number of hydrogen ions by diffusion is restrained compared with the generation of the ions, so that the hydrogen ion concentration will increase rapidly at the anode. Thus, when the β value is decreased while the value of α is kept constant, the current may decrease as a result of the coagulation of organic anions.

When the applied voltages are increased, the current densities increase. If the value of α is kept constant, the rate of the generation of hydrogen ions at the anode increases with an increase in the current densities, in accordance with Faraday's law. Therefore, the period of time until hydrogen ion concentration increases to a certain critical concentration will decrease with an increase in the current densities. Thus, the value of α/β_0 decreases with an increase in the applied voltages, *i. e.*, the current densities.

As the sample became soluble in water at about pH 7 and as the pH of the neutralization point was about 9 to 10, carboxyls of this sample are not neutralized completely below pH 9. Therefore, as the number of dissociated organic anions per molecule increases with an increase in the pHs, the number of hydrogen ions required to neutralize dissociated anions will increase with an increase in the pHs of the bath solution. Consequently, if the value of α and the current density are kept constant, the value of β_0 must decrease with an increase in the pHs of the solution.

If the solution is stirred, the diffusion layer of the hydrogen ions will decrease. As a result, the diffusion rate of hydrogen ions from the anode to the bulk solution increases upon an increase in the rate of the rotation of the electrode. Therefore, the increase rate of the hydrogen ion concentration at the anode during electrolysis will decrease with an increase in the rate of the rotation of the electrode when the other conditions are kept constant. Thus, if the value of α and the current density are kept constant, the value of β_0 must decrease, *i. e.*, α/β_0 increases with an increase in the rate of the rotation of the electrode.

Constant Current Deposition. In order to compare these findings with the results on constant-current deposition, we measured the relation between I and $I\cdot\tau^{1/2}$ in the constant-current deposition using the same sample as we used in studying the constant-voltage deposition: the results are shown in Fig. 10. $I\cdot\tau^{1/2}$ increases with an increase in the current densities. We calculated the values of $I_v\cdot\tau_v^{1/2}$ from the results of the constant-voltage deposition (see Fig. 7): they are shown in Fig. 10, where I_v is the arithmetic mean value of the current density at induction time τ_v (see Fig. 6). As is shown in Fig. 10, the values of $I_v\cdot\tau_v^{1/2}$ are comparable to the values of $I\cdot\tau^{1/2}$. The values of $I_v\cdot\tau_v^{1/2}$, calculated from Fig. 8, are shown against the pHs of the bath solution in Fig. 11. $I_v\cdot\tau_v^{1/2}$ increases with an increase in the pHs of the bath solution. These results can be explained by the same consideration as we used to describe the effects of the pHs of the solution on the α/β_0 in continuous-pulse deposition. Thus, the film formation in constant-voltage deposition can also be explained in terms of the coagulation of organic anions.

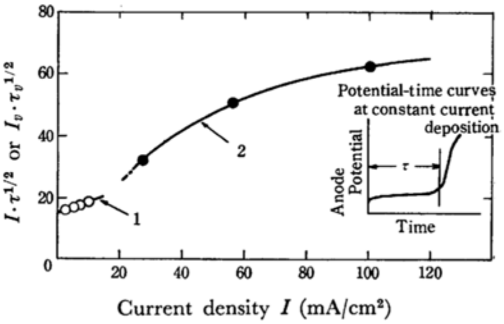

Fig. 10. Relation between $I\cdot\tau^{1/2}$ or $I_v\cdot\tau_v^{1/2}$ and current density.

1: $I\cdot\tau^{1/2}$, 2: $I_v\tau_v^{1/2}$, resin concentration 5% in weight, pH 7.7.

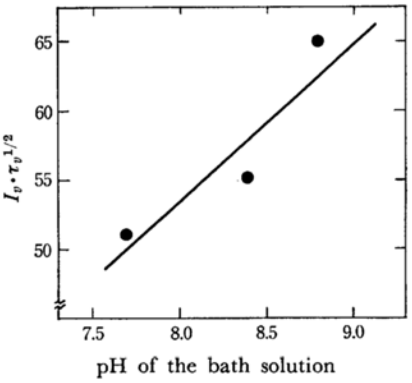

Fig. 11. Relation between $I_v\cdot\tau_v^{1/2}$ and pH.