Technical Paper

Mechanism of Electrophoretic Deposition of Water-soluble Resin I. Study of Critical Time, T_c^*

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With cationic acrylic copolymer resin, the critical time, T_c , was measured by the galvanostatic method. Especially, the effects of the degree of neutralization and the concentration of the resin on T_c were investigated in detail. The relation between T_c and I , $I^2T_c = K_1 + K_2I^2$, was theoretically derived on the basis of the idea that the deposited film is formed by flocculation of resin. The validity of the theory was confirmed by the experimental results. The mechanism was much better understood by the detailed theoretical discussion. The resin reacts with the electrolyzed products of water, and flocculates. The flocculated resin is carried onto the electrode surface by electrophoresis, and forms deposited film. The initial electrolyte concentration is influenced by the degree of neutralization and the concentration of the resin. The change of the initial electrolyte concentration has strong effect on the critical time. In the higher current density region, the electrophoresis of resin has strong effect on the critical time.

1 Introduction

In electrophoretic deposition of water-soluble resin, it is well known that there is a time lag, called the critical time, T_c , between the beginning of electrophoresis and the actual deposition. T_c may be interpreted as the time necessary for building of the atmosphere for the film formation. So, the study of the origin of T_c means that of the mechanism of electrophoretic deposition itself.

The mechanism of electrophoretic deposition has been studied by a number of authors^{1)~3)}. Hamaker⁴⁾, Hill⁵⁾, and Overbeek⁶⁾ studied T_c in relation to the stability of colloids in non-aqueous suspensions. Koelmans and Overbeek⁷⁾ interpreted T_c as the time required to build up a critical electrolyte concentration. Maeda et al.⁸⁾ applied the interpretation by Koelmans and Overbeek to the electrophoretic deposition of water-soluble resin. With water-soluble resin, the electrolytes accumulated on the electrode surface are electrolyzed products of water, that

is, H^+ ion at the anode and OH^- ion at the cathode. They derived the relation, $I\sqrt{T_c} = K$ (constant), between T_c and current density, I . Their basic idea, that deposited film is formed by flocculation of resin, will form the starting point for the present paper.

In our previous paper⁹⁾, taking into consideration of the re-dissolution of the once flocculated resin, we derived the relation, $I^2T_c = K_1 + K_2I^2$ (K_1, K_2 : constant). The relation is found to agree well with experimental results. The main purpose of the present paper is to elucidate the more precise mechanism through investigation of the effect of the resin concentration and the degree of neutralization of resin on T_c .

2 Experiment

2.1 Sample

In case of an anionic water-soluble resin, the resin may react with metal ion generated by anodic dissolution^{9), 10)}. To eliminate this reaction, a cationic water-soluble resin was used in the present work.

The cationic resin was synthesized by Shinto Paint Co., Ltd. through the following way: 17.5 parts of styrene, 35 parts of glycidyl methacrylate, and 35 parts of 2-ethylhexyl acrylate were

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copolymerized in isopropyl alcohol. Azobisisobutyronitrile was used as the polymerization initiator. The resulting copolymer was modified with 12.5 parts of di-*n*-propylamine. The resin was made water-soluble by neutralizing with acetic acid. The molecular weight determined by the end group analysis was about 800.

2.2 Experimental method

It is well known that electrode potential (vs. S.C.E.) increases rapidly, when the actual deposition begins⁷⁾. Utilizing this phenomenon, the critical time, T_c , was measured by the galvanostatic method. Fig. 1 shows the schematic

Fig. 1 Schematic diagram of experimental apparatus

1: Cell, 2: Anode, 3: Cathode, 4: Luggin capillary, 5: Sample solution, 6: Salt bridge, 7: Saturated potassium chloride solution, 8: Saturated calomel electrode, 9: Two pen recorder, 10: Galvanometer, 11: Voltage regulator, 12: DC power supply, 13: Resistance box

diagram of the experimental apparatus. A steel plate electroplated with Cu-Ni-Cr (1cm×1cm) was used as the cathode, and a carbon plate as the anode. All the measurements were made at $25 \pm 0.1^\circ\text{C}$ without any agitation. After each measurement, the solution was agitated to make a homogeneous state. After 2 or 3 measurements, the solution was changed with the new solution to avoid any aging effect. For each experiment, the most probable value was determined by the mean of 4 or 5 measurement values. The relative error was within $\pm 5\%$.

3 Theory

3.1 Relation between T_c and I

It is generally admitted that aqueous solution of water-soluble copolymer used for electrophoretic coating is not a true solution but a colloidal

solution^{9),11)}. So, we derive the relation between T_c and I according to the following model; colloidal particles react with the electrolyzed products of water at the electrode, and flocculate. The flocculated colloidal particles are carried onto the electrode surface by electrophoresis. They cover the electrode surface and form deposited film.

At first, it is assumed that the electric current is faradaic, and the generated electrolyte is taken away from the electrode surface only by diffusion. The electrolyte concentration, C , accumulated on the electrode surface is obtained by solving Fick's diffusion equation

$$\frac{\partial C(x, T)}{\partial T} = D \frac{\partial^2 C(x, T)}{\partial x^2} \quad (1)$$

with the following conditions

$$\text{initial condition } C(x, 0) = C_0 \quad (2)$$

$$\text{boundary condition } C(\infty, T) = C_0 \quad (3)$$

$$-D \left(\frac{\partial C}{\partial x} \right)_{x=0} = \frac{I}{F} \quad (4)$$

where F is Faraday constant, and I is the current density. C_0 and D are the initial concentration and diffusion constant of the electrolyte, respectively. From eqs. (1), (2), (3), and (4),

$$C(x, T) = C_0 + \frac{2I\sqrt{T}}{F\sqrt{\pi D}} \exp\left(-\frac{x^2}{4DT}\right) - \frac{xI}{FD} \left\{ 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{DT}}\right) \right\} \quad (5)$$

In order to discuss the reaction on the electrode surface, we assume the presence of the layer (thickness l) on the electrode surface and l satisfies the condition, $l^2/4DT \ll 1$. The resin is accumulated in the layer by electrophoresis. The electrolyte concentration accumulated in the layer is given approximately by

$$C(T) \cong C_0 + \frac{2I\sqrt{T}}{F\sqrt{\pi D}} \quad (6)$$

On the other hand, the critical electrolyte concentration, C_c , is given by⁸⁾

$$C_c = C_i + C_r \quad (7)$$

where C_i is the electrolyte concentration, above which the once flocculated resin does not redissolve. C_r is the concentration of the electrolyte which reacts with the accumulated resin. C_r should be proportional to the quantity of the accumulated resin. So, C_r is assumed to be given by

$$C_r = \alpha D_n \frac{Y}{l} = \alpha D_n \frac{\rho u I_0 T}{l} \quad (8)$$

where α is a constant which will depend on the resin, Y_0 is the quantity of the resin accumulated on a unit area of the electrode surface during time, T , and σ is the specific resistance of the solution. D_n , ρ , and u are the degree of neutralization, concentration, and mobility of the resin, respectively. The time, T_c' , required to build up the concentration, C_c , is calculated from eqs. (6), (7), and (8) as follows

$$\begin{aligned} C_c &= C_i + C_r = C_i + \alpha D_n \frac{\rho u I \sigma T_c'}{l} \\ &= C_0 + \frac{2I \sqrt{T_c'}}{F \sqrt{\pi D}} \end{aligned} \quad (9)$$

Assuming $(T_c' - T_i)/T_i \ll 1$, where $T_i = (C_i - C_0)^2 F^2 \pi^2 D / 4I^2$ is the time elapsed before C_i is built up,

$$T_c' \approx T_i = \frac{(C_i - C_0)^2 F^2 \pi^2 D}{4I^2} \quad (10)$$

If C_c is built up, change of the electrode potential is not yet observed till the electrode is covered by the deposit up to some extent¹¹. Therefore, the critical time, T_c , observed experimentally, is

$$T_c = \frac{Y_0}{\rho_f u_f \sigma_f I} + T_c' \quad (11)$$

where Y_0 is the minimum quantity of deposit to be observed, and σ_f is the specific resistance of the accumulated layer of the resin. ρ_f and u_f are the concentration and mobility of the flocculated resin, respectively. ρ_f is assumed to be equal to the resin concentration accumulated during T_c' .

$$\rho_f = \frac{\rho u \sigma I T_c'}{l} \quad (12)$$

We obtain the following eq. (13) from eqs. (10), (11), and (12).

$$\begin{aligned} T_c &= \frac{(C_i - C_0)^2 F^2 \pi^2 D}{4I^2} + \frac{4Y_0 l}{\rho u \sigma u_f \sigma_f (C_i - C_0)^2 F^2 \pi^2 D} \\ &= K_1 I^{-2} + K_2 \end{aligned} \quad (13)$$

$$I^2 T_c = K_1 + K_2 I^2 \quad (14)$$

If $K_2 \rightarrow 0$, eq. (14) is equivalent to the equation derived by Maeda et al¹⁷.

3.2 Discussions

In this section, we will discuss the effect of D_n and ρ on T_c . The mobility of the resin is related to the Zeta potential by Smoluchowski's equation,

$$u = \frac{\epsilon \zeta}{4\pi \eta} \quad (15)$$

where ϵ is the dielectric constant of the medium, ζ is the Zeta potential of the resin, and η is the viscosity of the medium. We assume that the Zeta potential is equal or proportional to the surface potential, Ψ_s . Ψ_s should be determined by the number of the ionized end groups of the resin. Finally, u is proportional to D_n . As C_0 is decreased with the increase of the concentration of acetic acid added to the solution to make the resin water-soluble, $(C_i - C_0)$ is increased with the increase of the concentration of acetic acid. The concentration of acetic acid is determined from the given values of D_n and ρ . So, $(C_i - C_0)$ is expressed as a function of D_n and ρ . Next, we consider about the specific resistance of the solution, σ . When the deposited film is kept in the solution after stopping electrophoresis, the film re-dissolves completely⁹. If the resin discharges directly at electrode surface, the deposited film may not re-dissolve. So, we consider that the discharge of the resin at electrode is a negligible reaction. In case of anionic resin, Brass⁹ and others^{21, 22, 12} reported the same result as ours about the discharge of the resin. Therefore, the resin does not contribute appreciably to the electric current and the electric conductivity may depend only on the concentration of acetic acid. The electric conductivity is expressed as a sum of the contribution from each ionic species as follows

$$\kappa = \left(\sum_i |Z_i| n_i \lambda_i \right) = \frac{1}{\sigma} \quad (16)$$

where κ is the specific conductance of a solution, Z_i is the electric charge of the i -th ion, n_i is the concentration of the i -th ion, and λ_i is the ionic equivalent conductance of the i -th ion. The concentration of acetic acid added to the solution is proportional to D_n and ρ . So, σ is inversely proportional to D_n and ρ .

It is generally known that the water-soluble resin flocculates at a certain degree of neutralization. Therefore, the flocculated resin, which exists on the electrode surface, should have a constant degree of neutralization independently of D_n and ρ . Thus, u_f is not affected by D_n and ρ . Furthermore, we neglect the change of the electrolyte concentration on the electrode surface after C_c is built up. When C_c is built up, the electrolyte concentration on the elec-

Table 1 Effect of ρ and D_n on different variables

	ρ	D_n	u	σ	$(C_i - C_o)$	K_1	K_2
A	Constant	Increase	D_n	D_n^{-1}	Increase, $f(D_n)$	$f^2(D_n)$	$f^{-2}(D_n)$
B	Increase	Constant	Constant	ρ^{-1}	Increase, $F(\rho)$	$F^2(\rho)$	$F^{-2}(\rho)$

$f(D_n)$: Function of D_n , $F(\rho)$: Function of ρ

trode surface is equal to C_f . So, σ_i is not affected by D_n and ρ .

Table 1 shows the result discussed above. Applied the relation, shown in Table 1, to eq. (13), we obtain the following equations,

In case of A,

$$T_c = K_1' f^2(D_n) I^{-2} + K_2' f^{-2}(D_n) \quad (17)$$

$K_1', K_2' : \text{constant}$

In case of B,

$$T_c = K_1'' F^2(\rho) I^{-2} + K_2'' f^{-2}(\rho) \quad (18)$$

$K_1'', K_2'' : \text{constant}$

where $f(D_n)$ is a function of D_n and $F(\rho)$ is a function of ρ . Eqs. (17) and (18) indicate that both D_n and ρ affect T_c in the similar manner. Considering that K_1 and K_2 are an order of magnitude of 10^{-5} , and 1, respectively⁹⁾, the values of T_c were calculated by eq. (13) for different values of I using appropriate

values of K_1 and K_2 . The calculated values are shown in Fig. 2 as a plot of $T_c^{-1/2}$ vs. I . It shows the expected effects of D_n and ρ on T_c .

4 Comparison with Experimental Results

Fig. 3 shows the effect of D_n on T_c as a plot of $T_c^{-1/2}$ vs. I , and Fig. 4 is a partially expanded one of Fig. 3. Fig. 5 shows the effect of ρ on T_c as a plot of $T_c^{-1/2}$ vs. I , and Fig. 6 is a partially expanded one of Fig. 5. In Figs. 3, 4, 5, and 6, it is found that, in the lower current density region, T_c becomes long with increasing of D_n or ρ . On the contrary, in the higher current density region, T_c becomes short the with increase D_n or ρ . It is

Fig. 2 Expected effect of D_n and ρ on T_c , calculated with eqs. (17) and (18)

1 : $K_1 = k_1$, $K_2 = k_2$, 2 : $K_1 = 2k_1$, $K_2 = 1/2 k_2$
 3 : $K_1 = 4k_1$, $K_2 = 1/4 k_2$
 k_1, k_2 : Appropriate constant

Fig. 3 Effect of D_n on T_c
 Lines show the calculated values with eq. (13)

1 : $\triangle$, $\rho = 5.0 \text{ wt}\%$, $D_n = 55\%$, 2 : $\circ$, $\rho = 5.0 \text{ wt}\%$, $D_n = 62\%$, 3 : $\times$, $\rho = 5.1 \text{ wt}\%$, $D_n = 68\%$, 4 : $\bullet$, $\rho = 5.1 \text{ wt}\%$, $D_n = 96\%$

Fig. 4 Effect of D_n on T_c
Lines show the calculated values with eq. (13)

1: $\triangle$, $\rho=5.0$ wt%, $D_n=55\%$, 2: $\circ$, $\rho=5.0$ wt%, $D_n=62\%$, 3: $\times$, $\rho=5.1$ wt%, $D_n=68\%$, 4: $\bullet$, $\rho=5.1$ wt%, $D_n=96\%$

Fig. 6 Effect of ρ on T_c
Lines show the calculated values with eq. (13)

1: $\triangle$, $\rho=3.0$ wt%, $D_n=71\%$, 2: $\times$, $\rho=5.1$ wt%, $D_n=68\%$, 3: $\circ$, $\rho=7.9$ wt%, $D_n=69\%$, 4: $\bullet$, $\rho=10.0$ wt%, $D_n=71\%$

Fig. 5 Effect of ρ on T_c
Lines show the calculated values with eq. (13)

1: $\triangle$, $\rho=3.0$ wt%, $D_n=71\%$, 2: $\times$, $\rho=5.1$ wt%, $D_n=68\%$, 3: $\circ$, $\rho=7.9$ wt%, $D_n=69\%$, 4: $\bullet$, $\rho=10.0$ wt%, $D_n=71\%$

noted that both D_n and ρ give similar effects on T_c . Comparing the experimental results with Fig. 2, the theoretical expectation is found to agree well with the experimental results. Fitting for the experimental results shown in Figs. 3 and 5, the values of K_1 and K_2 were determined. The calculated values of T_c with eq. (13) are shown in Figs. 3, 4, 5, and 6. Figs. 7 and 8 show the values of K_1 and K_2 as functions of D_n and ρ , respectively. The effects of D_n and ρ on K_1 and K_2 agree qualitatively with the expectation in eqs. (17) and (18), respectively. In Fig. 8, the discrepancy is seen only for 3 wt% solution. For the 3 wt% solution, the concentration of acetic acid is about 0.02 mol/l. So, the discrepancy may be due to the change of the degree of dissociation of acetic acid^{13), 14)}.

In eq. (13), the value of $K_1 I^{-2}$ decreases with increasing current density. If $K_1 I^{-2}$ is comparable with K_2 , the value of T_c will depend strongly on K_2 . K_2 indicates the time required to deposit the minimum quantity to be observed. Therefore, in the higher current density region, T_c is affected by the electrophoresis of the resin through K_2 .

Fig. 7 Effect of degree of neutralization on K_1 and K_2

Resin concentration is about 5 wt%

Fig. 8 Effect of resin concentration on K_1 and K_2

Degree of neutralization of resin is about 70%

5 Conclusion

The mechanism of the electrophoretic deposition of water-soluble resin was much better understood by the present detailed theoretical discussion. The validity of the theory was con-

firmed by general agreement of the theoretical expectation with behavior of T_c .

In consequence, the following are concluded.

1. The equation, $I^2 T_c = K_1 + K_2 I^2$, derived theoretically, agrees well with the experimental results, and can explain qualitatively the effects of the degree of neutralization and the concentration of the resin on T_c .

2. On the electrode surface, the resin reacts with electrolyzed products of water, and flocculates. The flocculated resin is carried onto the electrode surface by electrophoresis. It covers the electrode surface and forms deposited film.

3. The initial electrolyte concentration is influenced by the degree of neutralization and the concentration of the resin. The change of the initial electrolyte concentration has strong effect on the critical time, T_c .

4. In the higher current density region, the electrophoresis of the resin has strong effect on T_c .

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