Note

The Mechanism of Electrophoretic Deposition of Water-soluble Resin

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With acrylic copolymer resin, the critical time T_c were measured by the galvanostatic method. T_c is defined as the time elapsed before the actual deposition begins after starting electrophoresis.

The resin was made water-soluble by neutralization with acetic acid, and had positive charge in an aqueous solution. The molecular weight determined by the end group analysis was about 800. All measurements were made at $25 \pm 0.1^\circ\text{C}$ without any agitation. A steel plate electroplated with Cu-Ni-Cr ($1\text{cm} \times 1\text{cm}$) was used as the cathode and a carbon plate as the anode.

Fig. 1 shows the plot of $T_c^{-1/2}$ vs. I (current density).

Fig. 1 Critical time vs. current density
Solid lines show the calculated values with eq. (8)

A : 5 wt%, degree of neutralization 68%, pH 5.0

B : 3 wt%, degree of neutralization 71%, pH 5.0

Temperature 25°C

Koelmans and Overbeek¹⁾ interpreted T_c as the time required to build up a critical electrolyte concentration in case of the electrophoretic deposition of the suspensions. Maeda et al.²⁾ applied their interpretation into the electrophoretic deposition of water-soluble resin, and explained the relation between T_c and I . With water-soluble resin, the electrolyte accumulated on the electrode surface are the electrolyzed products of water, that is, H^+ ion at the anode and OH^- ion at the cathode. Their basic idea, *i.e.*, that the deposited film is formed by flocculation of resin, will form the basis for this paper. They obtained the relation between T_c and I shown by eq. (1)²⁾.

$$I\sqrt{T_c} = K \quad K: \text{constant} \quad (1)$$

Eq. (1) cannot explain the experimental results shown in Fig. 1. Nakamura et al.³⁾ also pointed out the discrepancy between eq. (1) and the experimental results on T_c in case of the deposition of maleic-linseed oil.

Fig. 2 shows the variation of the weight of deposit as a function of the time after stopping electrophoresis.

Fig. 2 Relation between the weight of deposit remained on the electrode and time after switching-off

5 wt%, degree of neutralization 69%, pH 5.0, Temperature 25°C , Current density 0.5 mA/cm^2 , Deposition time 360 sec

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sis. This phenomenon may be interpreted as follow: The resin reacts with OH^- ion and flocculates. But the once flocculated resin re-dissolves when enough OH^- ions which make an atmosphere are lost by diffusion.

Taking this phenomenon into consideration, we derived the relation between T_c and I . At first, we consider the critical electrolyte concentration, C_c , as shown by eq. (2).

$$C_c = C_i + C_r \quad (2)$$

Where C_i is the electrolyte concentration, above which the once flocculated resin does not re-dissolve. C_r is the electrolyte concentration which reacts with the resin. C_r should be in proportion to the quantity of the accumulated resin. So, we denote C_r as eq. (3).

$$C_r = \alpha D_n Y / l = \alpha D_n \rho u I \sigma T / l \quad (3)$$

where α is a constant which will depend on the resin, Y is the quantity of the resin accumulated on the electrode surface (unit area) during time T , l is the thickness of the accumulated layer, 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.

Secondly, it is assumed that I is faradaic current, and the generated electrolyte is taken away from the electrode surface only by diffusion. Eq. (4), derived from the diffusion equation, shows the electrolyte concentration, C , accumulated on the electrode surface (unit area) as a function of I and T .³⁾

$$C = C_o + 2I\sqrt{T}/F\sqrt{\pi D} \quad (4)$$

where F is faraday constant. C_o and D are the initial concentration and diffusion constant of the electrolyte, respectively. We can obtain the time, T_c' , required to build up the concentration, C_c , from eqs. (2), (3), and (4),

$$C_c = C_i + C_r = C_i + \alpha D_n \rho u I \sigma T_c' / l = C_o + 2I\sqrt{T_c'} / F\sqrt{\pi D} \quad (5)$$

Assuming $(T_c' - T_i)/T_i \ll 1$, where $T_i = (C_i - C_o)^2 F^2 \pi D / 4 I^2$,

$$T_c' \cong T_i + 2AT_i^{3/2} + \dots \cong T_i \quad (5')$$

where $A = \alpha D_n \rho u \sigma F \sqrt{\pi D} / 2l$

If C_c is build up, change of the electrode potential is not yet observed before the electrode is covered by the deposit to some extent^{2),5)}. Therefore, the critical time T_c , observed experimentally, is

$$T_c = Y_o / \rho_f u_f \sigma_f I + T_c' \quad (6)$$

where Y_o 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' .

$$\rho_f = \rho u \sigma I T_c' / l \quad (7)$$

We obtain the following eq. (8) from eqs. (5'), (6) and (7).

$$I^2 T_c = K_1 + K_2 I^2 \quad K_1, K_2: \text{constant} \quad (8)$$

Fitting for the experimental results in Fig. 1, K_1 and K_2 are determined to be 41.6×10^{-6} and 0.35 for 5 wt% solution, respectively, and 55.6×10^{-6} and 1.0 for 3 wt% solution, respectively. The calculated values are shown in Fig. 1, and found to agree well with the experimental results.

Details are to be published elsewhere.

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