

## Chemical deposition coating onto anodized aluminum plate from anionic polymer emulsion containing sodium citrate

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**Abstract:** The chemical deposition coating from an anionic acrylic copolymer emulsion containing sodium citrate onto anodized aluminum plates was repeated. In the absence of sodium citrate, the coating thickness decreased with the number of repeated use of the emulsion bath. However, in the presence of sodium citrate or potassium sodium tartrate, it was maintained to be constant. The reason for attainment of the desirable results was discussed.

**Key words:** Coating – chemical deposition – polymer emulsion – anodized aluminum – sodium citrate

### Introduction

We have been carrying out a series of investigations on a new type of polymer coating process using anionic polymer emulsion of which pH value is below about 3 onto an anodized aluminum plate [1–7]. We named it chemical deposition. The polymer coating obtained without applying an electric current cannot be removed by washing; it is a coating similar to a widely known electrodeposition coating process.

In the previous article [2], we pointed out a problem in that the amount of polymer deposited decreased with a repeated use of the emulsion bath. This is a serious disadvantage in applying this coating process industrially. In this article, we will try to resolve this problem.

### Experimental

#### Materials

Ethyl acrylate (EA) and methyl methacrylate (MMA) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Potassium persulfate

(KPS) of analytical grade was used. Sodium citrate and potassium sodium tartrate of reagent grade were used. Deionized water was distilled with a Pyrex distillator.

#### Emulsion

EA-MMA (60/40, molar ratio) copolymer emulsion was prepared by emulsifier-free emulsion copolymerization at 70 °C for 24 h under the conditions listed in Table 1. The emulsion was deionized by passing it through a column packed with the anion-exchange resin (Amberlite IRA-400).

#### Anodization of aluminum

An aluminum plate (JIS-A-1050) of 100  $\mu\text{m}$  in thickness was cut into small pieces (8  $\times$  21 cm), degreased with alkaline solution, and washed with distilled water. The pieces were then anodized at 20 °C for 30 min at a current density of 1 A/dm<sup>2</sup> in a bath consisting of 15 wt% sulfuric acid and 5.6 wt% aluminum sulfate, washed with distilled water, and dried under reduced pressure at room temperature.

\*) Part CXL of the series "Studies on Suspension and Emulsion"

Table 1. Preparation of EA-MMA (60/40, molar ratio) copolymer emulsion by emulsifier-free emulsion polymerization<sup>a)</sup>

| Ingredient             |      |     |
|------------------------|------|-----|
| EA <sup>b)</sup>       | (g)  | 96  |
| MMA <sup>c)</sup>      | (g)  | 64  |
| KPS <sup>d)</sup>      | (mg) | 800 |
| Water                  | (g)  | 600 |
| Diameter <sup>e)</sup> | (nm) | 540 |
| Tg <sup>f)</sup>       | (°C) | 15  |

<sup>a)</sup> Nitrogen, 70 °C, 24 h. <sup>b)</sup> Ethyl acrylate. <sup>c)</sup> Methyl methacrylate. <sup>d)</sup> Potassium persulfate. <sup>e)</sup> Measured by dynamic light scattering method. <sup>f)</sup> Calculated from Fox's equation:  $1/(T_g + 273) = W_e/249 + W_m/378$ ;  $W_e$  and  $W_m$  are weight fraction of EA and MMA, respectively

### Chemical deposition

The anodized aluminum plate (8 × 2.5 cm) was immersed without stirring in 50 ml of 10 wt% emulsion (immersion area, 20 cm<sup>2</sup>) at pH 2.5 or 3.7 for 10 min at 30 °C. The pH was adjusted with HCl. The coated plate was dried at 40 °C for 1 h and then at room temperature under reduced pressure. The amount of polymer deposited was measured by gravimetric method with a microbalance.

### Amount of dissolved aluminum ion

The amounts of aluminum ion contained in the film and dissolved in the emulsion bath were determined by aluminon absorption spectrophotometry [2] or isotachophoretic analysis.

### Measurement of $\zeta$ -potential

$\zeta$ -potentials of EA-MMA copolymer particles were measured in 10 mM KCl solutions of pH 5 containing various concentrations of sodium citrate using electrophoretic light scattering (Otsuka Electronics LEZA-600).

## Results and discussion

Figure 1 shows the variations of the amounts of polymer deposited (*Pd* value) and of the pH values with the number of the repeated use of the emulsion baths of which initial pH values were 2.5 and

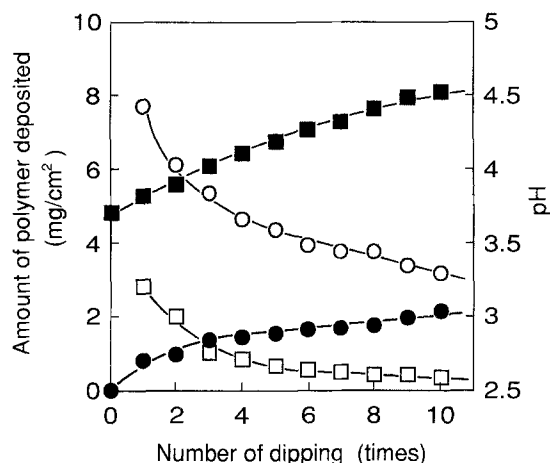


Fig. 1. Variations of the amounts of polymer deposited (○, □) and of pH values (●, ■) with the repeated use of the emulsion baths at 30 °C for 10 min. Initial pH with HCl: ○, ●, 2.5; □, ■, 3.7. Initial polymer solid, 10 wt%

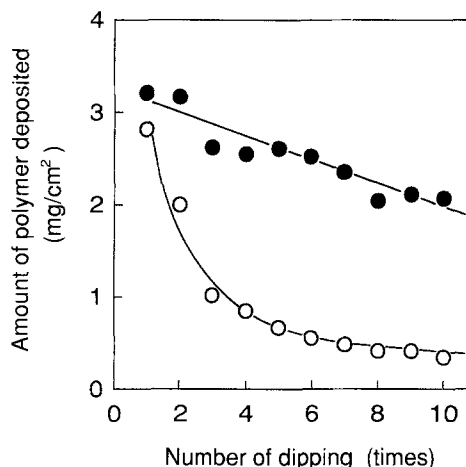


Fig. 2. Variations of the amounts of polymer deposited with the repeated use of emulsion baths at 30 °C for 10 min. Initial polymer solid, 10 wt%. ○: the pH was adjusted to 3.7 only in the first dipping. ●: the pH was adjusted to 3.7 in every dipping

3.7. In both cases, the *Pd* values decreased and the pH values increased with the number of the repeated use. This is a serious problem for applying this process industrially, as already described in the introduction.

In the previous article [2], it was shown that *Pd* value decreased with an increase in the initial pH

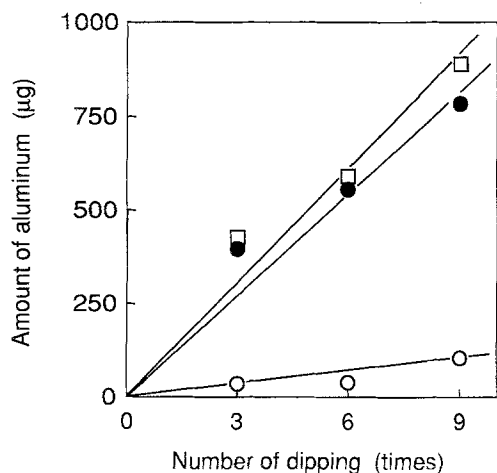


Fig. 3. Increases in the amount of aluminum accumulated in the emulsion bath (●) and in deposited polymer layers (○) with the repeated use of the emulsion bath (50 ml). Each dipping was always conducted at 30 °C for 10 min. Initial polymer solid, 10 wt%. The concentration of sodium citrate, 0.5 mM. □ indicates the total amount of aluminum dissolved

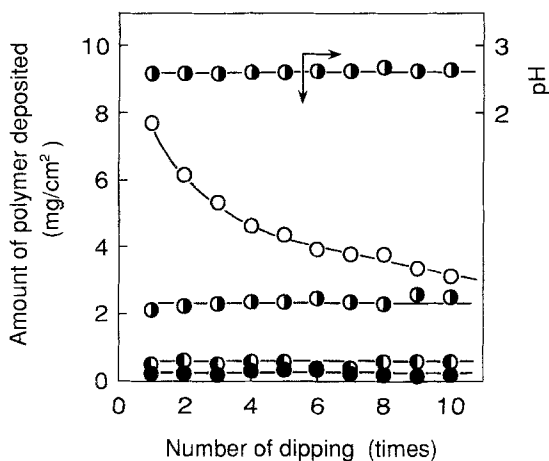


Fig. 4. Effects of the concentration of sodium citrate on the variations of the amount of polymer deposited and of the pH value with the repeated use of the emulsion baths at 30 °C for 10 min: Sodium citrate (mM): ○, 0; ●, 0.5; ◐, 3.0; ◑, 30. Initial pH, 2.5. Initial polymer solid, 10 wt%

value and this was derived from the reduction of solubility of aluminum ion from the anodized aluminum plate. Therefore, in order to suppress the decrease in the  $Pd$  value with the repeated use, the pH of the emulsion bath was always readjusted to 3.7 just before each dipping.

Figure 2 shows the results. The readjustment of the pH to 3.7 just before each dipping tends to

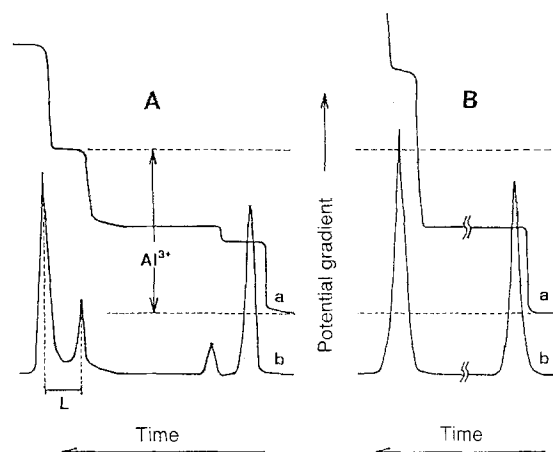


Fig. 5. Typical isotachopherograms of aluminum ion in the absence (A)/presence (B) of sodium citrate. a) Potential gradient curve. b) Differential curve

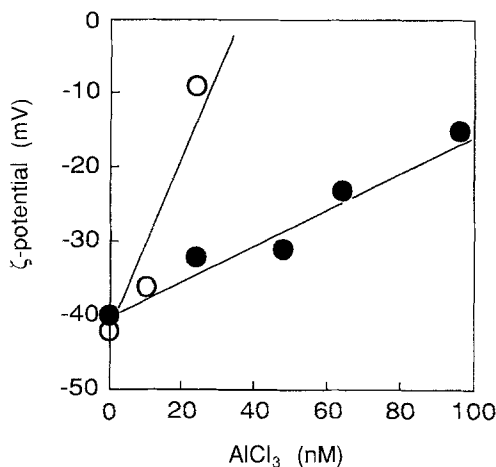


Fig. 6. Effect of the concentrations of AlCl<sub>3</sub> on ζ-potentials of EA-MMA (60/40, molar ratio) copolymer particles in 10 mM KCl solution of pH 5 (with HCl) in the absence (○)/presence (●, 5.0 nM) of sodium citrate

suppress the decrease in the  $Pd$  value with the repeated use, but it was not complete. This result was accord with that obtained at pH 2.5 [2]. In the previous article [2], it was also shown that a certain amount of aluminum ion dissolved from the plates accumulated in the emulsion bath with every dipping. As shown in Fig. 3, the amount of aluminum ion accumulated in the emulsion bath

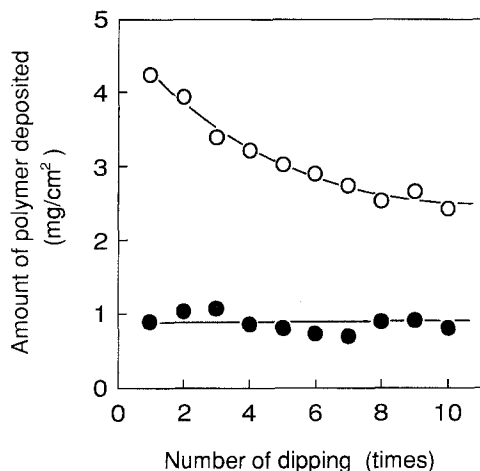


Fig. 7. Effect of the concentration of potassium sodium tartrate on the variation of the amount of polymer deposited with the repeated use of the emulsion bath at 30°C for 10 min: Potassium sodium tartrate (mM): ○, 1.0; ●, 10. Initial pH, 2.5. Initial polymer solid, 10 wt%

increased with the number of the repeated use. Only a part of aluminum ion was contained in the deposited polymer layer. Therefore, we tried to repeat the chemical deposition using the emulsion containing sodium citrate, which is known as a masking agent of  $\text{Al}^{3+}$ .

Figure 4 shows the effects of the concentration of sodium citrate on the variations of  $Pd$  value and pH value with the repeated use of the emulsion bath of which initial pH was 2.5. As will be seen, the purpose was clearly attained. That is, the decrease in  $Pd$  value with the repeated use was completely suppressed, though the  $Pd$  value decreased with an increase in the concentration of sodium citrate. The  $Pd$  value of 2 mg/cm<sup>2</sup> obtained in the presence of 0.5 mM sodium citrate gives a sufficient coating thickness to be used industrially. The pH value also remained constant.

Figure 5 shows a typical isotachopherogram of aluminum ion in the presence/absence of sodium citrate. The peak due to  $\text{Al}^{3+}$  which was observed in the absence of sodium citrate disappeared in the presence of sodium citrate. This indicates that the  $\text{Al}^{3+}$  was masked by sodium citrate.

Figure 6 shows the effect of the concentrations of  $\text{AlCl}_3$  on  $\zeta$ -potentials of EA-MMA copolymer

particles. In the absence of sodium citrate, the  $\zeta$ -potentials markedly decreased with an increase in the  $\text{Al}^{3+}$  concentration. Such a decrease of  $\zeta$ -potential should cause the marked drop in the movement of the particles toward the plate surface. On the other hand, in the presence of 5 mM sodium citrate the decrease was gentle.

Figure 7 shows the variation of  $Pd$  value with the repeated use of the emulsion bath containing potassium sodium tartrate, which is also known as a masking agent of  $\text{Al}^{3+}$ . Initial pH was 2.5. As will be seen, potassium sodium tartrate gave a result similar to that of sodium citrate.

From the above results, it is concluded that the anionic acrylic copolymer emulsion containing a small amount of masking agent for  $\text{Al}^{3+}$ , such as sodium citrate and potassium sodium tartrate, can be used repeatedly for the chemical deposition coating onto the anodized aluminum plate.

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