

# The Study of Twice Electrodeposition Coating. I. Topcoat Acrylic Resin–Primer: Epoxy Resin with Anticorrosion and Weather Resistance Performances

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**ABSTRACT:** The twice electrodeposition (ED) coating is defined as that by which the primer was coated on the metallic material by ED, then the topcoat was coated on the wet, uncured primer by ED again. It can be observed by the distinction of deposition yield and the change of current density during each process. The main object of this method is to improve anticorrosion and weather resistance of coating film simultaneously. Comparing the physical and chemical properties, it was found that the film obtained by the twice ED coating has superior weather resistance to the one-coat electrodeposited film formed by a coemulsion. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 233–240, 1997

## INTRODUCTION

Generally, resins used for the matrix of electrocoating include epoxy resin,<sup>1–4</sup> acrylic resin,<sup>5–7</sup> their copolymer,<sup>8–9</sup> and polyurethane resin.<sup>10</sup> Because of good anticorrosion and adhesion properties, epoxy resin is usually used as the primer in the automobile. On the contrary, acrylic resin used as the topcoat has the properties of good glossiness and weather resistance. Recently, the one-coat electrodeposited film containing epoxy and acrylic resin has been reported.<sup>11–13</sup> It was found that the method can be improved the properties of the deposited film.<sup>14,15</sup> Since the compatibility of resins in the coemulsion and the difference of the deposition rate of each resin may be occurred, the resin composition of film after continuous electrodeposition is not the same as the original coemulsion. Therefore, the reappearance of properties cannot be controlled correctly.

In this study, the secondary ED coating was

used for coating the acrylic resin film upon the wet, uncured film of tertiary amine–epoxy resin adduct to form the likely double-layer film. The purpose of this method is to make sure that the required characteristics can appear in the correct level, that is, the glossiness and weather resistance in the surface level (topcoat) and the anticorrosion and adhesion in the base level (primer).

The above-mentioned tertiary amine–epoxy resin adduct was prepared by reacting diglycidyl ether of bisphenol A (DGEBA) already grafted by the blocked diisocyanate compound, with *N*-methyl ethanol amine. Meanwhile, the acrylic resin was synthesized by the radical copolymerization of styrene, *n*-butyl acrylate, 2-hydroxy ethyl methacrylate, *N*-(*n*-butoxy methyl) acrylamid, and *N,N*-dimethyl amino ethyl methacrylate. Neutralization of these resins is accomplished by reacting all of the amino groups in the matrix with an organic acid, followed by dispersing to prepare the cationic emulsion.

The basic electrochemical properties of each emulsion were investigated first. Then, the distinction of deposition yield and the change of current density were measured to be approved the possibility of twice ED coating. In addition, the

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physical and chemical properties of one-coat film electrically deposited by a coemulsion containing the above resins were also observed for comparison.

## EXPERIMENTAL

### Material

All agents are used as received. The epoxy resin is Epon 1004 (Shell Co. USA) having the equivalent weight of per epoxy group of 900–1000. The cross-linking agent and blocking agent are toluene diisocyanate (TDI; 2,4/2,6 mix.) and 2-ethyl hexanol (2EH), respectively. *N*-methyl ethanol amine (MEA) is used as ring-opening, and the neutralizer is acetic acid.

The acrylic resin was prepared by monomers, including styrene (St), *n*-butyl acrylate (BA), 2-hydroxy ethyl methacrylate (HEMA), *N*-(*n*-butoxy methyl) acrylamide (NBMA), and *N,N*-dimethyl amine ethyl methacrylate (DMAEMA); and the neutralizer is lactic acid. Ethylene glycol mono-butyl ether (BCS) is used as the coalescing solvent. The initiator is AIBN (2,2'-azobisisobutyronitrile).

### Syntheses

#### Tertiary Amine–Epoxy Resin Adduct (Resin T)

First, 2EH–half-blocked TDI was prepared by charging 75.86 g (0.43 mol) TDI into a suitable reactor vessel with an electric stirrer under a nitrogen blanket. Then, 56.68 g (0.436 mol) 2EH was added slowly to the vessel and kept the reaction temperature under 18°C. Upon completion of the addition, the temperature of mixture was held at 40°C for another 1 h.

Two hundred grams of Epon 1004 and 400 mL toluene were charged into a suitable reactor vessel with stirrer and water remover and heated to the reflux temperature for removing azeotropically any water present. The reaction mixture was cooled to 80°C, followed by the addition of 2EH–half-blocked TDI under a nitrogen blanket. After the addition was completely charged, the mixture was held at this temperature for an additional 3 h. Then, 15.79 g (0.21 mol) MEA was added slowly to the mixture for ring-opening reaction. This step was kept at 80–90°C for 3 h. Finally, the tertiary amine–epoxy resin adduct (Resin T) was obtained when toluene was removed from the product by reduced pressure distillation.

#### Acrylic Resin (Resin A)

Into a reactor equipped with condenser, stirrer, thermometer, and dropping funnel 150 g BCS were charged and heated to 80°C. Then, a mixture of 48 g (0.46 mol) St, 100 g (0.78 mol) BA, 40 g (0.308 mol) HEMA, 80 g (0.512 mol) NBMA, 16 g (0.1 mol) DMAEMA, and 3.4 g AIBN was added to the reactor over a period of 3 h. The reaction was held at 100–110°C for additional 3 h. The final nonvolatile of the mixture was 66.5 wt %. All reaction equations are shown in Scheme 1.

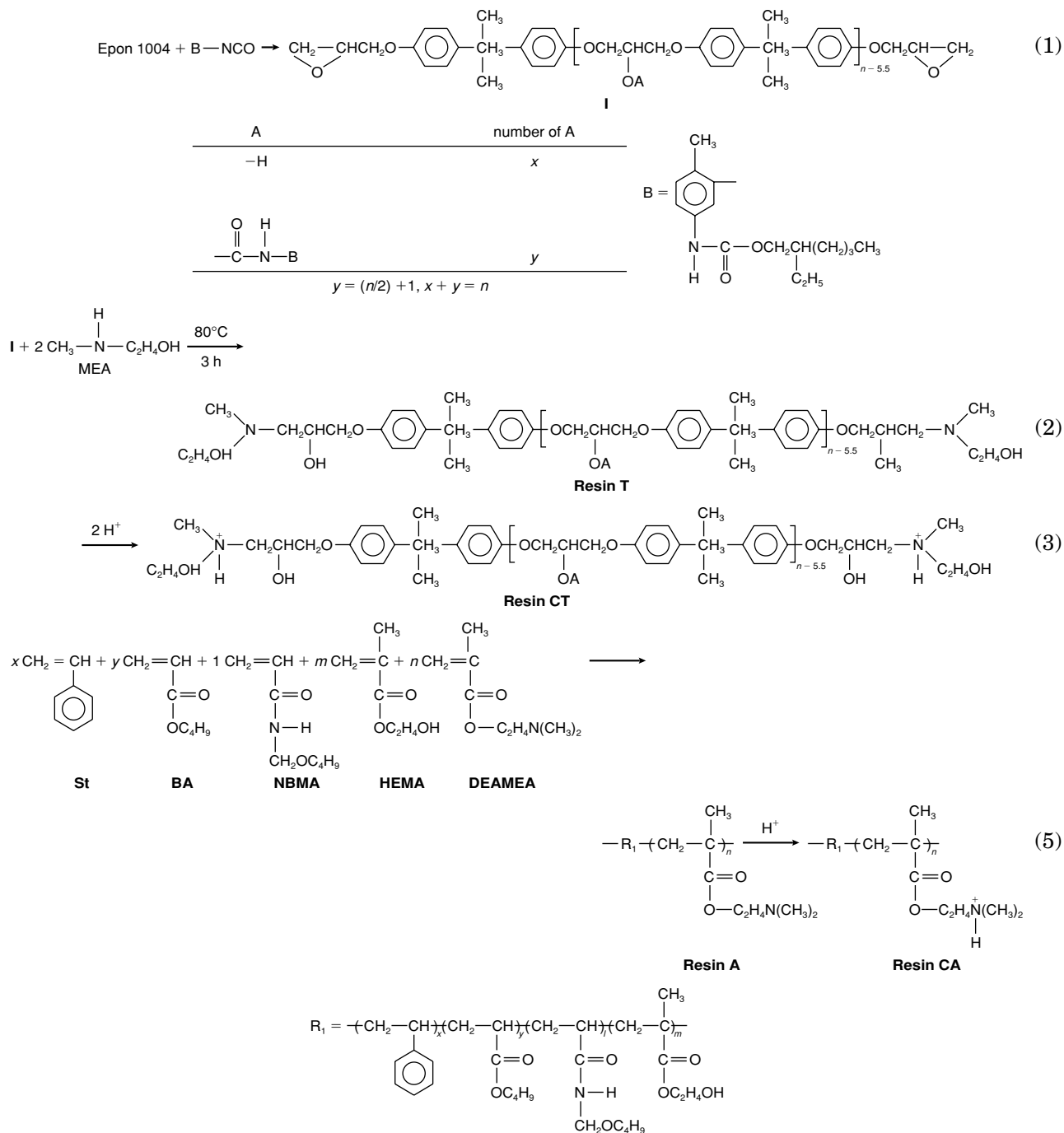
#### Preparation of Emulsion for Electrodeposition

The electrodepositable emulsion of resin T was prepared by charging 30 g of resin T into a suitable vessel with stirrer and heated to the soft point, followed by adding 15 g of BCS to the vessel and mixing completely. Then, a calculated amount of acetic acid was added for 100% neutralization to form the cationic resin T, referred to as resin CT. After the mixture was cooled to room temperature, 255 g of deionized water was added slowly, and the mixture was stirred completely to form the stable, electrodepositable emulsion CT having the resin concentration of 10 wt % and BCS content of 5 wt %.

In addition, emulsion CA was prepared by fully neutralizing 45 g of resin A with lactic acid to form the cationic resin A, referred to as resin CA, and then dispersing this resin CA with 255 g of deionized water. The resin concentration and BCS content of emulsion are also 10 and 5 wt %, respectively.

#### Twice Electrodeposition Coating

A piece of aluminum plate diving into two parts having the same surface area ( $A \text{ cm}^2$ ) and weight ( $W_0 \text{ mg}$ ) is completely immersed into emulsion CT and then connected with cathode of a direct current (DC) power supplier. Two stainless strips are used as anode and located each side of the aluminum plate in the bath. When a fixed voltage is applied, ED coating begins, and the resin is continuously deposited on the surface of the aluminum plate during the assigned time. After completion, the film-contained plate is removed from the bath and rinsed to obtain wet primer. One part of the aluminum plate is then immersed into emulsion CA for the secondary ED coating. The process is same as that mentioned above. Finally, these plates bake at 180°C for 30 min. Now,



Scheme 1

the weight of the part only containing the primer is  $W_1$  and the weight of another part proceeding twice ED coating is  $W_2$ . Thus, the deposition yield ( $\text{mg}/\text{cm}^2$ ) of primer is  $(W_1 - W_0)/A$  and the total deposition yield of final film is  $(W_2 - W_0)/A$ . The difference of both is the deposition yield of the secondary ED coating.

## RESULT AND DISCUSSION

### Electrochemical Properties of Each Emulsion

Under the following conditions, a stable emulsion CT and emulsion CA can be obtained. These conditions are 100% neutralization, 10 wt % resin

**Table I** Electrical Characteristics of Emulsions CT and CA

| Emulsion    | Electrical Characteristics |                         |                        |
|-------------|----------------------------|-------------------------|------------------------|
|             | pH                         | Conductivity<br>(mS/cm) | Rupture<br>Voltage (V) |
| Emulsion CT | 4.5                        | 0.56                    | > 420 <sup>a</sup>     |
| Emulsion CA | 3.1                        | 0.59                    | 390                    |

<sup>a</sup> The maximum output voltage of the power supplier can be supplied in our laboratory.

concentration, and 5 wt % BCS content in the emulsion. The electrochemical properties of emulsion CT and emulsion CA are shown in Table I. It is found that pH of emulsion CT is slightly higher than that of emulsion CA, but the bath conductivity of both emulsions are close. Moreover, the rupture voltage,<sup>16</sup> which occurs during deposition at high voltage and is usually ascribed merely to gas evolution from the electrolysis of water, is actually caused by electric discharge, as shown in Table I. As a result, the rupture voltage of emulsion CT is higher than that of emulsion CA and both are higher than 390 volts. However, this result indicates that as the applied voltage is below 200 volts, the defect of deposited film will never occur due to the rupture voltage.

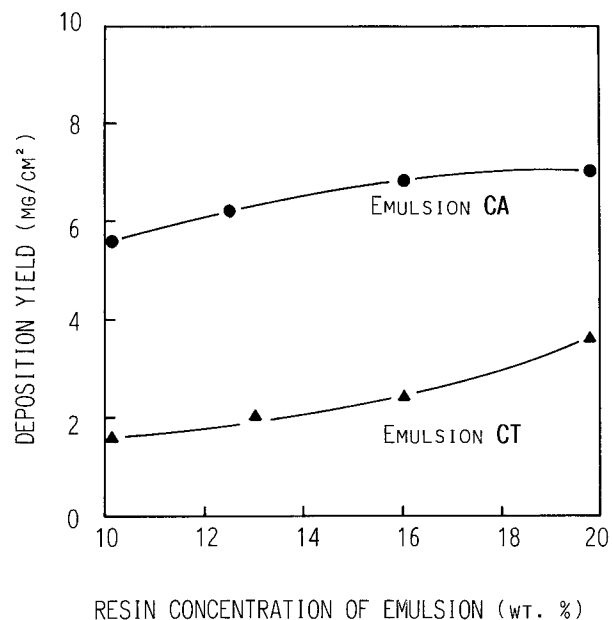
For ED coating, the thickness of film is directly affected by the resin concentration of emulsion, the deposition time, and the applied voltage. Hereafter, the thickness of film is replaced by the deposition yield (mg/cm<sup>2</sup>) in the sequential discussion. For the same emulsion under the same applied voltage, the deposition yield of film increases with the increase of resin concentration of its emulsion, as shown in Figure 1. The result is caused by the increase of the ionized resin particles in the emulsion at the higher resin concentration; but if the resin concentration is too high, it creates the problem of viscosity and makes the electrodeposition properties unusual. Consequently, the suitable resin concentration of emulsion is about 10–20 wt %. In addition, it is shown that the deposition yield of emulsion CA is always higher than that of emulsion CT at the same resin concentration.

Figure 2 shows the effect of deposition time on the deposition yield. It appears that the deposition yield increases with the increment of deposition time and finally tends to a limitation. The result obtained indicates that the film-forming rate becomes diminishing and finally balances to

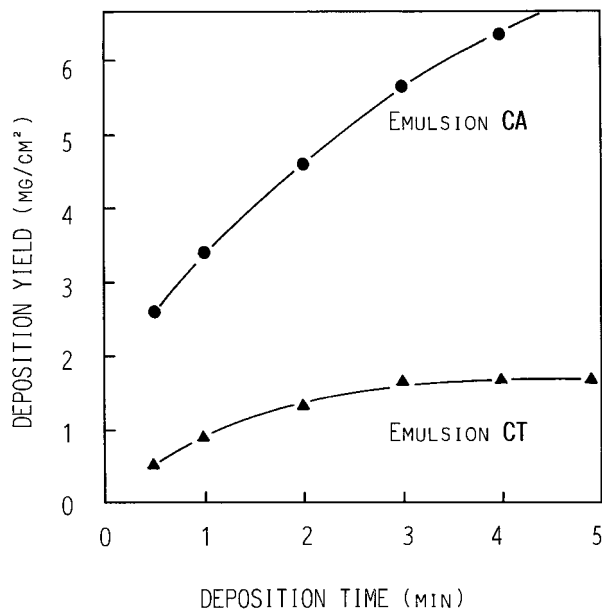
the redissolution rate of the deposited film so that the deposition yield increases to a limitation. On the other hand, the electric insulation of the polymeric film increases when the film grows up during ED coating. Moreover, the deposition yield of emulsion CA is higher than that of emulsion CT at the same applied voltage and deposition time.

In general, the higher the applied voltage, the more potential is gained in the system. Thus, the more thickness of film can be formed. Figure 3 shows the relationship between the applied voltage and the deposition yield at the same deposition time. The results follow the above explanation, but the increment tendency of emulsion CT is not apparent.

Simultaneously, the change of current density with time during ED coating is observed, as shown in Figure 4. It was found that the maximum current density occurs at the beginning, which accounts for the fastest deposition rate of resin at this time. The current density, then, decreases immediately due to the growth of the resinous film. Finally, it reduces to a minimum. Pierce et al.<sup>17</sup> reported that the area under the current density can represent the deposition yield. Consequently, the order of the deposition yield is emulsion CA > emulsion CT because the order of area under the curve in Figure 4 is emulsion CA > emulsion CT. The above result is the same as that shown in Figure 2. On the other

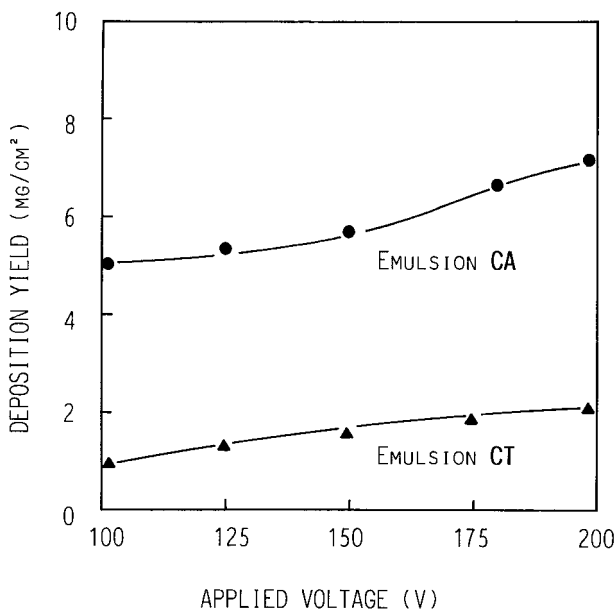


**Figure 1** The effect of resin concentration of emulsion on deposition yield: applied voltage, 150 V; deposition time, 3 min.

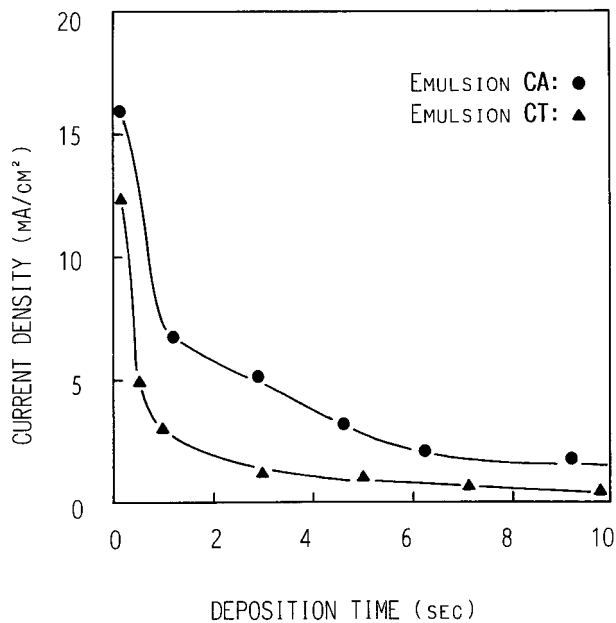


**Figure 2** The effect of deposition time on deposition yield: resin concentration of emulsion, 10 wt %; applied voltage, 150 V.

hand, the order of residual current density is emulsion CA > emulsion CT. It means that the electric resistance between electrodes (i.e., deposited film plus emulsion bath) in the emulsion CA is smaller than that of the emulsion CT bath. The result obtained indicated that the acrylic resin-



**Figure 3** The effect of applied voltage on deposition yield: resin concentration of emulsion, 10 wt %; deposition time, 3 min.



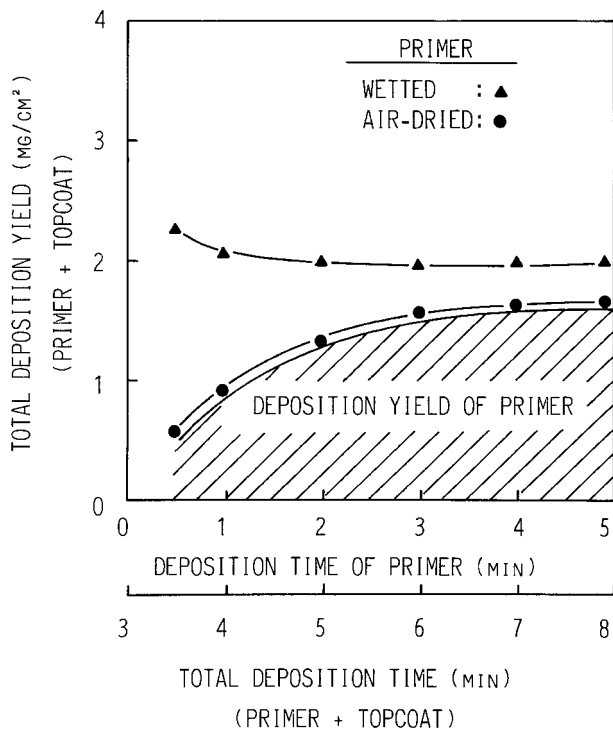
**Figure 4** The change of current density with time during primer electrodeposition: applied voltage, 150 V; resin concentration of emulsion, 10 wt %.

type wet film has better electrical conductivity than the epoxy resin-type wet film.

So far, the discussions are concerned with the basic properties of each emulsion. It concludes that emulsion CA can get the higher deposition yield than emulsion CT; meanwhile, its wet film has better electric insulation.

### Twice Electrodeposition Coating

Now, the twice ED coating formed by emulsion CT and emulsion CA is investigated. First, a series of different deposition yield (i.e., different thickness) of emulsion CT, referred as the primer, were electrically deposited on the metallic substrate; then the film formed by emulsion CA, referred as the topcoat, was deposited on the wet primer by the secondary (topcoat) ED coating. The possibility of twice ED coating can be approved by measuring the difference of deposition yield between the primer and final film (primer + topcoat); the results are shown in Figure 5. From the difference between the total deposition yield (▲) and the deposition yield of primer (shadow), it is shown that the secondary ED coating can truly occur when the primer keeps wet; and its deposition yield stays below 1.70 mg/cm<sup>2</sup>. The deposition yield of the topcoat decreases with the increase of the deposition yield of the primer because the



**Figure 5** The relationships between deposition time and deposition yield of twice electrodeposition coating. The primer (shaded area) is deposited by emulsion CT at different deposition times; the topcoat is deposited by emulsion CA at constant deposition time (3 min): applied voltage, 150 V; resin concentration of emulsion, 10 wt %.

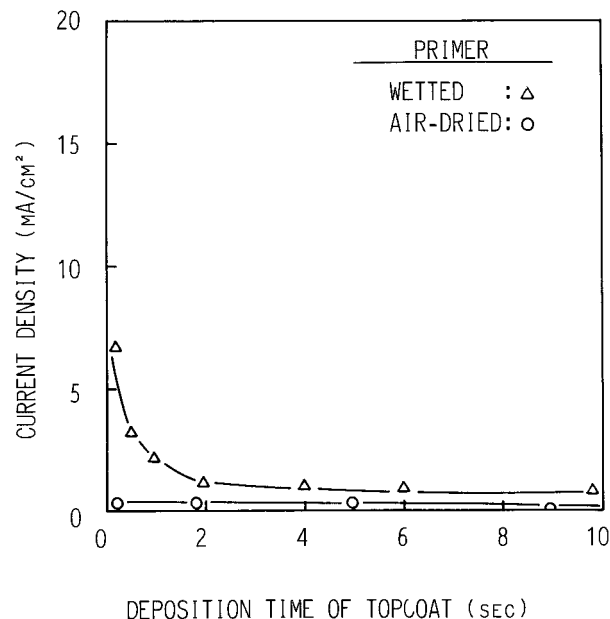
electric resistance of primer increases at the same time. In addition, when the primer was naturally dried over 30 min and immersed into emulsion CA for the topcoat ED, it was found that there is no deposition yield of topcoat to be observed. This result certainly indicates that keeping the primer wet can improve the topcoat ED.

On the other hand, the change of current density can account for the behavior of the secondary ED too (Fig. 6). The change of current density ( $\Delta$ ) can apparently be observed when the secondary ED is progressing upon the wet primer. It means the electrochemical reaction is really occurring at this time. On the contrary, when the primer is the air-dried film, there is almost no current density ( $\circ$ ) to be detected; that is, the secondary ED is difficult to progress under the this situation.

As a result, the twice ED coating of which the primer is resin T and the topcoat is resin A can be obtained. This film obtained is just like a double-layer film.

### The Comparison Between Film Obtained by Twice ED Coating and Coemulsion

A one-coat film containing two different resins, resin T and resin A, can be electrically deposited by a coemulsion obtained by mixing emulsion CT and emulsion CA. The resin composition of this one-coat film can be determined complicatedly by the quantitative analysis of Fourier-transform infrared (FTIR) spectroscopy. In previous studies,<sup>14,15</sup> it has reported that the resin composition of one-coat film is same as that of the coemulsion used. Thus, the resin composition of one-coat film can be represented directly by the coemulsion. For twice ED coating, the resin composition of film can be easily determined by the deposition yield of each process. Here, we notice that the deposited film is resin T or resin A, but the resin in the emulsion is the cationic-type resin T (resin CT) or the cationic-type resin A (resin CA); that is, the tertiary amino groups in resin T or resin A are fully converted to the tertiary amine acid salt type by neutralization. In Figure 7, the relationship between the resin composition of film and the deposition yield is plotted. It is shown that the deposition yield of one-coat film increases with the increase of resin A in the deposited film. The reason is caused by the higher deposition yield of emulsion CA than that of emulsion CT at the



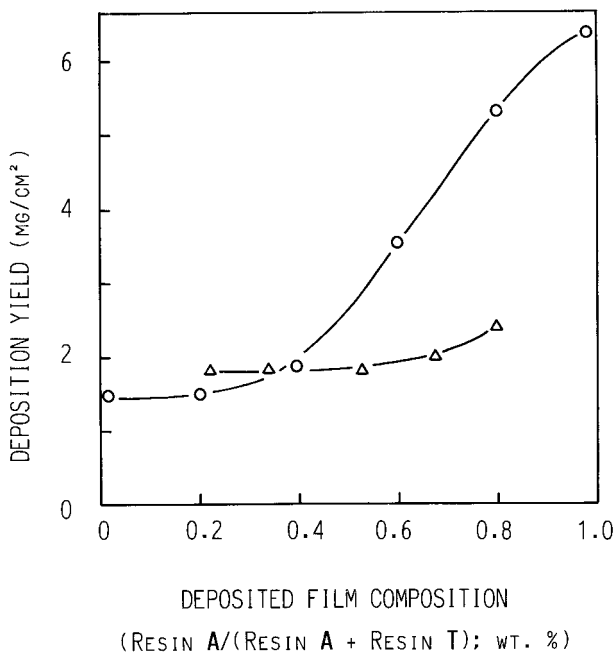
**Figure 6** The change of current density with time during topcoat electrodeposition: resin concentration of emulsion, 10 wt %; applied voltage, 150 V; deposition yield of primer, 0.5 mg/cm<sup>2</sup>.

same conditions, as already shown in Figures 1–3. But the change of deposition yield of twice ED coating with the resin composition is not remarkable. As comparing these curves, it is found that using the twice ED coating, a higher deposition yield can be gained when the ratio of resin A in the film is below 0.4, and the deposition yield of one-coat film becomes higher when the ratio of resin A in the film is over 0.4.

**Physical and Chemical Properties of Cured Film**

In Table II, it is shown that the physical and chemical properties, including adhesive strength, pencil hardness, alkali and acidic resistance, and salt spray resistance are not remarkably different between the cured films obtained from the twice ED coating and the coemulsion ED coating. Films obtained from these different methods have the required properties.

Comparing weather resistance ability, it is found that the cured film obtained by twice ED coating has superior weather resistance to that obtained by coemulsion ED coating, as shown in Figure 8. The reason for this result is that the surface content of film obtained by the twice ED



**Figure 7** The relationships between resin composition of deposited film and deposition yield: applied voltage, 150 V; deposition time, 5 min; resin concentration of emulsion, 10 wt %. Coemulsion electrodeposition coating is indicated by ○; twice electrodeposition coating is indicated by △.

**Table II Physical and Chemical Properties of the Cured Deposited Film**

| Properties                         | Method of Obtaining Cured Deposited Film |                                |
|------------------------------------|--|--------------------------------|
|                                    | Coemulsion                               | Twice ED <sup>f</sup> Coatings |
| Adhesive strength <sup>a</sup>     | 100/100                                  | 100/100                        |
| Pencil hardness <sup>b</sup>       | 2H                                       | 2H                             |
| Alkali resistance <sup>c</sup>     | OK                                       | OK                             |
| Acidic resistance <sup>d</sup>     | OK                                       | OK                             |
| Salt spray resistance <sup>e</sup> | OK                                       | OK                             |

<sup>a</sup> Determined by the standard method of JIS-0202 (1 mm<sup>2</sup> × 100).

<sup>b</sup> Measured by the Bräive Instruments B-400 with Mitsubishi pencils.

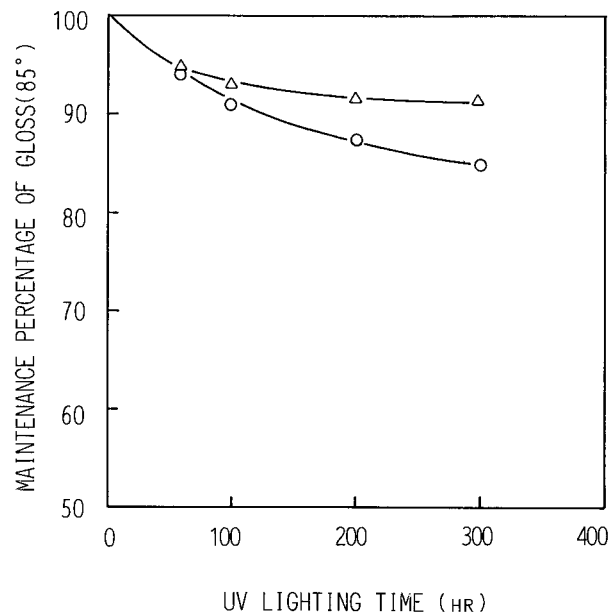
<sup>c</sup> Tested by dipping in 0.1N NaOH<sub>(aq)</sub> for 240 h.

<sup>d</sup> Tested by dipping in 0.2N H<sub>2</sub>SO<sub>4(aq)</sub> for 48 h.

<sup>e</sup> Evaluated by the standard method of JIS-Z2371, sprayed with 5% NaCl<sub>(aq)</sub> for 240 h.

<sup>f</sup> ED: Electrodeposition.

coating is pure acrylic resin (resin A). Contrarily, the content of film obtained by the coemulsion ED coating is the mixture of acrylic resin (resin A) and epoxy resin (resin T). It is known that acrylic resin has superior weather resistance to epoxy resin, so weather resistance can be improved.



**Figure 8** The effect of ultraviolet lighting time on maintenance percentage of gloss: deposition yield of film, 1.7–1.9 mg/cm<sup>2</sup>; ratio of resin A in the cured film, 0.4. Coemulsion electrodeposition coating is indicated by ○; twice electrodeposition coating is indicated by △.

## CONCLUSIONS

From the distinction of deposition yield and the change of current density during each ED process, the likely double-layer electrodeposited film can be confirmed; that is, a layer of acrylic resin, referred to as the topcoat, can be electrically deposited upon a layer of wet tertiary amine-epoxy resin adduct, referred to as the primer, which is also formed by ED. The deposition yield of the topcoat is deeply affected by the deposition yield of the primer. When the deposition yield of the primer increases, it decreases.

Compared with the one-coat film deposited by a coemulsion, it is found that the total deposition yield of twice ED coating is not apparently changed by the resin composition of the film when the ratio of acrylic resin below 0.8. But when the ratio is below 0.4, the total deposition yield of twice ED coating is higher than that obtained by the coemulsion. Although other physical and chemical properties are not apparently improved, the twice ED coating has better weather resistance caused by the pure content of acrylic resin in the surface of the cured film for comparing with the coemulsion ED coating.

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