

# FTIR Analysis of Electrodeposition Film from Emulsion of Two Cationic Resins

CHIN-PING YANG\* and YAHN-HAUR CHEN

Department of Chemical Engineering, Tatung Institute of Technology, Taipei, Taiwan, Republic of China

## SYNOPSIS

The resin composition of film deposited from coemulsion of two cationic resins (epoxy-amine adduct, *E*, was the main resin; cationic trimethylolpropane-toluene diisocyanate-dimethylaminoethanol/2-ethylhexanol resin, *T*, was used as crosslinker) was determined by Fourier Transform Infrared (FTIR) quantitative analysis. The electrodeposition properties of cationic resins and their coemulsions were compared to study the effects of resin composition of coemulsions on the resin composition of deposited films. The optimum resin composition of coemulsions was also found to produce deposited film with the best properties after curing.

## INTRODUCTION

Two or multi-component cationic coatings<sup>1-7</sup> can provide better storage stability of electrodeposition emulsions and better physical and chemical properties of electrodeposited films than a one-component system.<sup>8-16</sup> In reported papers,<sup>1-7</sup> most of the crosslinkers of two-component cationic coatings were uncharged resins. In this study, TMP-TDI-DMAE/2EH resin, containing tertiary amine groups, can be treated with acetic acid to form cationic crosslinkers. This resin can be codispersed with an epoxy-amine adduct, *E*, (a cationic resin with polyol groups) to form the emulsions of two cationic resins.

Infrared spectroscopy has traditionally been a useful tool for the identification and characterization of materials. Quantitative analysis is also possible through the use of the Beer-Lambert law. In this study, the functional groups (for example, the carbonyl group of *T* and hydrocarbon groups of *T* and *E*) were selected by FTIR quantitative analysis to determine the resin composition of electrodeposited

films. Moreover, the electrophoretic behavior of two-component emulsions, and the relationship between the resin composition of coemulsions and the resin composition of electrodeposited films, were investigated by comparing the electrodeposition properties of cationic resins and their coemulsions.

## EXPERIMENTAL

### Materials

Reagents used in the preparation of TMP-TDI-DMAE/2EH resin included the 2-dimethylaminoethanol (DMAE, Hanawa reagent pure grade), 2-ethylhexanol (2-EH, Wako extra pure grade), trimethylolpropane (TMP, Merck reagent pure grade), and toluene-2,4-diisocyanate (TDI).

Epon 1004 (diglycidyl ether of bisphenol A, commercially available from Shell Chemical Company, and possessing an epoxy equivalent weight of about 950) and diethylamine (Hanawa extra pure grade) were used in the preparation of epoxy-amine adduct (*E*).

Ethylene glycol mono-*n*-butyl ether (butyl cellosolve, BCS) (Wako EP grade) and acetic acid (Wako first grade) were used in the preparation of electrodeposition emulsion.

\* To whom correspondence should be addressed.

### Instruments

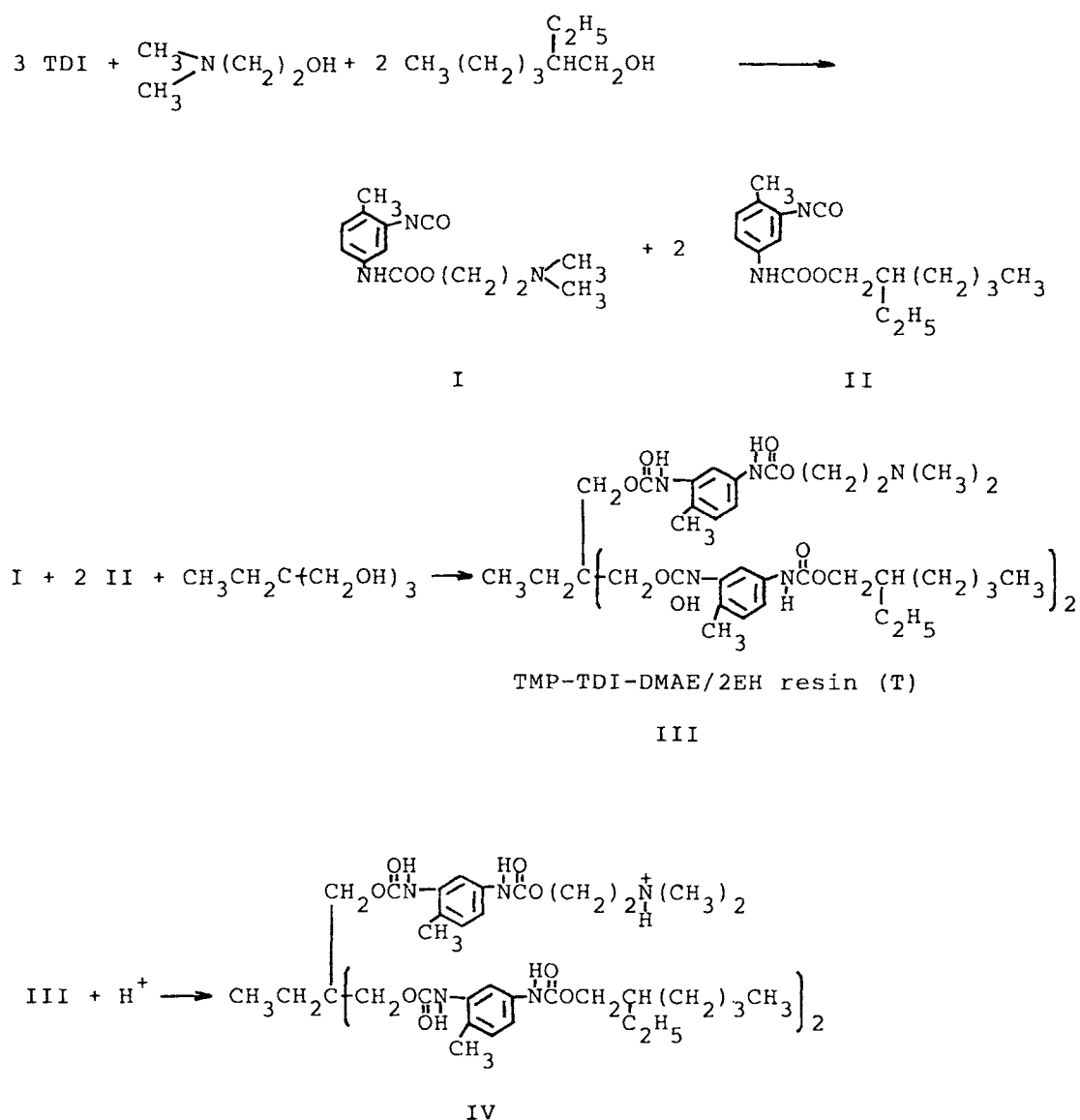
An electrodeposition apparatus<sup>16</sup> and a Jasco-7000 Fourier transform infrared spectrophotometer (FTIR) were employed. The electrodeposition apparatus included a glass reaction vessel with a cover, in which the copper electrode (used as anode) and aluminum plate (cathode), with a surface area of about 30 cm<sup>2</sup>, were hung. Approximately 200 mL of emulsion was placed in the glass vessel of the electrodeposition apparatus. The electrodes were immersed in the emulsion and electrodeposition was carried out at 50 V for 3 min. After deposition, the aluminum plate was rinsed with distilled water and

dried for 30 min in an air circulating oven at 100°C, then was reweighed to obtain the deposition yield of deposited film (mg/cm<sup>2</sup>).

### Synthesis

#### TMP-TDI-DMAE/2EH (T)

In a three-necked reaction vessel, a half-blocked TDI was prepared by slowly adding the mixture of 2-ethylhexanol (49.92 g, 0.384 mol) and dimethylaminoethanol (17.11 g, 0.192 mol) to TDI (100 g, 0.576 mol) over a period of about 40 min, below 20°C. At the completion of addition, the batch was

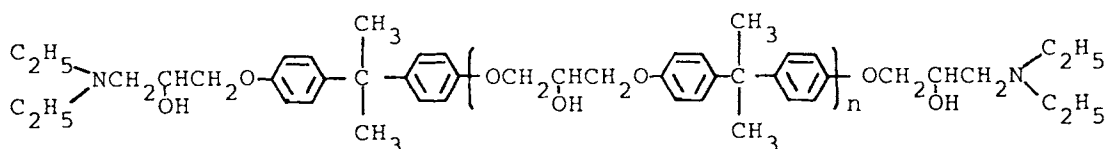
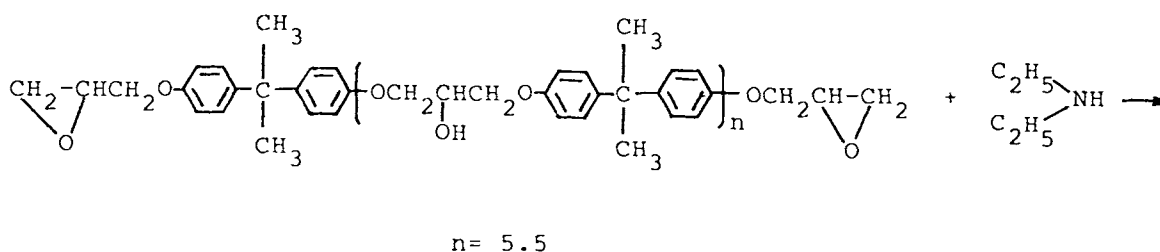


Scheme 1

kept below 20°C for an additional 40 min and then was heated to 40°C and held for 1 h. The solution of trimethylolpropane (25.7 g, 0.192 mol) in THF (50 g) was added dropwise in the reaction product after the reaction temperature was heated to 60°C. In the meantime, external cooling maintained the reaction temperature below 100°C. At the completion of addition, an additional 1 h at 100°C was maintained to give the TMP-TDI-DMAE/2EH resin (*T*) solution in THF. Finally, the obtained resin solution was distilled at 60°C under reduced pressure to remove THF.

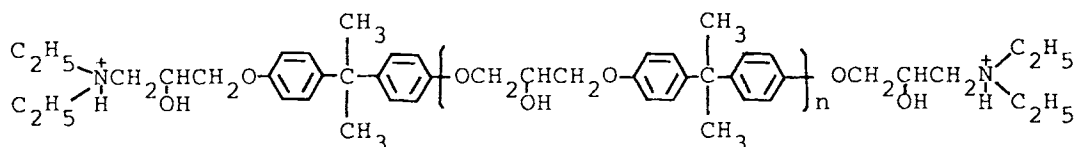
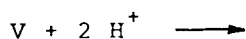
### Epoxy-Amine Adduct (*E*)

An epoxy resin (Epon 1004, 100 g) and toluene (100 mL) were charged into a three-necked flask. The mixture was heated to 80°C to dissolve the epoxy resin. 7.70 g (0.105 mol) of diethylamine was added into the flask. The whole mixture was kept at this temperature for about 2.5 h to give the resin solution of epoxy-amine adduct (*E*) in toluene. Finally, toluene was distilled off under reduced pressure. When cooled to room temperature, a golden, brittle solid of *E* was obtained.



Epoxy-Amine Adduct (*E*)

V



VI

Scheme 1 (continued from the previous page)

## Electrodeposition and Quantitative Analysis

### Calibration Curve

*E* and *T* resins, with various weight ratios, were mixed and well dissolved in THF, then were coated on potassium bromide (KBr) windows and dried. The dried films were analyzed in the absorbance mode and at a resolution of  $4\text{ cm}^{-1}$  by signal averaging 16 scans. The absorbance areas of carbonyl group ( $\text{C}=\text{O}$ ) stretching band (at approximately  $1900\text{--}1650\text{ cm}^{-1}$ ) and hydrocarbon (CH) stretching vibration (at approximately  $3000\text{--}2700\text{ cm}^{-1}$ ) were calculated and recorded. The  $[\text{C}=\text{O}]/[\text{CH}]$  absorbance area ratios (Abs. ratio) were plotted against the  $T/T + E$  weight ratios to derive the calibration curve.

### Quantitative Analysis

The electrodeposited film was dissolved in THF applied to a KBr window and then dried. The sample was analyzed under the same testing conditions as described above to get the  $[\text{C}=\text{O}]/[\text{CH}]$  Abs. ratio. From the  $[\text{C}=\text{O}]/[\text{CH}]$  Abs. ratio and calibration curve, we can get the resin composition of electrodeposited film.

### Gel Content

A 40% solid content solution, prepared by dissolving and mixing *E* and *T* resins in THF, was spread on aluminum foil and baked at  $180^\circ\text{C}$  for 40 min in an air oven to form a crosslinked film. The crosslinked film was immersed in acetone to reflux for 24 h. After drying, the gel content was calculated by dividing the residual weight by the initial weight of crosslinked film.

### Preparation of Electrodeposition Emulsion

The general process for the preparation of emulsions of *E* and *T* resins involved first the dilution of the mixed resins (*T* 5 g, *E* 5 g) with 4 g BCS to a solution with 40% solid content, and then the solution was treated with 0.5 mL HOAc (about 90 mol % of the total theoretical neutralization) and dispersed in 84 g deionized water to form a cationic emulsion of 10 wt % solid content.

### Electrodeposition

Approximately 100 mL of emulsion was placed in the glass vessel of the electrodeposition apparatus. The electrodes were immersed in the emulsion and electrodeposition was carried out at 50 V for 3 min. The cathode was removed from the emulsion,

washed with water, and successively heated to  $100^\circ\text{C}$  to obtain the deposition yield.

## RESULTS AND DISCUSSION

### Synthesis of TMP-TDI-DMAE/2EH (*T*) Resin and Epoxy-Amine Adduct (*E*)

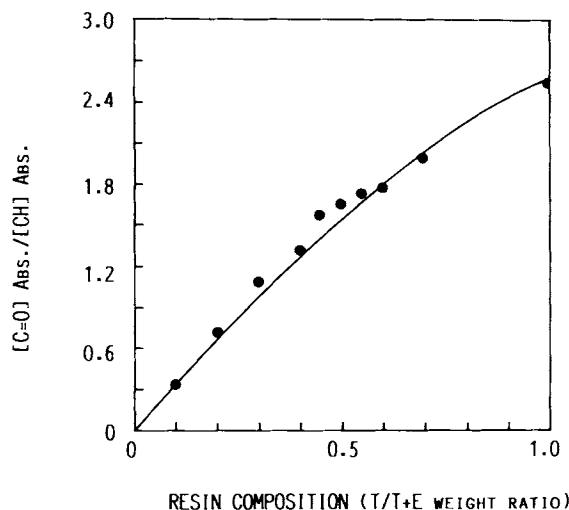
Tertiary amine groups were introduced into the molecule of TMP-TDI-DMAE/2EH resin (*T*) and epoxy-amine adduct (*E*) in the synthetic procedure, so both of the resins can be treated with acetic acid to form cationic resins and can be codispersed in deionized water to obtain emulsion. The synthetic procedures are shown in Scheme 1.

### The Mixing of Cationic Resins and Quantitative Analysis Calibration Curve

Infrared (IR) spectroscopy, which is sensitive to the functional group, has traditionally been a useful tool for the identification and characterization of materials. In this work, the IR quantitative analysis was used to study the electrodeposition behavior of two-component cationic resins system. The resins of two-component emulsion contain the cationic crosslinker *T*, having IR absorption of carbonyl  $[\text{C}=\text{O}]$  and hydrocarbon  $[\text{CH}]$  groups, and the polyol type *E* resin, having  $[\text{CH}]$  IR absorption. The strong  $[\text{C}=\text{O}]$  peak appears at  $1700\text{ cm}^{-1}$  and the peak of  $[\text{CH}]$  stretching vibration appears at  $2900\text{ cm}^{-1}$ . *E* and *T* resins with various weight ratios were well mixed and dissolved in THF, then were spread on KBr windows and dried. The samples were analyzed by IR spectroscopy. The absorbance areas of  $[\text{C}=\text{O}]$  stretching band (at approximately  $1900\text{--}1650\text{ cm}^{-1}$ ) and  $[\text{CH}]$  stretching vibration band (at approximately  $3000\text{--}2700\text{ cm}^{-1}$ ) were calculated. The  $[\text{C}=\text{O}]/[\text{CH}]$  ratios of absorbance areas were plotted against  $T/T + E$  weight ratios to give the calibration curve, as shown in Figure 1. It shows that the  $[\text{C}=\text{O}]/[\text{CH}]$  Abs. ratio increases with increasing "*T*" content.

### Electrodeposition Properties of *E* and *T* Deposition Yield

The relationships between deposition time and deposition yield of resins *T* and *E* are shown in Figure 2. For resin *E*, the deposition yield increased with the deposition time in the initial 2–3 min and reached a limit when an insulating film formed. For resin *T*, the deposition yield reached a limit after the initial 3–4 min. At the same deposition time, the

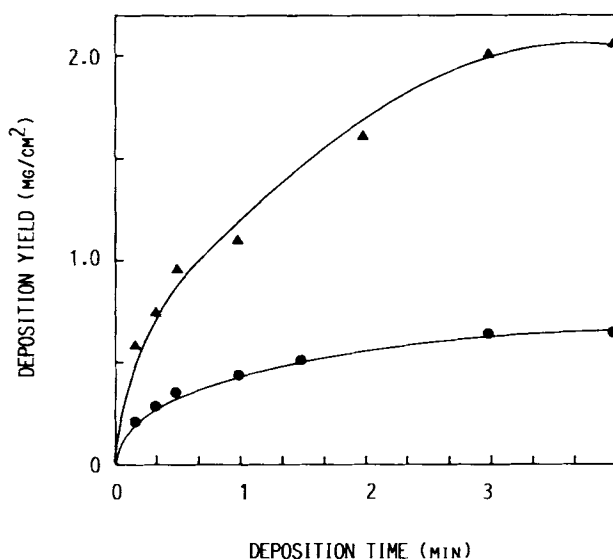


**Figure 1** The calibration curve of FTIR quantitative analysis of resin  $T/E$ .

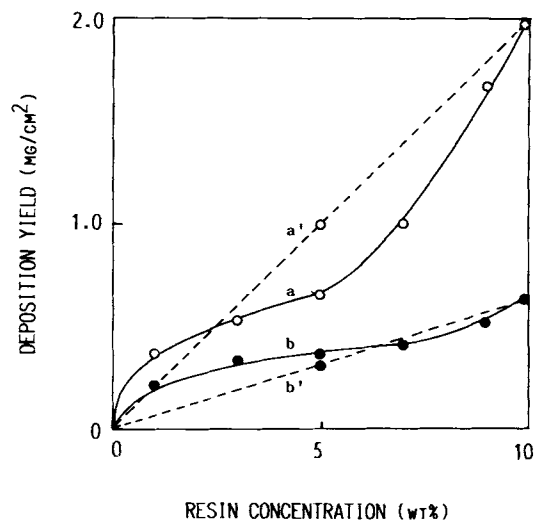
deposition yield of  $T$  is greater than that of  $E$ , that is, the deposition velocity of  $T$  is faster than that of  $E$ . This is probably due to the fact that  $T$  has lower molecular weight and its emulsion has higher conductivity.

### Effect of Resin Concentration on Deposition Yield

The effect of resin concentration on deposition yield is shown in Figure 3. The predicted deposition yields of dotted lines  $a'$  and  $b'$  were estimated to be proportional to the resin concentration (based on the



**Figure 2** Effects of deposition time on deposition yield. Resin concentration: 10 wt %, BCS content: 4 wt %, pH = 5.40, applied voltage: 50 V; (●), emulsion of  $E$ , conductivity =  $1.01 \text{ m}\Omega^{-1}/\text{cm}$ ; (▲), emulsion of  $T$ , conductivity =  $1.35 \text{ m}\Omega^{-1}/\text{cm}$ .

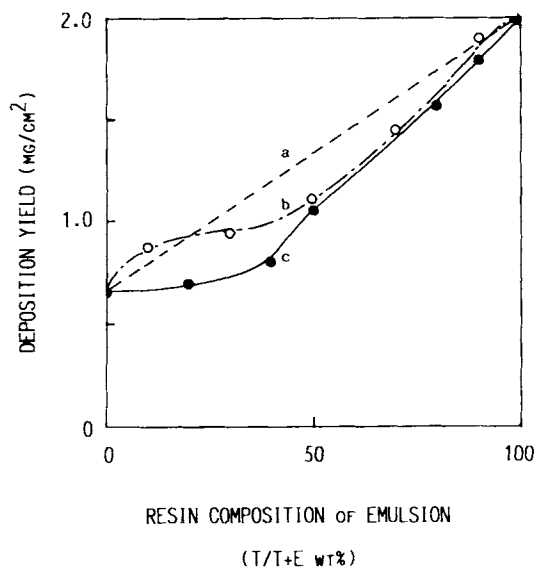


**Figure 3** Effects of resin concentration on deposition yield. BCS content: 4 wt %, pH = 5.4, applied voltage: 50 V, deposition time: 3 min; (----- $a'$ ), the predicted deposition yield of  $T$  based on the resin concentration of 10 wt %; (----- $b'$ ), the predicted deposition yield of  $E$  based on the resin concentration of 10 wt %; (—  $a$ ), actual deposition yield of emulsion of  $T$ ; (—  $b$ ), actual deposition yield of emulsion of  $E$ .

deposition yield of  $T$  being  $2.04 \text{ mg}/\text{cm}^2$  and  $E$  being  $0.66 \text{ mg}/\text{cm}^2$  at the resin concentration of 10 wt %). Lines  $a$  and  $b$  were the actual deposition yields of  $T$  and  $E$  at various resin concentrations. However, the figure shows that the actual deposition yield was not proportional to the resin concentration. At the lower resin concentration, the actual deposition yield was greater than the predicted value, but at the higher resin concentration, the actual deposition yield was lower than the predicted value. For example, the actual deposition yield of  $T$  was lower than the predicted value when the resin concentration was lower than 3 wt %. The actual deposition yield of  $E$  was greater than the predicted value at the resin concentration lower than 7 wt %, but the actual deposition was lower than the predicted value at the resin concentration higher than 7 wt %. Thus, the deposition yield was increased with, but was not proportional to, the resin concentration.

### The Deposition Yield of Coemulsion

The effects of resin composition of coemulsion on deposition yield are depicted in Figure 4. Line  $c$  is the actual deposition yield of coemulsion at various resin compositions. Line  $a$  is the connection of deposition yield of  $E$  and  $T$  (both at the resin concentration of 10 wt %). The values of data points shown on line  $b$  are calculated from the individual depo-



**Figure 4** Effects of resin composition of emulsion on deposition yield. Resin concentration: 10 wt %, BCS content: 4 wt %, pH = 5.4, applied voltage: 50 V, deposition time: 3 min; (-----), a, the connection of deposition yields of emulsions of  $T$  and  $E$  based on the resin concentrations of 10 wt %; (- · - · - ·), b, the addition of actual deposition yields of emulsions of  $T$  and  $E$  derived from Figure 3; (—), c, the actual deposition yield of coemulsion.

sition yield of  $T$  and  $E$  resin emulsions shown in Figure 3. For example, for a coemulsion with 10 wt % resin concentration and 0.7 of  $T/T + E$  weight ratio, the predicted yield is the sum of deposition yield of resin  $T$  at 3 wt % and that of resin  $E$  at 7 wt % when they were electrodeposited individually. Figure 4 shows that the actual deposition yield of coemulsion is related to the resin composition and the individual deposition velocity of  $E$  and  $T$ . The actual deposition yield of line c increases with the increase of  $T$  composition and, at the higher  $T$  composition ( $T/T + E$  weight ratio  $> 0.5$ ), it's almost equal to the predicted value of line b. However, the actual deposition yield of line c is lower than the predicted value of line b when the composition of  $E$  is higher than  $T$  ( $T/T + E < 0.5$ ). This is because the deposition velocity of  $T$  is faster than that of  $E$  and, at the composition with  $E$  and, at the composition with  $E$  higher than  $T$ , the higher than  $T$  the molecular chains of  $T$  are entangled by the ones of  $E$ , resulting in the lowering of deposition velocity.

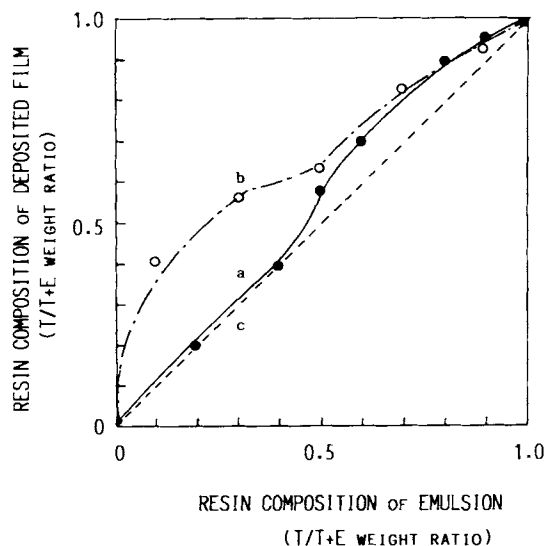
#### The Analysis of Resin Composition ( $T/T + E$ ) of Deposited Film

Figure 5 indicates the effect of resin composition of coemulsion on the resin composition of deposited film, where line a shows the observed  $T/T + E$

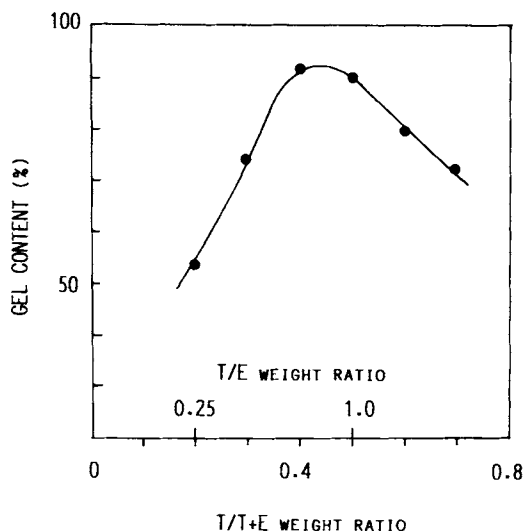
weight ratios of the deposited films and line b shows the calculated values from the individual deposition yield of resins  $T$  and  $E$ , as shown in Figure 3. Theoretically, line a is close to or equal to line c (the diagonal of Figure 5) if  $T$  and  $E$  are well mixed to form a stable coemulsion and are uniformly comigrated onto the substrate during the electrodeposition process. Line a is close to the predicted value of line b if the resin composition of deposited film is affected by the individual deposition velocity of  $E$  and  $T$ . Figure 5 shows that at the weight ratio ( $T/T + E$ ) lower than 0.4, the  $E/T$  coemulsion was uniformly deposited on the substrate, that is, the resin composition of coemulsion was equal to the resin composition of deposited film; however, when the  $T/T + E$  weight ratio was greater than 0.4, the resin composition of deposited film was close to the value of line b. This indicates that the electrodeposition was affected by the individual deposition velocity of  $T$  and  $E$  at higher composition of  $T$ , resulting in a higher content of  $T$  deposited on the substrate. Thus, in this condition, the resin composition of emulsion will be gradually changed during successive electrodeposition.

#### Gel Content of $T/E$ Mixed Film

Figure 6 shows the effect of composition of  $E/T$  mixed film on its gel content. It shows that the op-



**Figure 5** Effects of the resin composition of coemulsion on the resin composition of deposited film. Resin concentration: 10 wt %, BCS content: 4 wt %, pH = 5.25, applied voltage: 50 V, deposition time: 3 min; (—), a, actual value; (- · - · - ·), b, forecast value derived from actual deposition yields of emulsions of  $E$  and  $T$  of Figure 3; (-----), c, diagonal line.



**Figure 6** Effects of resin composition on gel content. Curing temperature: 180°C, curing time: 40 min.

imum composition of mixed film is at  $T/E$  weight ratio between 0.7–1. The theoretical  $T/E$  value of the best gel content is at the  $T/E$  weight ratio of 1.2 ( $T$ ,  $M_w = 1005$ , will decompose 3 mol of hydroxyl group in the curing process and will retain 3 -NCO groups to cure with  $E$ ,  $M_w = 2046$ , containing 7.5 mol hydroxyl groups. Thus the equivalent weights of  $T$  and  $E$  are 335 and 273). The theoretical  $T/E$  weight ratio of the best gel content is greater than the experimental value. This is probably due to the fact that at these curing conditions, some hydroxyl groups of  $E$  are not reacted with -NCO groups, but this must be proved experimentally. From Figures 5 and 6, the optimum resin compositions of coemulsion are between 0.4–0.45 ( $T/T + E$  weight ratios of deposited film are between 0.4–0.5).

## CONCLUSIONS

1. The deposition yields of  $E$  and  $T$  increase with increase in resin concentration, but the relationship of deposition yield and resin concentration is not directly proportional.
2. The actual deposition yield of coemulsion is related to the individual electrophoretic velocity of  $T$  and  $E$  and the resin composition of coemulsion. The deposition velocity of  $T$  is higher than that of  $E$ . At higher " $T$ " compositions ( $T/T + E$  weight ratio  $> 0.5$ ), the actual deposition yield of coemulsion is almost equal to the predicted deposition yield;

on the other hand, at higher composition of  $E$  ( $T/T + E < 0.5$ ), the actual value is lower than the predicted value.

3. At the  $T/T + E$  weight ratio, lower than 0.4,  $E$  and  $T$  are well mixed in the coemulsion to uniformly codeposit on the substrate; however, at the higher composition of  $T$  ( $T/T + E$  weight ratio greater than 0.4), the resin composition of deposited film is affected by the individual velocity of  $E$  and  $T$ , resulting in higher content of  $T$  deposited on the substrate. Thus, in this condition, the resin composition of coemulsion will be gradually changed during successive electrodeposition.

We thank the National Science Council of R.O.C. for their generous financial support (Grant NSC 80-0405-E-036-01).

## REFERENCES

1. C. C. Anderson and C. C. Sturni, U.S. Pat. 3,853,803 (1974).
2. O. D. Stepp, U.S. Pat. 3,956,091 (1976).
3. R. Kita and A. Kimi, *J. Coatings Tech.*, **48**, 616, 53 (1976).
4. M. S. Chattha, U.S. Pat. 4,178,321 (1979).
5. I. Hazan, U.S. Pat. 4,177,124 (1979).
6. T. L. Anderson, T. K. Debroy, and D. Y. Chung, U.S. Pat. 4,575,523 (1986).
7. K. W. Anderson and R. A. Hickner, U.S. Pat. 4,698,141 (1987).
8. C. C. Anderson and J. R. Marchetti, U.S. Pat. 3,939,051 (1976).
9. G. M. Kobe, Y. Manabe, and Y. Suematsu, U.S. Pat. 3,988,281 (1976).
10. R. D. Jerabek, J. R. Marchetti, and R. R. Zwack, U.S. Pat. 4,017,438 (1977).
11. J. R. Marchetti, R. R. Zwack, and R. D. Jerabek, U.S. Pat. 4,104,147 (1978).
12. C. P. Yang and Y. H. Chen, *Aegew. Makromol. Chem.*, **160**, 91 (1988).
13. C. P. Yang and L. T. Lee, *J. Polym. Sci. Polym. Chem. Ed.*, **28**, 1861 (1990).
14. C. P. Yang and L. T. Lee, *J. Appl. Polym. Sci.*, **41**, 1995 (1990).
15. C. P. Yang and L. T. Lee, *J. Appl. Polym. Sci.*, **42**, 1465 (1991).
16. C. P. Yang and Y. H. Chen, *J. Appl. Polym. Sci.*, **42**, 1097 (1991).

Received December 9, 1991

Accepted January 2, 1992