The Electrodeposition Properties of Coemulsion-Contained Quaternary Ammonium/Tertiary Amine Salt Epoxy–Amine Adducts and the Composition Analysis of Its Electrodeposited Film

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SYNOPSIS

Two-component electrodepositable coemulsion-contained quaternary ammonium resin **Q**, as a pigment grinding vehicle, and DGEBA–N-methylethanolamine (MEA) tertiary amine salt resin **T**, as the principal resin, were obtained and then deposited to form a resinous film on the cathode during electrodeposition. The resin composition of this deposited film was determined by the quantitative analysis of FTIR and it was found different from the resin composition of the original coemulsion. The electrodeposition behaviors of the coemulsion were deeply affected by the quaternary ammonium resin. In addition, the electrodeposition properties of emulsions dispersed by quaternary ammonium resin and tertiary amine salt resin were also studied for comparison. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The water-dispersible epoxy–amine resin can be applied to the field of cationic electrodeposition (CED) coating having many advantages such as good corrosion resistance, good throwing power, and uniform film. Therefore, CED is suitable for a primer coating of recessed metal parts in industry.

In practice, in the formation of CED coating compositions, an important factor is the introduction of pigments into the coating composition. The pigments are typically ground in a pigment grinding vehicle that acts as a dispersing agent to form a paste, and the resultant pigment paste is incorporated into the principal emulsion to give the coating composition proper color, opacity, application, and film properties. Therefore, the commercial epoxy resin-based CED coating always contains two different kinds of resins. One is a tertiary amine salt resin, as the principal or main resin, and the other is a quaternary ammonium resin, as a pigment grinding vehicle.[1-6] But the study of electrodeposition behavior of this two-component emulsion and

the analysis of its deposited film are seldom reported. In this study, a thermal cross-linkable quaternary ammonium resin was prepared by a DGEBA-type epoxy resin (Epon 1001) and a tertiary amine, derived by reacting N,N-dimethylethanolamine (DMEA) with toluene diisocyanate (TDI), of which half the isocyanate groups were previously blocked by 2-ethyl hexanol (2EH). On the other hand, a tertiary amine salt resin was directly synthesized by Epon 1004 and N-methylethanolamine (MEA). For simplification, the emulsion of quaternary ammonium resin did not contain any pigment and then was mixed with the emulsion of tertiary amine salt resin with different weight ratios to give a series of coemulsions for electrodeposition. The resin compositions of deposited films were determined by the quantitative analysis of FTIR. Meanwhile, other electrodeposition properties of the coemulsion, such as deposition yield, throwing power,[7-9] and rupture voltage,[10] were also studied.

EXPERIMENTAL

Materials

Epoxy resins used were Epon 1001 and Epon 1004 (Shell Chemical Co.) having an average epoxy

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equivalent weight of 475 and 945, respectively, and having an average hydroxyl equivalent weight of 345 and 303, respectively. Toluene diisocyanate (TDI) and 2-ethyl hexanol (2EH) were industrial products purchased from the domestic supply. N-Methylethanolamine (MEA) and N,N-dimethylethanolamine (DMEA) were EP grade products purchased from Fluka (Switzerland). Glacial acetic acid, as neutralizer, and ethylene glycol mono-n-butyl ether (BCS), as cosolvent, were purchased from Wako (Japan) and were also EP grade.

Apparatus

A Fourier-transform infrared (FTIR) spectrophotometer (JASCO FT/IR-7000) for quantitative analysis, an electrodeposition apparatus, and a throwing power tester were employed. In addition, a pH meter and a conductivity meter were also required.

Synthesis

Quaternary Ammonium Resin Q

First, 80.04 g (0.46 mol) TDI was charged into a 300 mL three-necked glass flask equipped with a magnetic stirrer in an inert nitrogen blanket. Then, 59.8 g (0.46 mol) 2EH was added into the flask drop by drop below 18°C. After 2EH was completely charged, the mixture was kept at 40°C over 40 min for a thorough reaction. The product was transparent, sticky, 2EH–half-blocked TDI.

Half (0.21 mol) of the blocked TDI was added slowly into another flask already containing 18.69 g (0.21 mol) DMEA and equipped with an electric agitator in an inert nitrogen blanket. The mixture was reacted at 80°C for 3 h, followed by neutralizing with 12.6 g (0.21 mol) acetic acid to give tertiary amine acid salt (I).

Into a 1000 mL five-necked glass vessel equipped with a Dean-Stock reflux trap and an electric stirrer, 100 g (0.21 mol) Epon 1001 and 200 mL toluene were added and heated to the reflux temperature (over 110°C) to remove water in the system by azeotropic distillation for 3 h. Then, to the mixture, cooled down to 80°C in an inert nitrogen blanket, 76 g (0.25 mol) 2EH–half-blocked TDI was slowly charged and kept at this temperature for an additional 3 h until the free isocyanate (— NCO) groups of TDI was reacted completely with the pendent hydroxyl groups of the epoxy resin. Finally, 95.13 g (0.21 mol) tertiary amine acid salt I was added into the vessel to progress the ring-opening reaction with

the terminal epoxy groups of epoxy resin at 80°C for 3 h. After toluene was distilled off under reduced pressure, 271.13 g thermal cross-linkable solid quaternary ammonium resin Q was obtained.

Tertiary Amine Acid Salt Resin T

One hundred grams Epon 1004 and 200 mL toluene were charged to a 1000 mL five-necked reactor equipped with an electric stirrer and heated to 80–90°C for complete mixing. Then, 7.88 g (0.105 mol) MEA was added into the mixture to progress the ring-opening reaction at 80°C for 3 h. The product was tertiary amine resin T'. When the calculated amount of acetic acid added for 100% neutralization, tertiary amine acid salt resin T was obtained.

Preparation of Emulsion

Thirty grams of the cationic resin obtained and 9 g BCS were charged to a reactor equipped with an electric stirrer and heated to 80–90°C for complete mixing. Deionized water, 261 g, was then added into the mixture slowly and agitated violently to disperse the resin into a water phase to form a stable emulsion, having a resin concentration of 10 wt % by total weight and BCS content of 3 wt %. A series of coemulsions were obtained by mixing the emulsion of resin Q and the emulsion of resin T with various weight ratios.

Quantitative Analysis by FTIR

Calibration Curve

The deposited film of quaternary ammonium resin Q becomes a quaternary ammonium hydroxide-containing resin, hereafter defined as resin Q', and tertiary amine acid salt resin T is reduced to resin T' during electrodeposition. However, when a coemulsion is formed by mixing the emulsions of resins Q and T, the deposited film will contain resins Q' and resin T' simultaneously. To establish the calibration curve for analyzing the deposited film of coemulsion by FTIR, the mixtures of resins Q' and T' by different weight ratios were prepared first. There were two methods to obtain resins Q' and T': (a) resin Q' was obtained by precipitating resin Q in 6N NaOH$_{(aq)}$, followed by rinsing and drying, and resin T' was obtained by the synthesis process mentioned above, or (b) resins Q' and T' were obtained directly from the electrodeposited films of the resin Q emulsion and the resin T emulsion, respectively. The mixtures were completely dissolved in tetrahydrofuran (THF), poured on a KBr window,

and dried. The dried samples were analyzed in the absorbance mode of FTIR. In the spectrum, the absorbance areas of the carbonyl group ($-CO-$) stretching band (around 1900–1650 cm^{-1}) and the methylene group ($-CH_2-$) stretching band (around 1600–1400 cm^{-1}) were calculated and recorded individually. Finally, the [$-CO-$]/ [$-CH_2-$] absorbance ratio (Abs. ratio) were plotted against the weight ratio [$Q'/(Q' + T')$] to obtain the calibration curve.

Quantitative Analysis of Electrodeposited Film

The electrodeposited film was rinsed, dried, and dissolved in THF, followed by pouring on the KBr window and drying completely. The sample was analyzed by FTIR under the mentioned conditions to obtain the [$-CO-$]/[$-CH_2-$] Abs. ratio and compared to the calibration curve. Thus, the resin composition of the electrodeposited film could be determined.

Measurements

Throwing Power

The ability of a coating system to deposit film in recessed areas is called the throwing power. Throwing power of the emulsion was measured by a tube penetration test. The testing process was mentioned in a previous paper.[11]

Rupture Voltage

By exceeding a certain voltage, surface faults in the deposited film in the emulsion bath appear such as keloid, pit, etc. At the same time, the electric current and bath temperature apparently increases. This voltage is called rupture voltage or plague voltage for the deposited film. The testing method was mentioned in a previous paper.[12]

RESULTS AND DISCUSSION

Synthesis

The main reactions for preparing resins **Q**, **T**, and **T'** are shown in Scheme 1. The carbamate group containing tertiary amine salt **I** was synthesized by reacting DMEA with 2EH–half-blocked TDI and then was neutralized by acetic acid. The thermal cross-linkable quaternary ammonium resin **Q** was synthesized by reacting an half amount of pendent hydroxy groups of Epon 1001 with 2EH–half-blocked TDI, followed by the ring-opening reaction

of terminal epoxy groups with adduct **I**. On the other hand, tertiary amine resin **T'** was obtained directly by the ring-opening reaction of Epon 1004 with MEA. By neutralizing resin **T'** with acetic acid, tertiary amine salt resin **T** was obtained.
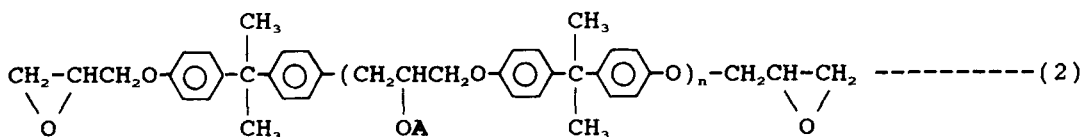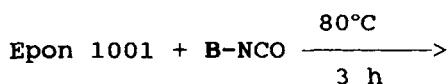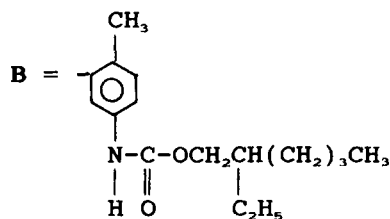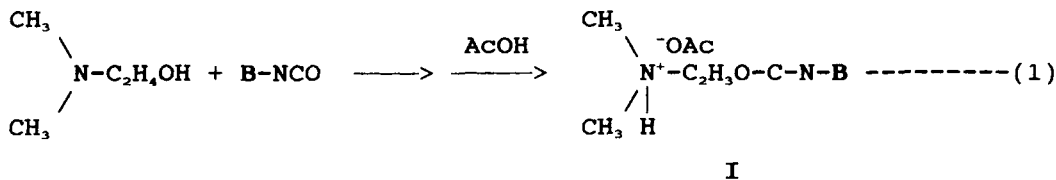
Water-emulsification of Resins Q and T

Stable emulsion of resin means dispersing and suspending the resin particle in the water phase, with no precipitation for a long period of time. It is affected by the hydrophility of resin, the pH value of dispersion solution, and the content of the cosolvent. Figure 1 shows the emulsion pattern of resins **Q** and **T**. The dispersion solution of resin **Q** has better emulsion stability because it contains the hydrophilic quaternary ammonium structure. The range of stable emulsion of resin **Q** is larger than that of resin **T**. In addition, the emulsion of resin **Q** is stable in acid and basic media, but the emulsion of resin **T** is stable only at pH < 7.

Figure 2 is the relationship between deposition yield and deposition time as the processing the electrodeposition in the emulsion bath. It was found that the deposition yield of resin **T** was higher than that of resin **Q** at the same deposition time and up to a limit of 1.75 mg/cm^2, with the deposition time over 3 min, because the deposition rate and the dissolution rate of the wetted film in the emulsion bath will keep a balance at this time. But the deposition yield of resin **Q** increased with increasing of deposition time.

It is concluded that resin **Q** has better water solubility and easily disperses to form stable emulsion for electrodeposition; meanwhile, the deposition yield is lower than for resin **T** but can increase by increasing the deposition time.
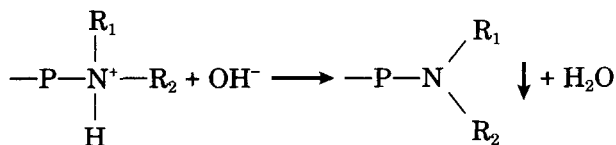
Calibration Curve

For two-component systems, the composition ratio can be determined by the quantitative analysis of IR, if one component possesses a special stretching band in IR spectrum but the other does not. Now we try to use this method to determine the resin composition of electrodeposited film of coemulsion in this study. Beginning in this work, the calibration curve, the defined resin composition of mixture to the Abs. ratio of some special function group, was prepared first. We already knew that a tertiary amine acid salt resin is reduced to a tertiary amine resin and deposited on the cathode during electrodeposition.[13] The main electrochemical reaction is
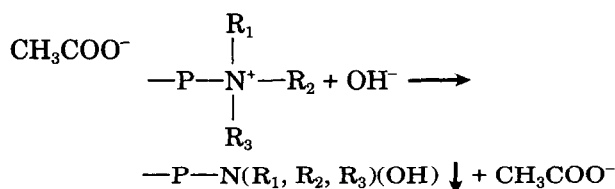
$$CH_3 \backslash N-C_2H_4OH + B-NCO \xrightarrow{AcOH} \longrightarrow$$

$$CH_3 / $$

$$\begin{array}{c} CH_3 \\ \backslash \quad ^-OAc \\ N^+-C_2H_3O-C-N-B \quad \text{---------}(1) \\ / | \\ CH_3 \quad H \end{array}$$

I

$$B = \begin{array}{c} CH_3 \\ \text{(benzene ring)} \\ N-C-OCH_2CH(CH_2)_3CH_3 \\ | \quad \| \quad | \\ H \quad O \quad C_2H_5 \end{array}$$

$$\text{Epon 1001 + B-NCO} \xrightarrow[3\ h]{80°C}$$

$$CH_2-CHCH_2O-\text{(ring)}-\overset{CH_3}{\underset{CH_3}{C}}-\text{(ring)}-(CH_2CHCH_2O-\text{(ring)}-\overset{CH_3}{\underset{CH_3}{C}}-\text{(ring)}-O)_n-CH_2CH-CH_2 \quad \text{----------}(2)$$
$$\backslash / \qquad \qquad \qquad \qquad OA \qquad \qquad \qquad \qquad \backslash /$$
$$O \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad O$$

II

A	number of A
-H	x
O H ‖ | -C-N-B	y

$$y = (n/2)+1, \quad n = 1.97$$

Scheme 1

$$\begin{array}{c} R_1 \\ | \\ -P-N^+-R_2 + OH^- \longrightarrow -P-N \overset{R_1}{\underset{R_2}{\diagdown}} \quad \downarrow + H_2O \\ | \\ H \end{array}$$
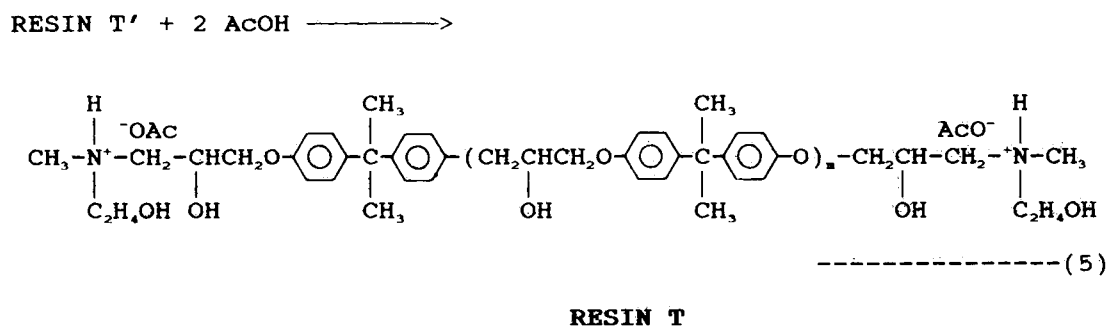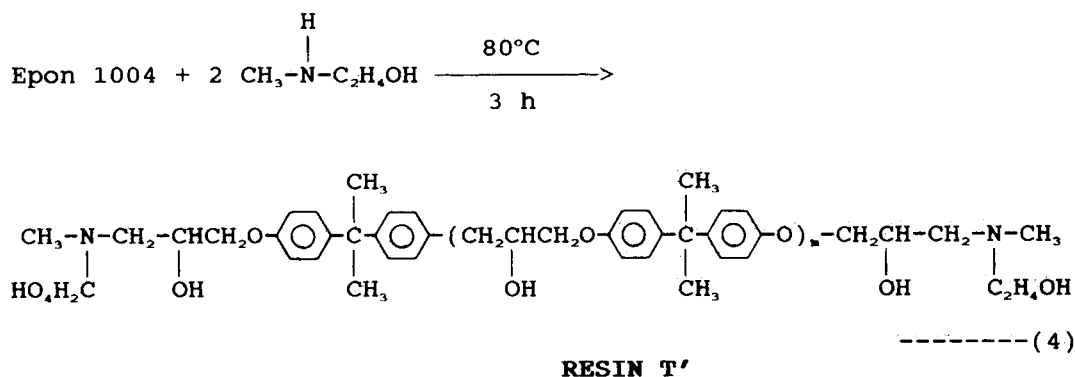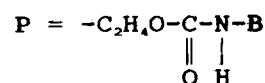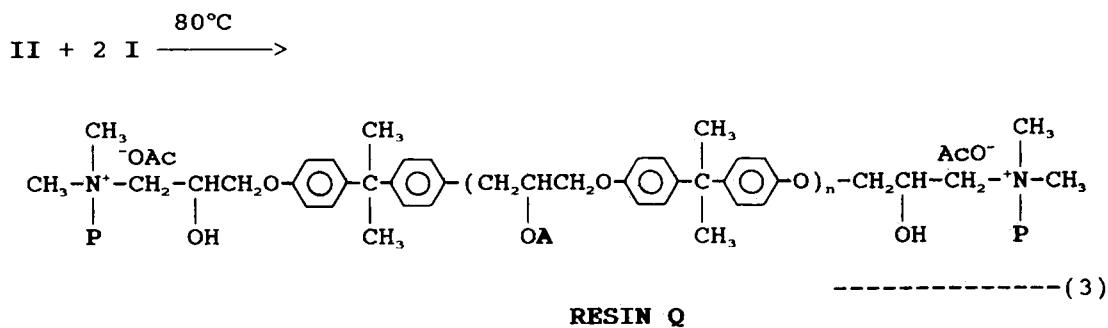
where —P— is a polymer chain; on the other hand, a quaternary ammonium resin became a poor-soluble hydroxyl quaternary ammonium resin during electrodeposition.[12] The main electrochemical reaction is

$$CH_3COO^- \begin{array}{c} R_1 \\ | \\ -P-N^+-R_2 + OH^- \longrightarrow \\ | \\ R_3 \end{array}$$

$$-P-N(R_1, R_2, R_3)(OH) \downarrow + CH_3COO^-$$

where —P— is a polymer chain. Thus, the main composition of the deposited film of coemulsion are hydroxyl quaternary ammonium resin **Q′** and tertiary amine resin **T′**. These two resins were mixed with various weight ratios for preparing the calibration curve.

Since resin **Q′** containing the blocked TDI has a carbonyl group (—CO—) and resin **T′** does not, the absorbance ratio of carbonyl to methylene groups ([—CO—]/[—CH_2—] Abs. ratio) increased when the content of resin **Q′** in the mixture increased. For this relationship, the [—CO]/ [—CH_2—] Abs. ratio was plotted against the weight ratio of resin **Q′** in the mixture [Q′/(Q′ + T′)] to give the calibration curve shown in Figure 3, where the resins used for creating the A line were obtained by method (a) mentioned in the Experimental section and did not contain any acetic acid.

II + 2 I $\xrightarrow{\ 80°C\ }$

$$CH_3-\overset{CH_3}{\underset{P}{\overset{|}{\underset{|}{N^+}}}}-CH_2-\overset{|}{\underset{OH}{CHCH_2}}O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\langle O\rangle-(CH_2\overset{|}{CHCH_2}O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\langle O\rangle-O)_n-CH_2\overset{|}{\underset{OH}{CH}}-CH_2-\overset{CH_3}{\underset{P}{\overset{|}{\underset{|}{N^+}}}}-CH_3$$

-OAc ... OA ... AcO^-

-------------(3)

RESIN Q

$$P = -C_2H_4O-\overset{O}{\overset{||}{C}}-\overset{H}{\overset{|}{N}}-B$$

Epon 1004 + 2 $CH_3-\overset{H}{\overset{|}{N}}-C_2H_4OH$ $\xrightarrow[3\ h]{\ 80°C\ }$

$$CH_3-\overset{}{\underset{HO_4H_2C}{\overset{|}{N}}}-CH_2-\overset{|}{\underset{OH}{CHCH_2}}O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\langle O\rangle-(CH_2\overset{|}{\underset{OH}{CHCH_2}}O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\langle O\rangle-O)_n-CH_2\overset{|}{\underset{OH}{CH}}-CH_2-\overset{}{\underset{C_2H_4OH}{\overset{|}{N}}}-CH_3$$

--------(4)

RESIN T'

RESIN T' + 2 AcOH $\longrightarrow$

$$CH_3-\overset{H}{\underset{C_2H_4OH}{\overset{|}{\underset{|}{N^+}}}}-CH_2-\overset{|}{\underset{OH}{CHCH_2}}O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\langle O\rangle-(CH_2\overset{|}{\underset{OH}{CHCH_2}}O-\langle O\rangle-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\langle O\rangle-O)_n-CH_2\overset{|}{\underset{OH}{CH}}-CH_2-\overset{H}{\underset{C_2H_4OH}{\overset{|}{\underset{|}{N^+}}}}-CH_3$$

-OAc ... AcO^-

-------------(5)

RESIN T

Scheme 1 (*Continued from the previous page*)

Therefore, the A line went through the original point. In fact, a small amount of acetate ion (CH_3COO^-) still remained in the film and affected the [— CO —] absorbance intensity. Resins Q' and T' were also collected from the deposited films of pure one-component emulsions to give another calibration curve (B line) for comparison. It was shown that the Abs. ratio of the B line is higher than that of the A line at the same resin composition because of the residue of acetate ion in the deposited film.

Hereafter, we will use the B line as the real calibration curve.

Electrodeposition Properties of Coemulsion

Deposition Yield

A series of coemulsions were obtained by mixing physically the emulsion of resin Q and the emulsion of resin T with various weight ratios. Some of elec-
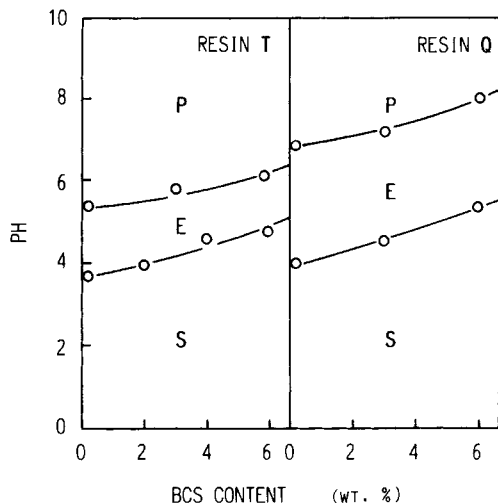
Figure 1   Effects of pH and BCS cosolvent content on the emulsion behavior of resin T and resin Q; resin concentration: 10 wt %; P: precipitation; E: stable emulsion; S: solution.
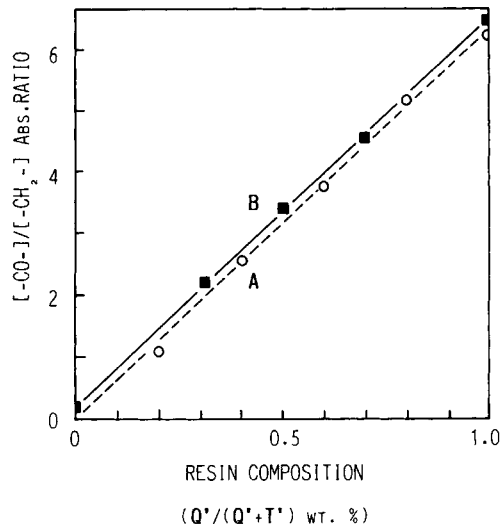
Figure 3   The calibration curve of the mixing resin by FTIR quantitative analysis; (A, dashed line) resins obtained from method (a); (B, solid line) resins obtained from method (b).

trodeposition behaviors of the coemulsion will be studied as follows: First, effects of the resin composition of coemulsion on deposition yield is shown in Figure 4. It was found that all deposition yields of coemulsions with different resin compositions were between the deposition yield of pure resin T, $Q/(Q + T) = 0$, and the deposition yield of pure resin Q, $Q/(Q + T) = 1$, and decreased by increasing resin Q content in the coemulsion. But the tendency was not linear. As small amounts of resin Q emulsion were added into resin T emulsion, the deposition yield decreased remarkably; on the contrary, as resin T emulsion was added into resin Q emulsion, the

change of the deposition yield was not significant. This means that the amount of resin Q in the coemulsion affects deeply the deposition yield of film.

The Composition Analysis of Deposited Film

The resin composition of the deposited film of coemulsion can be determined by calculating the $[-CO-]/[-CH_2-]$ Abs. ratio from the IR spectrum and then comparing this ratio with the
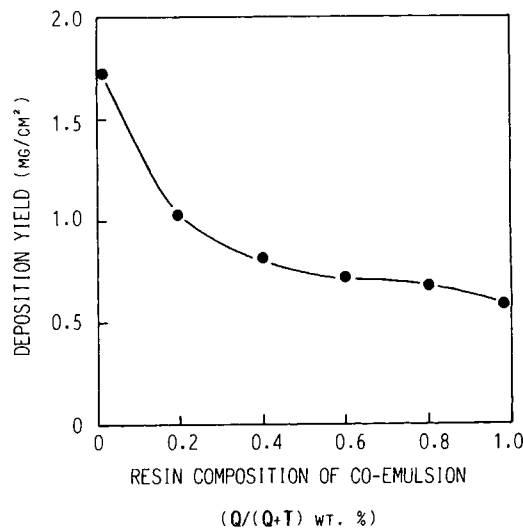
Figure 2   The effect of deposition time on deposition yield; applied voltage: 100 V; deposition time: 3 min.

Figure 4   The effect of resin composition of the coemulsion on deposition yield; applied voltage: 100 V; deposition time: 3 min.

calibration curve (**B** line) already shown in Figure 3. Figure 5 shows the resin composition of coemulsion vs. the resin composition of the deposited film obtained from this coemulsion. It was shown that the content of resin **Q'** in the deposited film is higher than the content of resin **Q** in the coemulsion; in other words, the resin composition of the deposited film is different from the resin composition of its original coemulsion. This result may be caused by the faster electrodeposition rate of resin **Q'**.

Throwing Power and Conductivity

In general, the conductivity of emulsion, contributed mainly by the ionized resin, influences the throwing power remarkably. The higher the conductivity of emulsion, the higher the throwing power. In this study, it was found that the conductivity of the emulsion of pure resin **T**, $Q/(Q + T) = 0$, is higher than that of pure resin **Q**, $Q/(Q + T) = 1$, at the same conditions; thus, the throwing power of pure resin **T** is naturally higher than that of pure resin **Q**, as shown in Figure 6. When the two emulsions were mixed, the throwing power and conductivity of this coemulsion were just between the values of pure resin **T** and resin **Q** and decreased by increasing the content of resin **Q** in the coemulsion.

Rupture Voltage

Rupture voltage is affected by the resin itself and the thickness of the deposited film. Usually, the better the electric insulation of the deposited film or
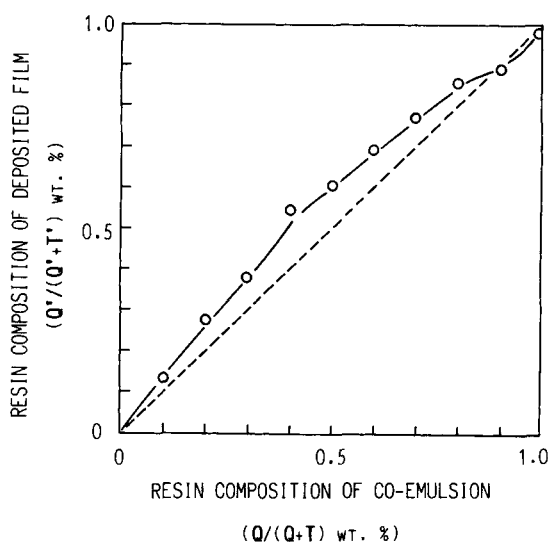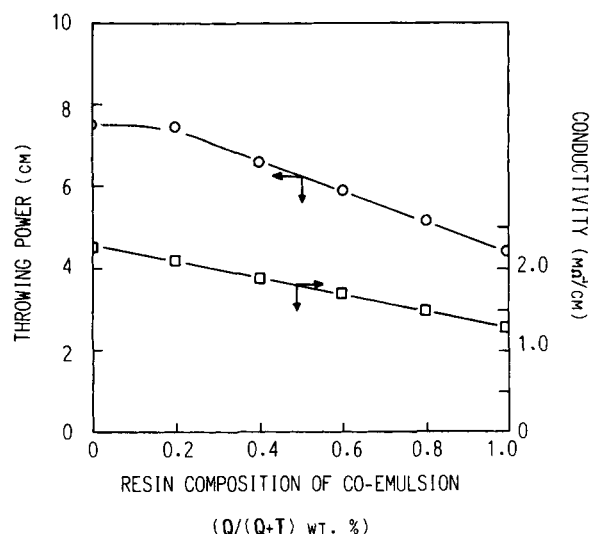

Figure 6   Effects of resin composition of the coemulsion on throwing power (testing conditions: 100 V; 30 s) and bath conductivity.

the thicker the deposited film, the higher the rupture voltage. Figure 7 shows that the rupture voltage of the deposited film of pure resin **T**, $Q/(Q + T) = 0$, is 380 V and that of pure resin **Q**, $Q/(Q + T) = 1$, is 340 V. Therefore, we predict that the rupture voltage of the coemulsion ought to be between 380 and 340 V theoretically. But the result was unusual. It was found that the rupture voltage decreased as the fraction of resin **Q**, $Q/(Q + T)$, in the coemulsion increased from 0 to 0.4 [Fig. 7(A)]. When $Q/(Q + T)$ was 0.4, the rupture voltage was only 240 V, below each of the two rupture voltages (380 and 340 V). But when $Q/(Q + T)$ was over 0.4 [Fig. 7(B)], the rupture voltage began to increase, and until $Q/(Q + T)$ was over 0.8, the rupture voltage was close to 340 V, the same as the rupture voltage of pure resin **Q**. This unusual phenomenon may be concerned with the resin composition and the thickness of deposited film. In Figure 5(A), when $Q/(Q + T)$ was below 0.4, the main content of the deposited film was the tertiary amine resin **T'**, but the deposition yield decreased from 1.7 to 0.8 mg/cm². The main reason for the rupture voltage decreasing even below 340 V was due to the thickness of film becoming thinner, not because of the change of the resin composition of the film. When $Q/(Q + T)$ was over 0.4 [Fig. 5(B)], the distinction of deposition yield was not apparent, but the main content of the film gradually changed to resin **Q'**. The reason for the rupture voltage to increase again may be the change of the resin composition of the deposited film.

Figure 5   Resin composition of the coemulsion vs. resin composition of the deposited film.

Applied Voltage

In general, the deposition yield increases with increasing the applied voltage, as with pure resin **Q** shown in Figure 8. But the deposition yield of pure resin **T** decreased with increasing applied voltage from 50 to 150 V. This result indicates that since the deposition rate of the resin is lower than the hydrolysis rate of water at lower voltage, the gas channels in the deposited film will not be sealed off easily and the wetted film is not electrically insulated completely during the electrodeposition. Therefore, the resin will be deposited continuously. As the applied voltage increases, the gas channels are sealed off easily because of a faster deposition rate and the wetted film in the emulsion bath becomes more electrically insulated immediately. Therefore, the deposition yield will increase no longer. When the coemulsion was formed, the relationship between deposition yield and applied voltage is changed by the resin composition of the coemulsion. For example, at $Q/(Q + T) = 0.2$, the deposition yield of the coemulsion decreased as applied voltage increased. This electrodeposition behavior of the coemulsion was similar to the pure resin **T** emulsion, because at this time, the main content of the coemulsion is resin **T**. At $Q/(Q + T) = 0.5$, the deposition yield increased when the applied voltage increased. This electrodeposition behavior is like pure resin **Q**. This finding indicates that the influ-
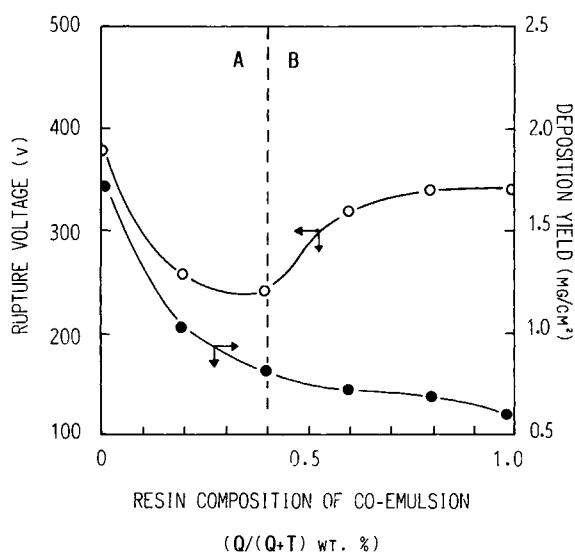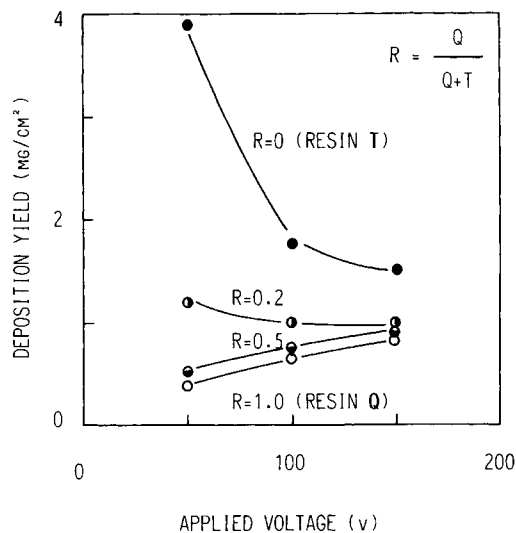

Figure 8 The effect of applied voltage on deposition yield; resin concentration: 10 wt %; BCS content: 3 wt %; deposition time: 3 min.

ence of resin **Q** is more important than that of resin **T** in this two-component system.

CONCLUSION

The conclusions are the following:

1. The quaternary ammonium resin **Q** has better solubility and its dispersion solution can be kept at a stable emulsion pattern at wide pH range. In addition, the deposition yield of its emulsion increases with the increase of deposition time and, finally, up to a limit.
2. For two-component emulsion systems, the resin composition of the deposited film can be investigated by the quantitative analysis of FTIR. The result shows that the resin **Q** content in the deposited film is slightly higher than the resin **Q** content in the original coemulsion.
3. The value of the throwing power of the coemulsion is between the throwing powers of resins **Q** and **T** and is changed by the resin composition. But the rupture voltage has an unusual change because of the influence of both the resin composition and the thickness of the film.
4. The relationship between deposition yield and applied voltage in the coemulsion has completely different results due to the differ-

Figure 7 Effects of resin composition of the coemulsion on (O) rupture voltage and (●) deposition yield, which came from Figure 4.

ent resin compositions of the coemulsion and it was found that resin **Q** plays the more important role in affecting the electrodeposition behavior in the two-component emulsion system.

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