Emulsification and Electrodeposition of Mixtures of Cationic Resins. I. Cationic Resin and Nonionic Cross-Linker

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SYNOPSIS

The emulsification and electrodeposition properties of two resins system (cationic epoxy–amine adduct, III, was the main resin; nonionic trimethylolpropane–toluene diisocyanate-2-ethylhexanol resin, II, was used as cross-linker) were investigated and the compositions of their electrodeposited films were obtained by Fourier transform infrared (FTIR) quantitative analysis to study the coemulsion and electrophoretic behaviors. The optimum resin composition of coemulsion was also found to provide the deposited film having the best properties. The results indicate that the molecules of nonionic cross-linker II are entangled by the ones of cationic resin III during the dispersion process and they can be codeposited on the cathodic substrate after a voltage has been applied. Moreover, at the condition of stable coemulsion of the two-component system, the resin composition of electrodeposited film is almost equal to the resin composition of the coemulsion and is not affected by the applied voltage or resin concentration. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Two or multicomponent cationic coatings[1-9] can provide better storage stability of electrodeposition emulsions and better physical and chemical properties of the electrodeposited film than can one-component systems.[10-18] In previous papers,[1-9] most of the cross-linkers for two-component cationic coatings were uncharged resins; however, the codeposition behavior of uncharged cross-linker and cationic resin is not well understood. In our previous studies,[19,20] two-component electrodepositable resins containing a cationic main resin and a cationic cross-linker were synthesized; in the meantime, the resin composition of their electrodeposited film were determined by FTIR quantitative analysis to investigate their electrophoretic behavior. The results indicate that the resin composition of deposited film is affected by the individual deposition velocity of the cationic main resin and cationic cross-linker.

In this work, a nonionic cross-linker **II**, TMP–TDI–2EH resin, and a cationic main resin **III**,

amine–epoxy adduct, were synthesized. The coemulsion and electrodeposition properties of this two-component system and the compositions of their electrodeposited film determined by FTIR quantitative analysis were obtained to study the coemulsion and electrophoretic behaviors. Moreover, the optimum resin composition of coemulsion was also found that gave deposited film with the best properties.

EXPERIMENTAL

Materials

Reagents used in the preparation of TMP–TDI–2EH resin (**II**) included 2-ethylhexanol (2EH, Wako extrapure grade), trimethylolpropane (TMP, Merck reagent pure grade), and toluene-2,4-diisocyanate (TDI).

Reagents used in the preparation of di(2-methyl isobutyl ketiminoethyl)amine (DKI) include reagent pure grade of diethylene triamine (DETA), methyl isobutyl ketone (MIBK, Hayashi reagent pure grade), and 50w-x8 ion-exchange resin (Merck). The detailed synthetic procedures were described in the previous publication.[15]

Epon 1004 (diglycidyl ether of bisphenol A, commercially available from Shell Chemical Co. and possessing an epoxy equivalent weight of about 950), diethylamine, diethanolamine, methylethanolamine (Hanawa extrapure grade), and DKI were used in the preparation of epoxy–amine adduct (III).

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

Instruments

An electrodeposition apparatus[18] 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^2 were hung. 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. After deposition, the aluminum plate was rinsed with distilled water and dried for 30 min in an air-circulating oven at 100°C, then reweighed to obtain the deposition yield of deposited film (mg/cm^2).

Synthesis

TMP–TDI–2EH Resin (II)

In a three-necked reaction vessel, a half-blocked TDI was prepared by slowly adding 2EH (74.9 g, 0.576 mol) to TDI (100 g, 0.576 mol) over a period of about 40 min below 10°C. At the completion of addition, the batch was kept below 20°C for an additional 40 min and then heated to 40°C and held for 1 h. The trimethylolpropane (25.7 g, 0.192 mol) was added portion by portion after the reaction temperature was heated to 60°C. At the completion of addition, an additional 1 h at 120°C was held to give the TMP–TDI–2EH resin (II).

Epoxy–Amine Adduct (III)

An epoxy resin (Epon 1004, 100 g) and toluene (100 mL) were charged into a three-necked flask, then heated to 80°C to dissolve the epoxy resin. The mixture of methylethanolamine (6.3 g, 0.084 mol) and DKI (5.67 g, 0.021 mol) was added and the whole mixture was kept at the temperature for about 2.5 h to give the resin solution of epoxy–amine adduct (III) in toluene. Finally, toluene was distilled off under reduced pressure. When cooled to room temperature, a golden, brittle solid of resin III was obtained.

Electrodeposition and Quantitative Analysis

Calibration Curve

II and III resins with various weight ratios were mixed and well dissolved in THF, then coated on potassium bromide (KBr) windows and dried. The dried films were analyzed in the absorbance mode and at a resolution of 4 cm^{-1} by signal averaging 16 scans. The absorbance areas of carbonyl group [C=O] (at approximately 1900–1650 cm^{-1}) and hydrocarbon [CH] stretching vibration (at approximately 3000–2700 cm^{-1}) were calculated and recorded. The [C=O]/[CH] absorbance area ratio (abs. ratio) were plotted against the II/(II + III) 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 at the same testing conditions as described above to get the [C=O]/[CH] abs. ratio. From the [C=O]/[CH] abs. ratio and calibration curve, we can obtain the resin composition of electrodeposited film.

Gel Content

A 40 wt % solid content solution, prepared by dissolving and mixing II and III in THF, was spread on aluminum foil and baked at 180°C for 40 min in an air oven to form a cross-linked film. The cross-linked 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 cross-linked film.

Preparation of Electrodeposition Emulsion

The general process for the preparation of coemulsion of II and III involved, first, the dilution of mixed resins (II 5 g, III 5 g) with 4 g BCS to a solution with 71 wt % solid content, and then the solution was treated with 0.5 mL HOAc (about 90 mol % of the total theoretical neutralization) and dispersed in 86 g deionized (D.I.) water to form a coemulsion 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°C to obtain the deposition yield.

RESULTS AND DISCUSSION

Synthesis of TMP–TDI–2EH Resin (II) and Epoxy–Amine Adduct (III)

The resins of two-component cationic coatings in reported patents generally consist of a nonionic cross-linker and a cationic main resin; however, their codeposition behavior is not well understood. In this work, the nonionic cross-linker II (TMP–TDI–2EH resin) and cationic main resins III (amine–epoxy adducts) were synthesized. These resins can be dissolved in BCS and treated with acetic acid to codisperse in D.I. water to form emulsion. The synthetic procedures of resins II and III are shown in Scheme 1.

Emulsification and Electrodeposition Properties of Resins II and III

Preparation of Stable Emulsion

The states of aqueous dispersion of resins II and III in deionized water are shown in Table I. Resin II, containing no hydrophilic group, is difficult to dissolve in water. It requires a lower resin concentration and higher BCS content to make resin II easier to be solubilized or dispersed in water (see Table I, nos. 1 and 2). Resin III, containing tertiary amine groups, can be neutralized with acetic acid to yield cationic resin, whereas cationic resin can be soluble in water or other hydrophilic solvents. The characteristics of cationic resin, pH value, resin concentration, and BCS content determine the dispersibility of the resin and, hence, they will affect the state of emulsion. The order of solubilities of resins III in aqueous dispersions is III-d > III-b, c > III-a, as shown in Table I (nos. 3–14). This is because the solubilities of resins III in aqueous solution depend on the degree of hydrophilicity of their end groups. Resin III-d, containing DKI that can be hydrolyzed to generate primary amine groups, has the best solubility; moreover, because of the hydrophilic terminal hydroxyl groups, the solubilities of resins III-b and III-c in aqueous systems are better than that of III-a. In conclusion, for resins III with a resin concentration of 10 wt %, stable emulsions are obtained when the resin concentration of the

solution is kept at 10 wt %, BCS content at 4 wt %, and pH 4.9–5.1. For III-a, precipitation occurs when the BCS content is lower than 4 wt %, and for III-d, the aqueous dispersion appears to be in solution when the BCS content is higher than 4 wt %.

Electrodeposition of Emulsions

The effects of resin concentration on deposition yield of emulsions of resins III are shown in Figure 1. The deposition yield increases with increasing resin concentration of the emulsion. At the same resin concentration, the order of deposition yields of emulsions prepared from resins III is III-d > III-a > III-b,c. This is because resin III-d containing primary amine group will form more charged groups during the neutralization process, resulting in the highest deposition yield. Moreover, III-b and III-c, which contain hydrophilic hydroxyl end groups, improve the redissolving tendency of deposited films and have lower deposition yields than that of III-a. The emulsions prepared from II have no deposition yield at various resin concentration because there is no charged group in its polymer chain.
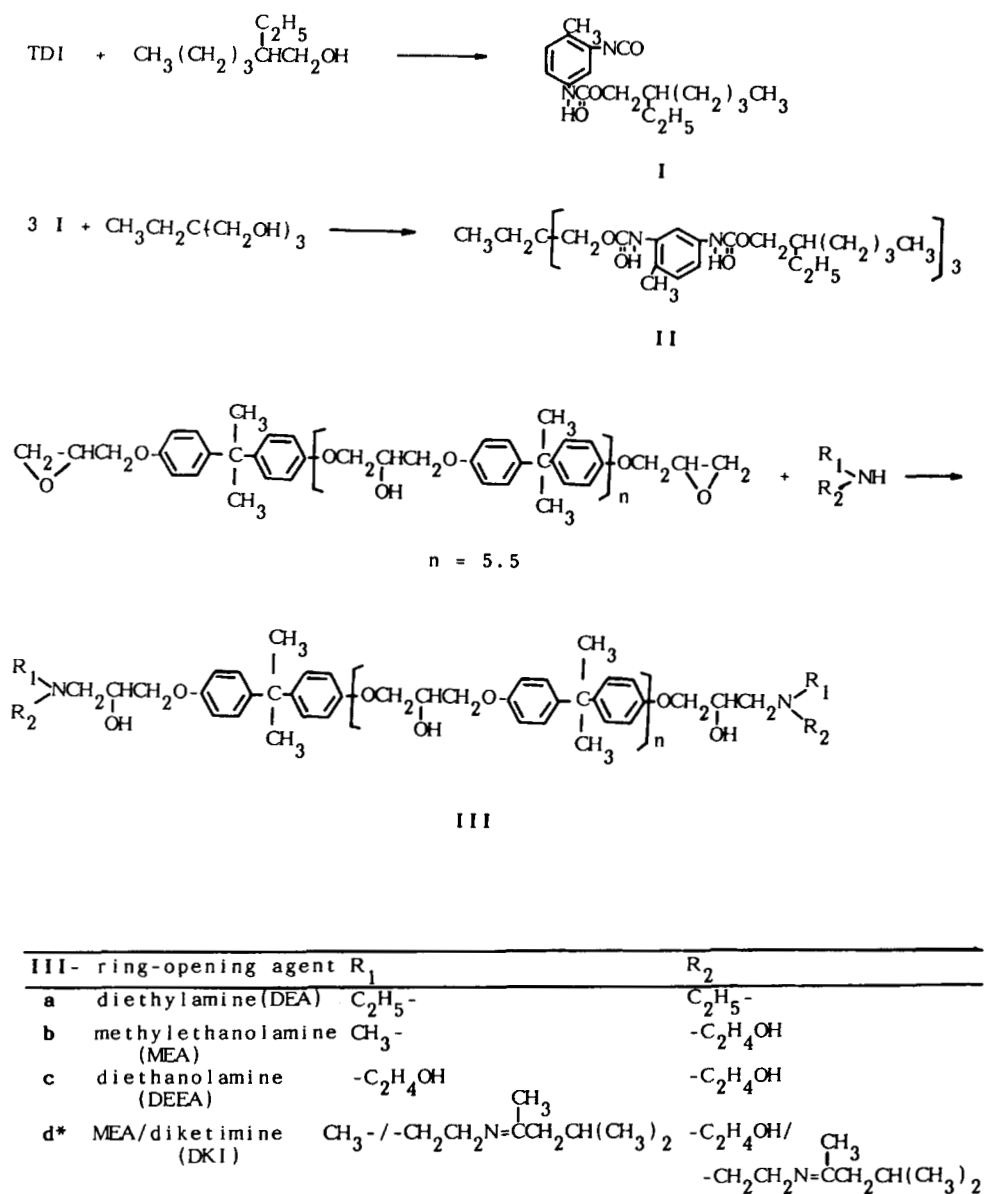
Properties of Mixtures of Cationic Resins and Nonionic Cross-Linker

Calibration Curve

The resins of two-component emulsions containing the nonionic cross-linker II have the IR absorption of carbonyl [C=O] and hydrocarbon [CH] groups, and the polyol type resin III have [CH] IR absorption. The strong [C=O] peak appears at 1700 cm^{-1} and the peak of [CH] stretching vibration appears at 2900 cm^{-1}. Resins II and III with various weight ratios were well mixed and dissolved in THF, then spread on KBr windows and dried. The samples were analyzed by IR spectroscopy. The absorbance areas of the [C=O] stretching band (at approximately 1900–1650 cm^{-1}) and the [CH] stretching vibration band (at approximately 3000–2700 cm^{-1}) were calculated. The [C=O]/[CH] ratios of the absorbance area were plotted against II/(II + III) weight ratios to give the calibration curve, as shown in Figure 2. It shows that the [C=O]/[CH] abs. ratio increases with increasing content of resin II.

Gel Content of II/III Mixed Film

The II/III mixed films with various weight ratios were cured at 180°C for 40 min. The effects of the blocked —NCO group/— OH group molar ratio of the mixed film on gel content are shown in Figure

$$TDI \ + \ CH_3(CH_2)_3\overset{\overset{\displaystyle C_2H_5}{|}}{C}HCH_2OH \ \longrightarrow$$

(structure **I**)

$$3 \ I \ + \ CH_3CH_2C(CH_2OH)_3 \ \longrightarrow$$

(structure **II**)

n = 5.5

(structure **III**)

III-	ring-opening agent	R_1	R_2
a	diethylamine (DEA)	C_2H_5-	C_2H_5-
b	methylethanolamine (MEA)	CH_3-	$-C_2H_4OH$
c	diethanolamine (DEEA)	$-C_2H_4OH$	$-C_2H_4OH$
d*	MEA/diketimine (DKI)	$CH_3-/-CH_2CH_2N=\overset{\overset{\displaystyle CH_3}{|}}{C}CH_2CH(CH_3)_2$	$-C_2H_4OH/ -CH_2CH_2N=\overset{\overset{\displaystyle CH_3}{|}}{C}CH_2CH(CH_3)_2$

*MEA/DKI = 4/1 (by mole)

Scheme 1

3. Theoretically, the blocked —NCO/—OH molar ratio of cured film having the best gel content is 1.0 (i.e., one free —NCO group reacted with one —OH group during curing). However, from Figure 3, it shows that the —NCO/—OH molar ratio of mixed film having the best gel content is at about 0.55–0.65 (i.e., **II/III** weight ratios are between 4.5/5.5 and 5/5). It appears that some hydroxyl groups are not reacted with —NCO groups under this condition.

States of Aqueous Codispersion of Mixtures of Resins II/III

The factors affecting the codispersion state of cationic resins in D.I. water, as described above, are pH, BCS content, resin concentration, and the nature of cationic resin. For the mixture of resins **II/III**, **III** have hydrophilic groups (amine salt which is formed by treating **III** with acetic acid), but **II** has no hydrophilic group, so the composition of **II**/

Table I   The Effect of Resin Composition on Properties of Aqueous Dispersion

No.	Resin	Resin Concentration (wt %)	BCS Content (wt %)	Resin Composition[a]	pH	Remarks
1	II	2	4	—	5.60	P[b]
2	II	2	10	—	5.67	E[c]
3	III-a	10	2	—	4.87	P
4	III-a	10	4	—	4.90	E
5	III-a	10	6	—	4.84	E
6	III-b	10	2	—	4.95	E
7	III-b	10	4	—	5.03	E
8	III-b	10	6	—	5.04	E
9	III-c	10	2	—	5.05	E
10	III-c	10	4	—	5.06	E
11	III-c	10	6	—	5.01	E
12	III-d	10	2	—	5.20	E
13	III-d	10	4	—	5.17	E
14	III-d	10	6	—	5.18	S[d]
15	II/III-a	10	4	0.3	5.03	E
16	II/III-a	10	4	0.4	5.00	P
17	II/III-b	10	4	0.1	5.05	E
18	II/III-b	10	4	0.4	4.97	E
19	II/III-b	10	4	0.5	5.04	P
20	II/III-c	10	4	0.1	4.97	E
21	II/III-c	10	4	0.4	5.05	E
22	II/III-c	10	4	0.5	5.02	P
23	II/III-d	10	4	0.5	5.18	E
24	II/III-d	10	4	0.6	5.15	E
25	II/III-d	10	4	0.7	5.23	P

[a] Resin composition: II/II + III, by weight.
[b] P: precipitate.
[c] E: emulsion.
[d] S: solution.

III also plays an important part in affecting the codispersion state. The lower content of II in the aqueous codispersion favors the attainment of a stable emulsion. Table I shows the effects of resin composition (II/II + III, by weight) on the codispersion state. For II/III-a (nos. 15 and 16), the aqueous codispersion is a stable emulsion when the resin composition (II/II + III, by weight) is lower than 0.4, but precipitation occurs when the resin composition is higher than 0.4. For aqueous codispersions of II/III-b, II/III-c (nos. 17–22), and II/III-d (nos. 23–25), the maximum values of resin compositions for forming stable coemulsion are about 0.5 and 0.7. This fact shows that molecules of nonionic II are entangled by molecules of resins III to codisperse in D.I. water. Thus, the order of hydrophilic nature of resin III and the tendency of forming stable coemulsion of II/III are the same (i.e., III-d > III-b, c, > III-a).

Electrodeposition of II/III Coemulsion

Effect of Applied Voltage on Deposition Yield

The effects of applied voltage on deposition yield of II/III-d coemulsion are shown in Figure 4. The deposition yield of coemulsion is almost directly proportional to the applied voltage. Meanwhile, at the same resin concentration of 10 wt %, the deposition yield of II/III-d coemulsion is higher than that of the III-d emulsion alone. This may be due to the effects of redissolution and equivalent weight per charged resin unit.
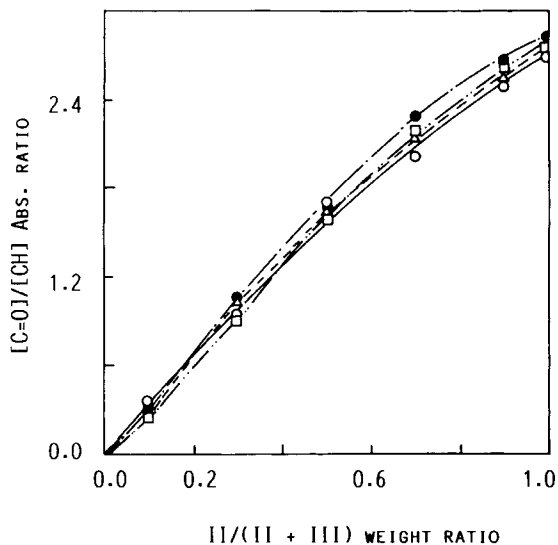
Effect of Resin Concentration on Deposition Yield

At the resin composition (II/III-d, by weight) of 1/1 and 2/3, the effects of resin concentration on deposition yield are shown in Figure 5. At conditions providing stable coemulsions, as expected, the de-
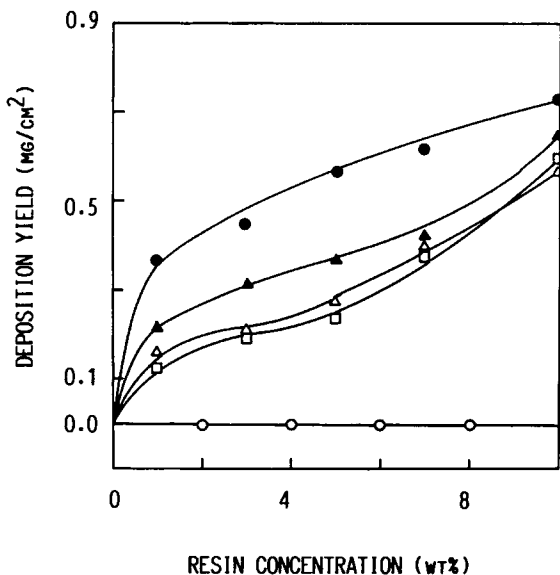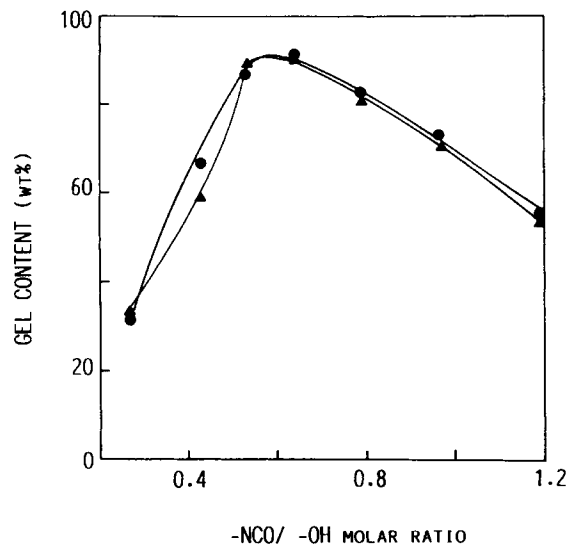
Figure 1 The effects of resin concentration on deposition yield of emulsions of resins III and II. applied voltage: 50 V; deposition time: 3 min; BCS: 4 wt %; (▲) III-a, pH 5.0; (□) III-b, pH 5.1; (△) III-c, pH 5.1; (●) III-d, pH 5.2; (○) II, pH 5.6.

Figure 3 The effects of — NCO/— OH molar ratio on gel content: (●) II/III-d; (▲) II/III-b.

position yield increases with increasing resin concentration; however, at a higher concentration (e.g., 15 wt %), the aqueous dispersion precipitates and

gives a lower deposition yield. Figure 5 also shows that the deposition yield of coemulsion containing higher "II" composition is higher than that of coemulsion containing lower "II" composition. The reason here is similar to the reason given for Figure

Figure 2 The relationship between $II/II + III$ weight ratio and $[C=O]/[CH]$ abs. ratio: (— O —) II/III-a; (···△···) II/III-b; (–··–□–··–) II/III-c; (–· ● ·–) II/III-d.
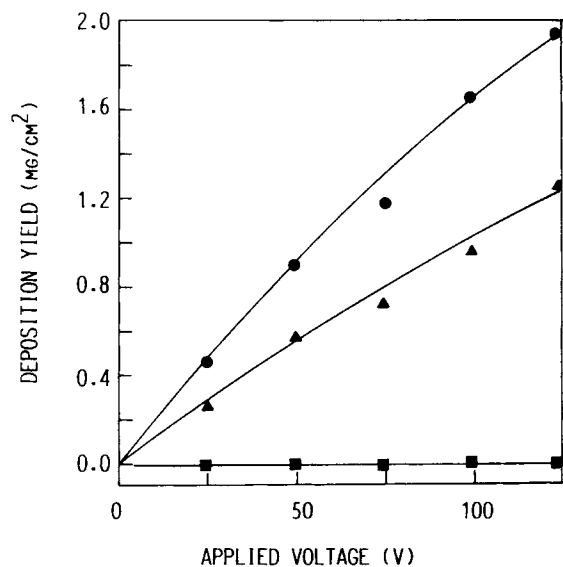
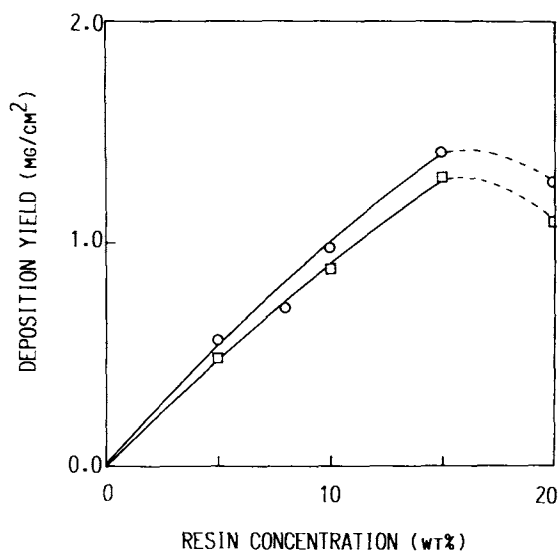**Figure 4** The effects of applied voltage on deposition yield of II/III-d coemulsion and III-d emulsion: deposition time 3 min; resin concentration: 10 wt %; BCS content: 4 wt %; (●) II/III-d weight ratio = 1, pH 5.2; (▲) III-d, pH 5.2; (■) II, pH 5.0.

Figure 5   The effects of resin concentration on deposition yield of **II/III-d** coemulsion: applied voltage: 50 V; deposition time: 3 min; BCS content: 4 wt %; pH 5.2; (———) stable emulsion; (- - - - -) unstable emulsion; (○) **II/III-d** = 1/1 (by weight); (□) **II/III-d** = 2/3 (by weight).
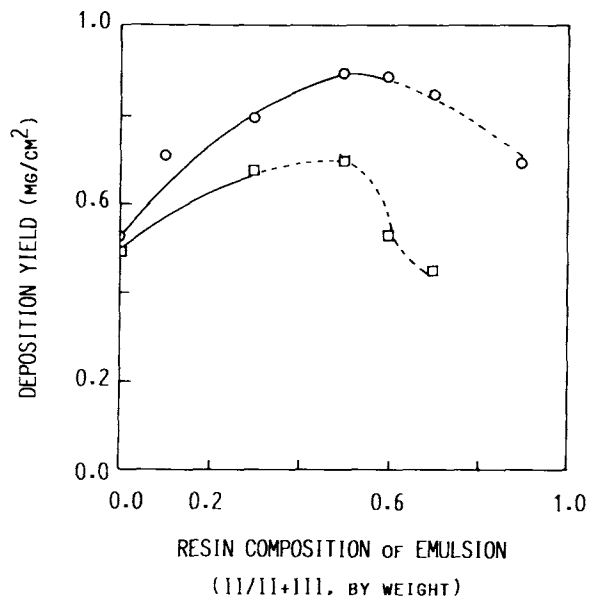

Figure 6   The effects of coemulsion resin composition on deposition yield: applied voltage: 50 V; deposition time: 3 min; BCS content: 4 wt %; pH 5.0; (○) **III-d**; (□) **III-a**; (———) stable emulsion; (- - - - -) unstable emulsion.

4, i.e., due to the effect of redissolving and equivalent weight per charged resin unit.

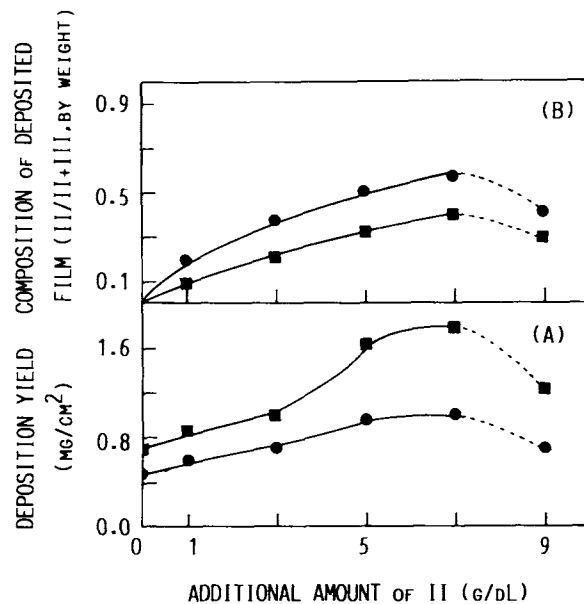## Effect of Resin Composition of Coemulsion on Electrodeposition Yield

At a constant resin concentration of 10 wt %, the effects of coemulsion resin composition on deposition yield are shown in Figure 6. The deposition yield of coemulsion increases with increasing level of **II** and gradually goes to a limit. When levels of **II** are greater than the limit, the deposition yield decreases because of the formation of precipitation. At conditions providing stable emulsions, increasing the level of **II** decreases the amount of charged molecules but increases the equivalent weight per charged resin unit. So, the effect of equivalent weight per charged resin unit on deposition yield is larger than the effect of charged molecules on deposition yield.

Effects of Adding II in III-d Emulsions on the Deposition Yield and Resin Composition of Deposited Film

At a constant concentration of **III-d,** the effects of an additional amount of **II** on the deposition yield and resin composition of deposited film are shown in Figure 7. At additional "**II**" concentrations providing stable coemulsions, the deposition yield and
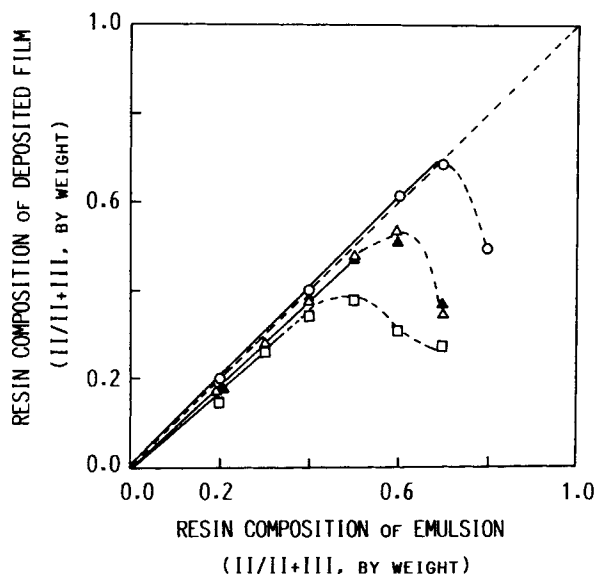

Figure 7   The effects of adding **II** in **III-d** emulsion on the deposition yield and composition of deposited film: applied voltage: 50 V; deposition time: 3 min; BCS content: 4 wt %; pH 5.10–5.20; (———) stable emulsion; (- - - -) unstable emulsion; (●) **III-d** emulsion with a constant "**III-d**" concentration of 5 g/dL; (■) **III-d** emulsion with a constant "**III-d**" concentration of 10 g/dL.
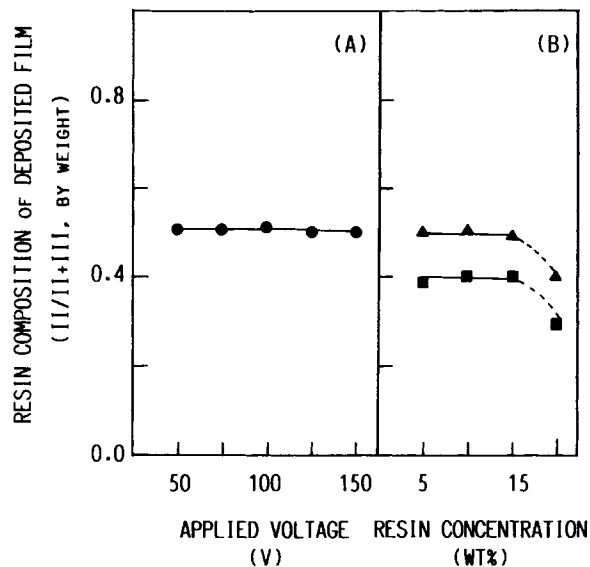
resin composition of deposited films increase with increasing additional amount of **II**; too high an additional "**II**" concentration causes coagulation and precipitation of **II** and lowers the level of **II** in the deposited film. It shows that the molecules of nonionic **II** are entangled by the ones of charged **III** to codeposit on the cathodic substrate.

Effect of Coemulsion Resin Composition on the Composition of Deposited Film

At a constant resin concentration of 10 wt %, the effects of coemulsion resin composition on the resin composition of electrodeposited film are shown in Figure 8. It shows that at conditions providing stable emulsions the amount of **II** in the electrodeposited film increases with increasing "**II**" content in the coemulsion. The "**II**" content in the electrodeposited film is close to the value of ideal blending (the diagonal line of Fig. 8, supposing that the resin composition of coemulsion equals the resin composition of electrodeposited film). However, too high a "**II**" content causes precipitation of **II** and makes the "**II**" content in the deposited film lower than the "**II**" content of coemulsion. According to the hydrophilic level of resins **III**, for forming stable coemulsions and making the resin composition of coemulsion equal to that of deposited film, the maximum "**II**" contents for **III-a, III-b** (or **III-c**), and **III-d** are 0.4, 0.5, and 0.7, respectively.

Figure 8 The effects of emulsion resin composition on the resin composition of deposited film: applied voltage: 50 V; deposition time: 3 min; resin concentration: 10 wt %; BCS content: 4 wt %; pH 5.10; (□) **II/III-a**; (○) **II/ III-b**; (△) **II/III-c**; (▲) **II/III-d.**

Figure 9 The effects of applied voltage and resin concentration on the resin composition of deposited film: applied voltage: 50 V; deposition time: 3 min; BCS content: 4 wt %; pH 5.10–5.20; (——) stable emulsion (-----) unstable emulsion; (●) **II/III-d** = 1 (by weight); (▲) **II/ III-d** = 1 (by weight); (■) **II/III-d** = 2/3 (by weight).

From Figure 3 and 8, the optimum resin compositions of coemulsions for obtaining better gel content of deposited films are between 4.5/5.5 and 5/5 (**II/III-d**, by weight) (i.e., the wt % of **II/II** + **III-d** are between 40 and 50).

Effects of Applied Voltage and Resin Concentration on the Resin Composition of Deposited Film

The effects of applied voltage and resin concentration on the resin composition of electrodeposited film are shown in Figure 9. Figure 9(A) shows that the emulsion micelles are not broken up at voltages applied from 0 to 150 V so that the resin composition of deposited film will not change at these voltages.

Figure 9(B) shows that at conditions providing stable coemulsions resins **II/III** can be uniformally codispersed in D.I. water and can keep the resin composition of electrodeposited film constant. However, when the total resin concentration goes beyond a limit, the hydrophobic **II** coagulates to cause precipitation and lowers the resin composition of electrodeposited film.

CONCLUSIONS

1. The deposition yield of emulsion of ionic **III** increases with increasing the applied voltage

and resin concentration. The deposition yield of emulsion of nonionic **II** is zero.

2. The deposition yield of **II/III-d** coemulsion increases with increasing total resin concentration, and at the same resin concentration, its value is higher than that of individual **III-d** emulsion.

3. At constant "**III-d**" concentration, the deposition yield of coemulsion increases with increasing "**II**" concentration. This is because the nonionic **II** is entangled by the charged **III** to codeposit on the cathodic substrate.

4. Under stable coemulsion conditions, the resin composition of electrodeposited film is not affected by the applied voltage or resin concentration.

5. Under stable coemulsion conditions, the resin composition of deposited film is almost equal to the coemulsion resin composition.

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