Coemulsion and Electrodeposition Properties of Mixtures of Cationic Epoxy Resin and Cationic Acrylic Resin Containing Butoxymethylamide Groups

CHIN-PING YANG* and YAHN-HAUR CHEN

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

SYNOPSIS

Butyl acrylate, styrene, N,N-dimethylaminoethylmethacrylate, and N-(n-butoxymethyl)acrylamide were copolymerized to prepare a cationic acrylic copolymer (I) containing butoxymethylamide groups. This copolymer can be mixed with an epoxy–amine adduct (II), acetic acid, and deionized (D.I.) water to form a coemulsion containing two cationic resins. The electrophoretic codeposition of the coemulsion and physical and chemical properties of the deposited film were investigated. The resin composition of film deposited from coemulsion was determined by Fourier transform Infrared (FTIR) quantitative analysis to study the coemulsion and electrophoretic codeposition behavior. The applicability of this two-component coemulsion in primer–surfacer (pricer) electrodeposition paint was also discussed. The results indicate that at any coemulsion resin composition the resin composition of electrodeposited film is almost equal to the coemulsion resin composition. The throwing power of emulsion increases with increasing applied voltage, as expected. However, the throwing power of coemulsion is almost equal to that of the II emulsion but greater than that of the I emulsion. Furthermore, all cured films derived from mixtures of I/II show excellent adhesive strength, good hardness, and high levels of salt spray resistance. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Electrodeposition has become increasingly important in the coating industry because it offers higher paint utilization, stronger throwing power, better corrosion protection, lower environmental contamination, definitely smoother coverage, and better adaptability to the automatic process when compared with nonelectrophoretic coatings.

Since the Ford Motor Co. first commercially applied anionic electrodeposition, the process has been used almost universally in such high-value coating operations as priming motor cars, electrical appliances, and many other commercial articles.

Cationic resins are polymers with basic moieties in the form of primary,[1,2] secondary, or tertiary amines,[3,4] or quaternary ammonium,[5,6] sulfonium,[7,8]

or phosphonium groups,[9,10] neutralized with organic acids. The most frequently used cationic resins include acrylic copolymers,[11,12] epoxy resins and their copolymers,[13,14] and polyurethanes.[15,16] Epoxy resins and their copolymers offer higher levels of corrosion resistance and, hence, have been adopted to provide the first or prime coat to a variety of products such as automotive bodies. Acrylic copolymers provide better weather resistance and outstanding gloss, suitable for application as topcoats.

In our previous studies,[17] the composition of films electrodeposited from the coemulsion of cationic epoxy resin and nonionic blocked toluene diisocyanate cross-linker were determined by FTIR quantitative analysis to investigate their electrophoretic behavior. The results indicate that, under the conditions providing stable coemulsion, the composition of electrodeposited film is almost equal to the resin composition of the coemulsion. However, the electrophoretic codeposition properties of mixtures of cationic epoxy resin and cationic acrylic

resin are not well understood. In this study, a cat-ionic acrylic resin containing butoxymethylamide groups and a cationic epoxy–amine adduct containing hydroxyl groups were mixed and their coemulsion was electrodeposited to obtain a primer–surfacer ("pricer") paint providing higher levels of corrosion resistance and weather resistance. Furthermore, the composition of film deposited from this coemulsion was determined by FTIR to determine the codeposition and coemulsion behavior.

EXPERIMENTAL

Materials

Monomers used in the preparation of cationic acrylic copolymer **I** included butyl acrylate (BA), styrene (ST), N,N-dimethylaminoethylmethacrylate (DMAEMA), and N-(n-butoxymethyl)acrylamide (NBMA) (Wako first grade). Epon 1004 [poly (glycidyl ether of bisphenol A), commercially available from Shell Chemical Co. and possessing an epoxy equivalent weight of about 950] and diethylamine (Hanawa extrapure grade) were used in the preparation of epoxy–amine adduct **II**. Ethylene glycol mono-n-butyl ether (butyl cellosolve, BCS) (Wako EP 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 the anode) and aluminum plate (the cathode), with a surface area of about 30 cm^2, were hung. Approximately 300 mL of the 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 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

Cationic Acrylic Resin I'

n-Butanol (50 g) was first charged into a reactor equipped with a condenser, stirrer, thermometer, dropping funnel, and inert nitrogen blanket. The reactor was heated to 110°C and then the mixture of n-butanol (50 g), ST (20.8 g, 0.2 mol), BA (76.8 g, 0.6 mol), DMAEMA (31.4 g, 0.2 mol), NBMA (31.6 g, 0.2 mol), and 2,2'-Azobisisobutyronitrile (AIBN) (2.4 g, about 1.5 wt % of the total monomers amount) was added by dropping a funnel over a 3 h period. At the completion of addition, the reaction was allowed to continue at 110°C. During reaction, the conversion and viscosity of the intermediate were tested at 1 h intervals. The conversion was determined by distilling the particular sample at 80°C under reduced pressure to remove n-butanol and unreacted monomers. More than 9–10 h, including the time of adding monomers, was needed to make the conversion approach 100%. After the reaction, n-butanol was removed under reduced pressure to give a viscous acrylic copolymer **I'** containing butoxymethylamide and tertiary amine groups.

Epoxy–Amine Adduct II'

An epoxy resin (Epon 1004) (250 g, 0.132 mol) and toluene (150 mL) were charged into a three-necked flask. The mixture was heated to 80°C to dissolve the epoxy resin. Diethylamine (19.25 g, 0.263 mol) was then added into the flask. The whole mixture was kept at that temperature for about 2–3 h until no free epoxy groups (IR spectrum [910 cm^{-1}]) were evident to give the resin solution of the epoxy–amine adduct (**II'**) in toluene. Finally, toluene was distilled off under reduced pressure. When cooled to room temperature, a golden, brittle solid of the epoxy–amine adduct (**II'**) was obtained.

Preparation of Electrodeposition Emulsion

The general process for the preparation of coemulsion of the **I/II** mixture involved, first, the dilution of the mixed resins (**I'**, 25 g; **II'**, 25 g) with 20 g BCS at 60°C to a solution with 70 wt % solid content, and treatment of the solution with 2.25 mL HOAc (about 90% of the total theoretical neutralization) followed by dispersion in 430 g deionized (D.I.) water to form a cationic coemulsion of 10 wt % solid content.

Electrodeposition

Approximately 300 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 heated to 120°C to obtain the deposition yield (mg/cm^2).

FTIR Quantitative Analysis

Calibration Curve

Resins I' and II' with various weight ratios were well mixed and 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] stretching band (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 ratios (Abs. ratio) were plotted against I'/(I'+II') 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 obtain the [C=O]/[CH] Abs. ratio. From the [C=O]/[CH] Abs. ratio and calibration curve, we can obtain the resin composition of the electrodeposited film.

Gel Content

A 40 wt % solids content solution, prepared by dissolving and mixing I' and II' resins in THF, was spread on aluminum foil and baked at 190°C for 40 min in an air oven to form a cross-linked 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 the cross-linked film.

Throwing Power and Rupture Voltage

The throwing power of emulsion was determined by the tube penetration test method. The apparatus and testing procedures of throwing power and rupture voltage were described previously.[18]

RESULTS AND DISCUSSION

Synthesis of Cationic Acrylic Copolymer (I) and Epoxy–Amine Adduct (II)

The mixture of monomers of ST, BA, DMAEMA, and NBMA was charged into the reactor by a dropping funnel over a period of 3 h at 110°C to prepare an acrylic copolymer I' containing butoxymethyl-amide groups. During the reaction, the conversion

and viscosity of intermediate were tested at 1 h intervals. Effects of reaction time on conversion and viscosity of the intermediate are shown in Figure 1. More than 9–10 h was needed to make the conversion approach 100%. The viscosity of product increased with increasing reaction time in the initial 9 h. The acrylic copolymer I' can be mixed with acetic acid to form the cationic acrylic resin I. The synthetic procedures for cationic I and epoxy–amine adduct II' are shown in Scheme 1.

Electrodeposition Yields of Resins I and II Emulsions

The relationships between deposition time and deposition yield of resins I and II are shown in Figure 2. For resin II, 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 I, the deposition yield does not reach a limiting value within 3–4 min. At the same deposition time, the deposition yield of I is greater than that of II, i.e., the deposition velocity of I is faster than that of II.

The Properties of the Mixture of I/II

Gel Content

Figure 3 shows the effect of composition of I'/II' mixed film on its gel content after thermal curing. It shows that the gel content is greater than 95% when the composition of mixed film (I'/I'+II', by

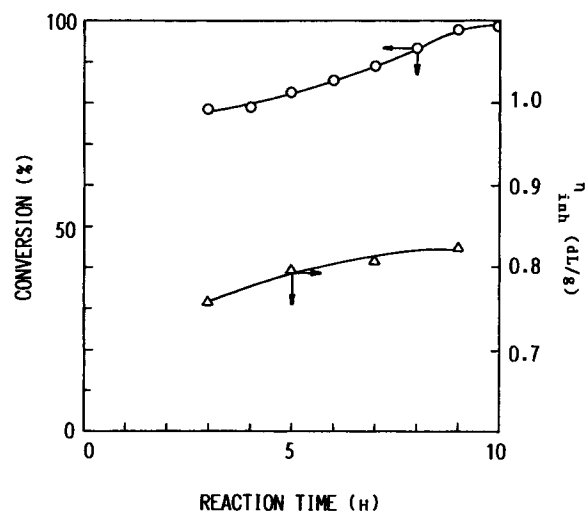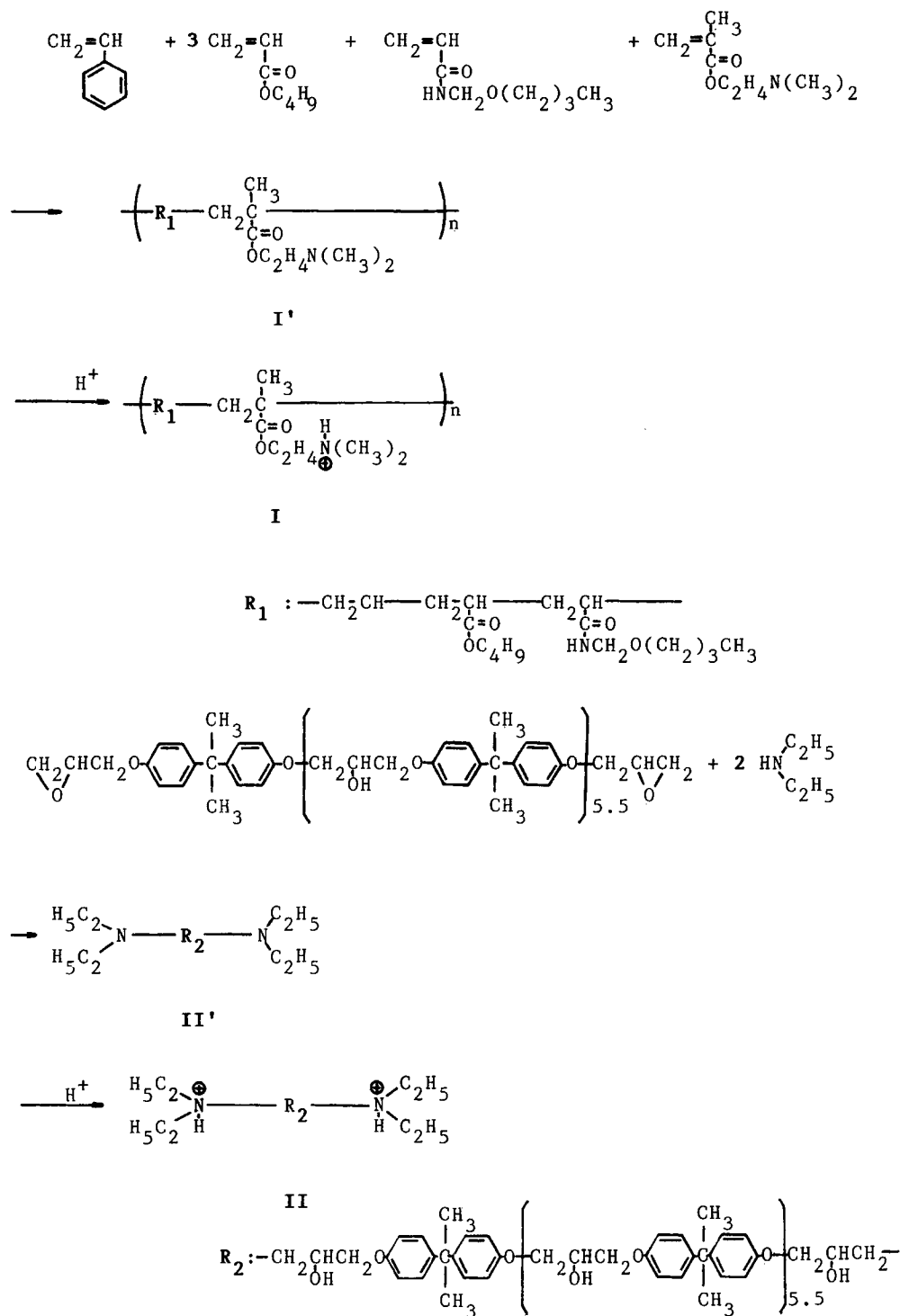**Figure 1** Conversion and viscosity of acrylic copolymer vs. reaction time during copolymerization. Reaction temperature: 110°C.

$$CH_2=CH \quad + \ 3\ CH_2=CH \quad + \ CH_2=CH \quad + \ CH_2=C$$

(phenyl ring) $\overset{|}{C}=O$ $\overset{|}{C}=O$ $\overset{CH_3}{\underset{C=O}{|}}$

OC_4H_9 $HNCH_2O(CH_2)_3CH_3$ $OC_2H_4N(CH_3)_2$

$$\longrightarrow \quad \left(R_1 - CH_2\overset{CH_3}{\underset{C=O}{\overset{|}{C}}} \right)_n$$

$OC_2H_4N(CH_3)_2$

I'

$$\overset{H^+}{\longrightarrow} \quad \left(R_1 - CH_2\overset{CH_3}{\underset{C=O}{\overset{|}{C}}} \quad \overset{H}{} \right)_n$$

$OC_2H_4\overset{\oplus}{N}(CH_3)_2$

I

$R_1 : -CH_2CH - CH_2CH - CH_2CH-$

$\overset{|}{C}=O \quad \overset{|}{C}=O$

$OC_4H_9 \quad HNCH_2O(CH_2)_3CH_3$

$$CH_2CHCH_2O-\text{(ring)}-\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}-\text{(ring)}-O\left[CH_2\overset{OH}{\underset{|}{CH}}CH_2O-\text{(ring)}-\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}-\text{(ring)}-O\right]_{5.5}CH_2CHCH_2 \ + \ 2\ HN\overset{C_2H_5}{\underset{C_2H_5}{}}$$

$$\longrightarrow \quad \overset{H_5C_2}{\underset{H_5C_2}{}}N - R_2 - N\overset{C_2H_5}{\underset{C_2H_5}{}}$$

II'

$$\overset{H^+}{\longrightarrow} \quad \overset{H_5C_2}{\underset{H_5C_2}{}}\overset{\oplus}{\underset{H}{N}} - R_2 - \overset{\oplus}{\underset{H}{N}}\overset{C_2H_5}{\underset{C_2H_5}{}}$$

II

$R_2: -CH_2\overset{OH}{\underset{|}{CH}}CH_2O-\text{(ring)}-\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}-\text{(ring)}-O\left[CH_2\overset{OH}{\underset{|}{CH}}CH_2O-\text{(ring)}-\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}-\text{(ring)}-O\right]_{5.5}CH_2\overset{OH}{\underset{|}{CH}}CH_2-$

Scheme 1

weight) is higher than 0.6 (molar ratio of butoxy-methylamide groups contained in **I'** and hydroxyl groups contained in **II'** is equal to 0.65 as the composition of the mixed film is equal to 0.6). Moreover, the gel content of pure acrylic resin **I'** (i.e., $\mathbf{I'}/\mathbf{I'}+\mathbf{II'}$ = 1, by weight) is equal to 95%. The results indicate that the butoxymethylamide group can react with itself as well as with hydroxyl groups, i.e., **I'** is self-
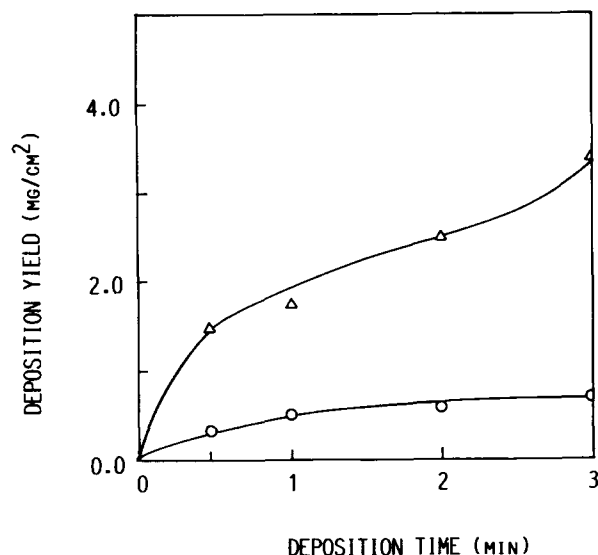
Figure 2   Effects of deposition time on deposition yield of **I** and **II** emulsions. Resin concentration: 10 wt %; BCS content: 4 wt %; applied voltage: 50 V; (△) **I** emulsion, pH 5.20; (○) **II** emulsion, pH 5.02.

curable and it can cure with **II'** at the proper curing conditions. Thus, at the lower "**I'''**" composition (e.g., **I'**/**I'**+**II'** weight ratio lower than 0.5), there is not an adequate amount of resin **I'** to be cured with resin **II'** because parts of resin **I'** have self-cured; therefore, the gel content of the mixture will be decreased.
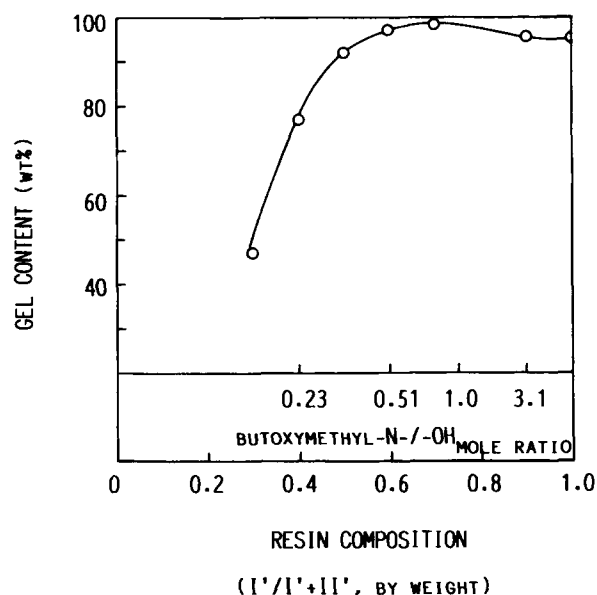
Figure 3   Effects of resin composition on gel content. Curing temperature: 190°C; curing time: 40 min.

Calibration Curve

The resins of two-component emulsion contain the cationic acrylic resin **I'**, having IR absorption of carbonyl [$C=O$] and hydrocarbon [CH] groups, and the polyol type **II'**, having [CH] IR absorption. The strong [$C=O$] peak appears at 1700 cm^{-1} and the peak of the [CH] stretching vibration appears at 2900 cm^{-1}. **I'** and **II'** resins 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 areas were plotted against **I'**/**I'**+**II'** weight ratios to give the calibration curve, as shown in Figure 4. It shows that the [$C=O$]/[CH] Abs. ratio increases with increasing "**I'''**" content.

The Deposition Yield of Coemulsion

The effects of resin composition of coemulsion on deposition yield are depicted in Figure 5. Line **A** is the actual deposition yield of coemulsion at various resin compositions. The values of data points shown on line **B** are calculated from the individual deposition yield of **I** and **II** emulsions. For example, for a coemulsion with 10 wt % resin concentration and 0.8 of **I**/**I**+**II** weight ratio, the predicted yield is the sum of deposition yield of resin **I** at 8 wt % and that
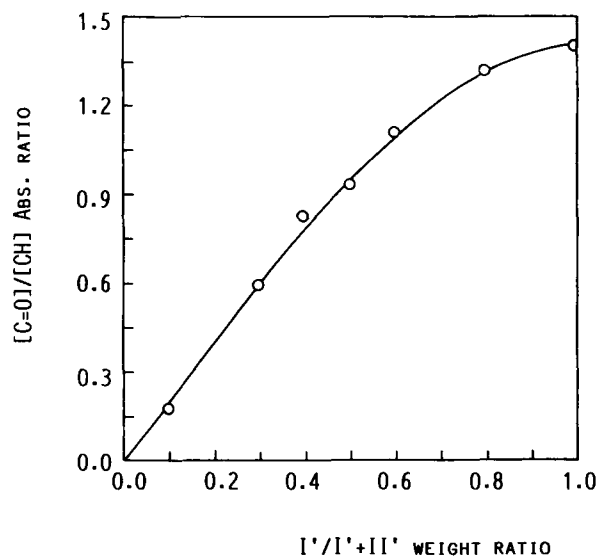

Figure 4   Calibration curve.

of resin **II** at 2 wt % when they were electrodeposited individually. Figure 5 shows that the actual deposition yield of line **A** increases with the increase of **I** composition and, at the lower **I** composition (**I**/**I**+**II** weight ratio < 0.5), it is almost equal to the predicted value of line **B**. However, the value of line **A** is higher than the predicted value of line **B** when the composition of **I** is higher **II** (**I**/**I**+**II** weight ratio > 0.5). This is probably due to the effects of codispersing uniformity of **I** and **II** in D.I. water, but this must be proved by further studies.

The Analysis of Resin Composition (I'/I'+II') of Deposited Film

Figure 6 indicates the effect of resin composition of coemulsion on the resin composition of deposited film, where line **A** shows the observed **I**/**I**+**II** weight ratios of the deposited films and line **B** shows the calculated values from the individual deposition yield of resins **I** and **II**. Line **A** is close to line **C** (the diagonal of Fig. 6), i.e., **I** and **II** are well mixed to form a stable coemulsion and are uniformly comigrated onto the substrate during the electrodeposition process. This is probably because the molecule backbone of acrylic resin **I** is extremely flexible and can readily entangle with **II** to obtain a uniform coemulsion. However, the predicted value of line **B** is much higher than the actual value of line **A**. This result suggests that the electrodeposition properties

Figure 6   Effects of resin composition of coemulsion on resin composition of deposited film. Resin concentration: 10 wt %; BCS content: 4 wt %; pH 5.0–5.2; applied voltage: 50 V; deposition time: 3 min; (O) actual value; (△) predicted value.

of coemulsion are different from those of individual **I** and **II** emulsions. As can be seen from Figures 3 and 6, to obtain the better thermal curing properties of the deposited film, the resin composition must be higher than 0.6.
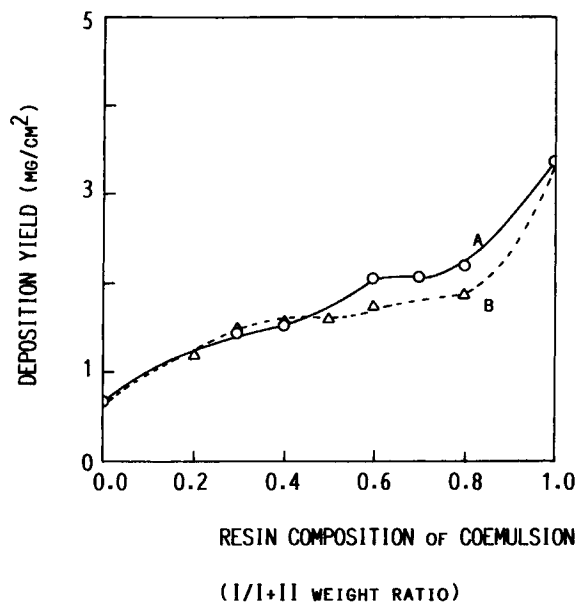

Figure 5   Effects of coemulsion resin composition on deposition yield. Applied voltage: 50 V; deposition time: 3 min; resin concentration: 10 wt %; BCS content: 4 wt %; (O) actual value; (△) predicted value.
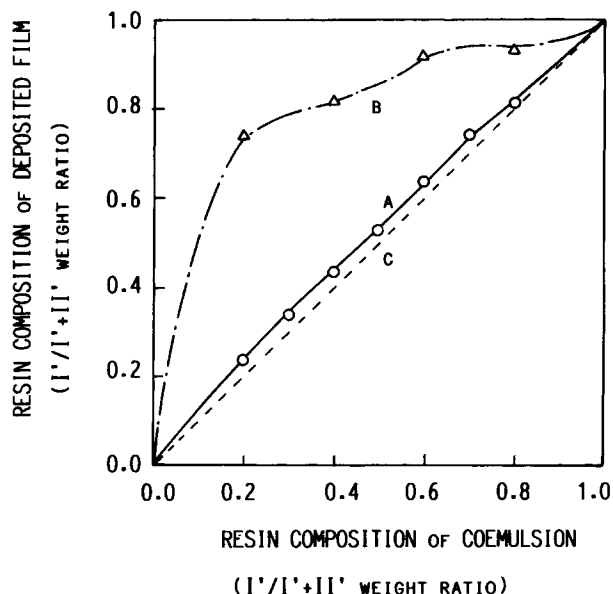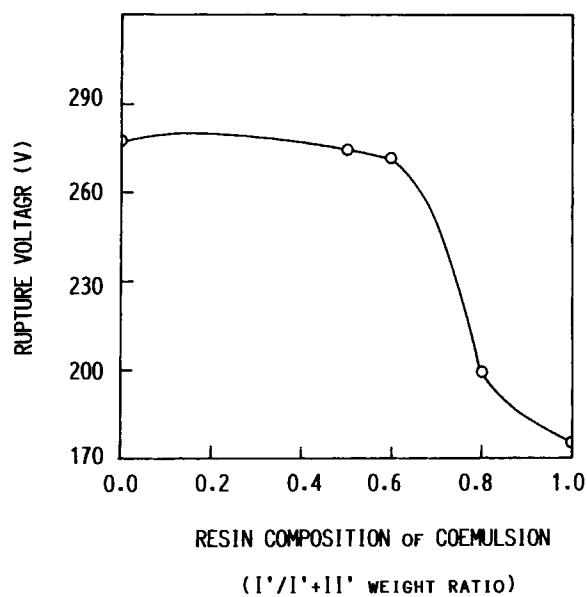

Figure 7   Effects of resin composition on rupture voltage. Resin concentration: 10 wt %; BCS content: 4 wt %.
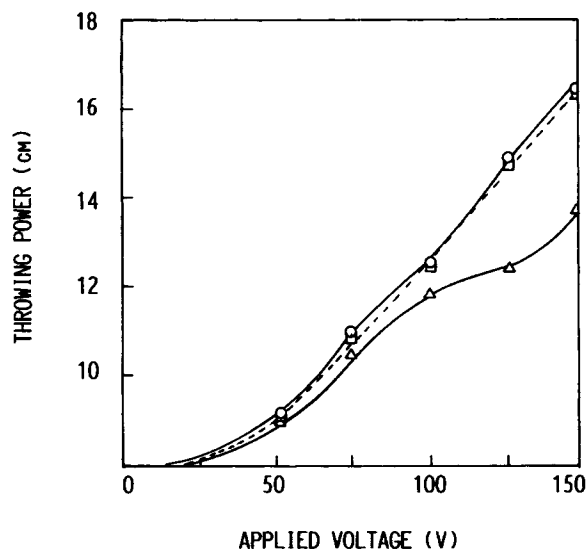
Figure 8 Effects of applied voltage on throwing power. Resin concentration: 10 wt %; BCS content: 4 wt %; deposition time: 2 min; ($\triangle$) I emulsion; ($\bigcirc$) II emulsion; ($\square$) coemulsion of I/II mixture.

Rupture Voltage

Effects of coemulsion resin composition on rupture voltage are shown in Figure 7. The rupture voltages of individual emulsions of I and II are 170 and 280 V. From Figure 7, the rupture voltage of coemulsion is not proportional to the resin composition. As the II composition approaches 40%, the rupture voltage

of coemulsion suddenly reaches a higher level. Thus, applied voltage of acrylic resin I can be improved by blending a proper amount of cationic epoxy resin II into the acrylic resin I emulsion.

Throwing Power

The relationships between applied voltage and throwing power of I/II coemulsion and individual I and II emulsions are shown in Figure 8. The throwing power has a tendency to increase with increasing voltage. This can be readily rationalized by taking into account the higher potential drop leading to a deeper penetration of the cationic resin into the shielded portions. The throwing powers of the emulsions are II = II/I > I. This might be explained by the fact that the throwing power of the codispersed emulsion was affected more significantly by II.

Physical and Chemical Properties of Codeposited Film

Physical and chemical properties of cured deposited films are shown in Table I. All cured films showed excellent adhesive strength, good hardness up to 1–3 H, and high acidic and alkali resistance. However, the cured deposited film derived from acrylic resin I showed less salt spray resistance and the film derived from the cationic epoxy resin system showed less weather resistance when they were compared to those derived from a mixture of cationic acrylic

Table I   Physical and Chemical Properties of the Cured Deposited Films

Properties	1[a]	2[b]	3[c]	4[d]
Adhesive strength[e]	100/100	100/100	100/100	100/100
Pencil hardness (H)[f]	1	3	2	2
Salt spray resistance[g]	> 3 mm	< 1 mm	< 1 mm	< 1 mm
Alkali resistance[h]	99.0	99.2	99.4	99.5
Acidic resistance[i]	99.3	99.1	99.2	99.6
Weather resistance[j]	O	$\triangle$	O	O

[a] Acrylic copolymer I.

[b] A self-curable cationic Epon 1004–diethylamine adduct with pendant 2-ethylhexanol-blocked isocyanate groups.

[c] Mixture of cationic I and II; resin composition of coemulsion: I/I + II weight ratio = 0.6.

[d] Mixture of cationic I and II; resin composition of coemulsion: I/I + II weight ratio = 0.7.

[e] Determined by the standard method of JIS D-0202 (1 mm^2 × 100).

[f] Measured with Mitsubishi pencils by using a Bravive-Instruments B-4000.

[g] Evaluated by the standard method of JIS Z-2371, sprayed with 5% aqueous NaOH for 240 h.

[h] Tested by dipping in 0.1N aqueous NaOH for 240 h; expressed as the weight percentage of the weight of cured film after dipping corresponding to the one before dipping.

[i] Tested by dipping in 0.2N aqueous H_2SO_4 for 48 h; the value recorded as the wt % as described in the preceding footnote.

[j] The level of weather resistance was judged by the gloss maintenance percentage of film after 500 h UV radiation corresponding to the one before radiation. The gloss of film was tested by the ProGloss at 85° (Models Pro-3, supplied by Hunter Associates Lab, Inc.). When the gloss maintenance percents were > 90%, 50–89%, and < 49%, the level of weather resistance were presented as O, $\triangle$, and X, respectively.

resin and cationic epoxy resin. The results indicate that the coemulsion prepared from the mixture of cationic acrylic resin **I** and cationic epoxy resin **II** can give a superior primer–surfacer coating with higher levels of corrosion and weather resistance.

CONCLUSIONS

1. At the same conditions, the deposition yield of acrylic resin **I** is greater than that of epoxy resin **II**, i.e., the deposition velocity of **I** is faster than that of **II**.
2. The mixtures of resins **I** and **II** at various weight ratios can all be well codispersed in D.I. water to form stable coemulsions. Thus, the resin compositions of electrodeposited films are almost equal to the coemulsion resin compositions.
3. The electrodeposition properties of the **I/II** coemulsion are different from those of the individual **I** and **II** emulsions. Thus, the resin composition of deposited film cannot be predicted by individual deposition yield of **I** emulsion and **II** emulsion.
4. To obtain better thermal curing properties of deposited film, the resin composition of coemulsion must be higher than 0.6.
5. The rupture voltage of coemulsion can be increased by increasing the resin **II** content in the coemulsion.
6. The coemulsion prepared from the mixture of **I/II** can give a superior primer–surface coating with higher levels of corrosion and weather resistance.

REFERENCES

1. R. D. Jerabek and R. J. Marchetti, U.S. Pat. 3,922,253 (1975).
2. R. D. Jerabek, U.S. Pat. 3,799,854 (1974).
3. F. E. Kemper and H. Spoor, U.S. Pat. 3,994,989 (1976).
4. S. L. Buchwalter, J. F. Bosso, and R. M. Christenson, U.S. Pat. 4,248,753 (1981).
5. J. F. Bosso and M. Wismer, U.S. Pat. 3,839,252 (1974).
6. J. F. Bosso and M. Wismer, U.S. Pat. 4,071,428 (1978).
7. M. Wismer and J. F. Bosso, U.S. Pat. 4,066,592 (1978).
8. J. F. Bosso and M. Wismer, U.S. Pat. 3,894,922 (1975).
9. L. C. Sturni and J. F. Bosso, U.S. Pat. 3,936,405 (1976).
10. J. F. Bosso and M. Wismer, U.S. Pat. 3,926,165 (1976).
11. C. C. Anderson and J. R. Marchetti, U.S. Pat. 3,939,051 (1976).
12. G. M. Kobe, Y. Manabe, and Y. Suematsu, U.S. Pat. 3,988,281 (1976).
13. T. L. Anderson, T. K. Debroy, and D. Y. Chung, U.S. Pat. 4,575,523 (1986).
14. K. W. Anderson and R. A. Hickner, U.S. Pat. 4,698,141 (1987).
15. M. Ramasri, G. S. Srinivasa, P. S. Sampathkumaron, and M. M. Sirshalkar, *J. Coat. Technol.,* **61**(777), 129 (1989).
16. G. Pampouchidis and H. Homig, U.S. Pat. 4,179,425 (1979).
17. C. P. Yang and Y. H. Chen, *J. Appl. Polym. Sci.,* to appear.
18. C. P. Yang and Y. H. Chen, *J. Appl. Polym. Sci.,* **42,** 1097 (1991).