

Coemulsion and Electrodeposition Properties of Mixtures of Polyoxypropylene-Modified Cationic Epoxy Resin and Nonionic Trimethylolpropane-Toluene Diisocyanate-2-Ethylhexanol Crosslinker

CHIN-PING YANG* and YAHN-HAUR CHEN

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

SYNOPSIS

The emulsification and electrodeposition properties of mixtures of polyoxypropylene- (POP) modified cationic epoxy resin (III) and nonionic trimethylolpropane-toluene diisocyanate-2-ethylhexanol (TMP-TDI-2EH, V) were investigated and the compositions of their electrodeposited films were obtained by Fourier Transform Infrared (FTIR) quantitative analysis to study the effects of "soft segment" (oxypropylene groups) contained in resin III on the coemulsion and electrophoretic behavior. The results indicate that the deposition yield and throwing power of emulsion of resin III are highly dependent on its average molecular weight (M_w). Resin III with higher M_w has higher deposition yield but lower throwing power. Moreover, the deposition yield of V/III coemulsion also increases with increasing the M_w of III. On the other hand, the throwing power of V/III coemulsion is not related to the M_w of III but is influenced by the amount of soft segments in III. Increasing soft segment content in III increases the throwing power of the coemulsion. Furthermore, at the conditions providing stable coemulsion, the composition of the electrodeposited film is almost equal to the resin composition of the coemulsion. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Two or multi-component cationic coatings¹⁻⁸ can provide better storage stability for electrodeposition emulsions and better physical and chemical properties of the electrodeposited films than one-component systems.⁹⁻¹⁶ In the earlier papers,¹⁻⁵ most of the crosslinkers of two-component cationic coatings were uncharged resins; however, the codeposition behavior of uncharged crosslinker and cationic resin is not well understood.

In our previous studies,⁶⁻⁸ the compositions of the films electrodeposited from coemulsions of cationic resin/cationic crosslinker or cationic resin/nonionic crosslinker were determined by Fourier Transform Infrared (FTIR) quantitative analysis to investigate their electrophoretic behavior. The

results indicate that in the "cationic resin/cationic crosslinker" coemulsion system,⁶⁻⁷ the composition of the deposited film is affected by the individual deposition velocities of the main resin and crosslinker; on the other hand, in the "cationic resin/nonionic crosslinker" coemulsion system,⁸ the composition of the electrodeposited film is almost equal to the resin composition of the coemulsion.

The cationic resins in our studies described above were diglycidylether of bisphenol A (DGEBA) type resin. The toughness of coatings derived from DGEBA resins is poor, so soft segments such as polymethylene ethers are usually introduced into the backbones of DGEBA resins to improve the toughness. In this study, a polyoxypropylene resin (POP), Epon 828 and bisphenol A were copolymerized to produce POP-modified cationic resin with various contents of soft segment (oxypropylene group). The coemulsion and electrodeposition properties of POP-modified cationic resins/nonionic crosslinker were investigated and the composition of the deposited

* To whom correspondence should be addressed.

film is obtained by FTIR quantitative analysis to study the effects of soft segment content on the co-deposition and coemulsion properties.

EXPERIMENTAL

Materials

Reagents used in the preparation of POP-modified cationic resin (III) included bisphenol A (Honscho Co.), DER 732 and 736 (a POP epoxy resin possessing epoxy equivalent weight of 305–335 and 175–205, Dow Chemical Co.). Epon 828 (a DGEBA epoxy resin possessing an epoxy equivalent of 184–192, Shell Chemical Co.) and diethylamine (Hanawa extra pure grade).

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

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.

Instruments

An electrodeposition apparatus and a Jasco-7000 FTIR spectrophotometer were employed. The detailed scheme of the electrodeposition apparatus was shown in a previous publication.¹⁵ A copper electrode (anode) and aluminum plate (cathode) with a surface area of about 30 cm² were used. Approximately 200 mL of emulsion was placed in the glass vessel of the electrodeposition apparatus. After deposition, the aluminum plate was rinsed with distilled water and dried in an air circulating oven at 100°C, then reweighed to obtain the deposition yield of deposited film (mg/cm²).

Synthesis

POP-Modified Cationic Epoxy Resins (III)

POP-modified cationic resins (III-e) was prepared by first charging 50 g (0.22 mol) of bisphenol A and 70.2 g (0.11 mol) of DER 732 into a three-necked flask equipped with an electric stirrer, a reflux condenser, and an inert nitrogen blanket. The batch was then mixed and heated to approximately 120°C and held for about 5 h until no free epoxy groups were evident. The epoxy equivalent weight (EEW) was determined by the pyridium chloride method.¹⁷

Epon 828, 82.5 g (0.22 mol), was then introduced into the batch and held for about 7 h at 120°C until the EEW of POP-modified epoxy resin (II) become a constant. The batch was then cooled to 60°C and 8.05 g (0.11 mol) of diethylamine was added slowly. After reheating to 100°C and then holding for an additional 2 h, the resultant POP-modified cationic epoxy resin (III-e) was obtained.

TMP-TDI-2EH Resin (V)

A nonionic TMP-TDI-2EH crosslinker (V) was prepared by first adding 74.9 g (0.576 mol) of 2-ethylhexanol slowly to 100 g of toluene-2,4-diisocyanate over a period of approximately 1 h, while mixing under a blanket of dry nitrogen gas and externally cooling the batch to maintain the reaction temperature below 10°C. The batch was then heated to 40°C and held for 2 h to obtain a partially blocked 2,4-toluene diisocyanate (IV). Trimethylolpropane 25.7 g, (0.192 mol), was then introduced slowly over 1 h while slowly heating the batch to 60°C. The batch was then held for about 1 h at this temperature until all isocyanate groups were consumed as indicated by an infrared scan. The resultant product was nonionic TMP-TDI-2EH crosslinker (V).

Preparation of Electrodeposition Emulsion

The general process for the preparation of coemulsion of III-b/V mixture involved first the dilution of the mixed resins (III-b, 5 g; V, 5 g) with 4 g BCS to a solution with 70 wt % solid content. The solution was treated with 0.5 mL AcOH (about 90% of the total theoretical neutralization) and dispersed in 86 g deionized (DI) water to form a cationic coemulsion of 10 wt % solid content.

FTIR Quantitative Analysis

Calibration Curve

Resins III and V with various weight ratios were well mixed and dissolved in tetrahydrofuran (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 the carbonyl group [C=O] stretching band (at approximately 1900–1650 cm⁻¹) and the 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 the V/(V + 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 the calibration curve, the composition of deposited film was obtained.

Gel Content

A 40 wt % solid content solution, prepared by dissolving and mixing III and V in THF, was spread on aluminum foil and baked at 190°C for 40 min in an air oven to form a crosslinked film. The crosslinked film was immersed in acetone and refluxed for 24 h. After drying, the gel content was calculated by dividing the residual weight by the initial weight of crosslinked film.

Throwing Power

The throwing power of emulsion was determined by the tube penetration test method. The apparatus and testing procedure of throwing power was described in a previous publication.¹⁵

Measurement of Average Molecular Weight (M_w)

A gel permeation chromatograph (GPC) (Shimadzu LC-6A) and a TSK-GEL G-3000 column were used to test the M_w of resins III. Testing conditions were employed as follows: temperature, 40°C; solvent, THF; flow rate, 1 mL/min; standard, Epon 828, 1001, 1004, and 1007.

RESULTS AND DISCUSSION

Synthesis of POP-Modified Cationic Epoxy Resin (III)

The synthetic procedures for POP-modified cationic epoxy resins (IIIa-e) and nonionic TMP-TDI-2EH crosslinker (V) are shown in Scheme 1. Resins III was prepared by first reacting an excess of bisphenol A with DER 732 (or DER 736) at 120°C for about 5 h until no free epoxy groups were evident in the product resin I. Resin I containing terminal hydroxyl groups was then reacted with Epon 828 at 120°C until the EEW of the resultant POP-modified epoxy resins (II) reached a constant. The EEW was tested by the pyridium chloride method. The relationships between the EEW of resultant II and reaction time is shown in Figure 1. Seven to eight hours or even

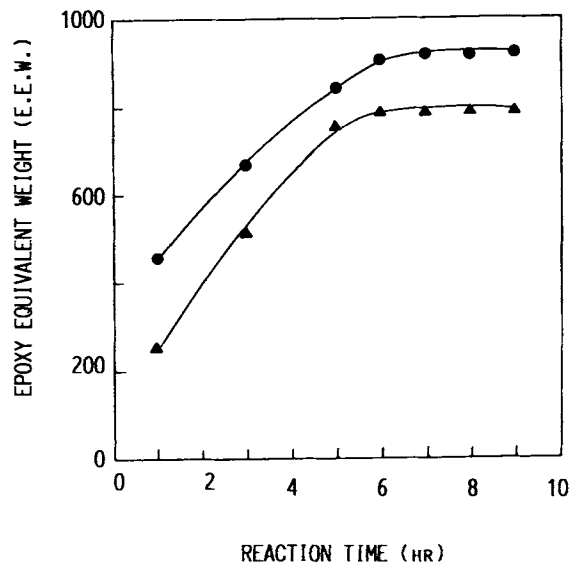


Figure 1 Effects of reaction time on epoxy equivalent of weight. (●) DER 732 modified bisphenol A (II) reacted with Epon 828; (▲) DER 736 modified bisphenol A (II) reacted with Epon 828; reaction temperature: 120°C.

longer, must be employed to ensure complete reaction. The M_w of resins IIa-e determined by GPC are very close to the predicted M_w (Scheme 1). After the completion of the above reaction, the resultant II containing various contents of soft segment (oxypropylene groups, R) was then reacted with diethylamine (essentially stoichiometrically equivalent to the epoxide groups present) to produce POP-modified cationic resins IIIa-e.

Properties of Resins IIIa-e

Electrodeposition Yield

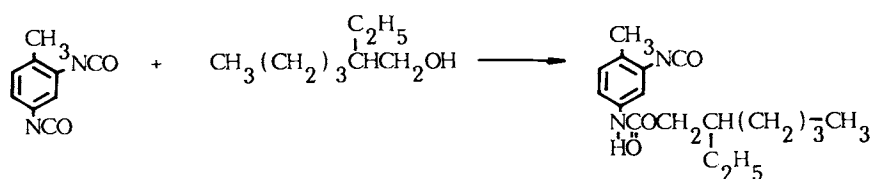
Electrodeposition was carried out in a beaker of the emulsion of cationic resin III at 25°C. After deposition, the coated panels were washed with water and baked in order to dry the film. The effects of electrodeposition time and applied voltage on the deposition yield of IIIa-e emulsions are shown in Figures 2(A) and (B). Figure 2(A) shows that the deposition yields of IIIa-e emulsions increase with the deposition time in the initial 3-4 min and reach a limit when an insulating film forms. It appears that the deposition yields of IIIa-e emulsions also increase with increasing applied voltage [Fig. 2(B)]. At the same applied voltage and time, the resin with higher M_w gives a higher deposition yield. This may be attributable to the increase of colloidal weight per charged unit, which leads to higher efficiency when electrodeposited.

Scheme 1 (Continued from the previous page)

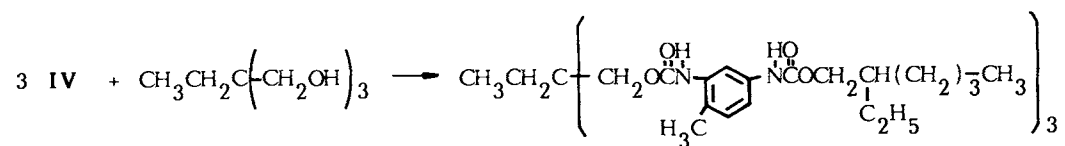
II, III-	a	b	c	d	e
BPA : DER : Epon 828		3:1:3	2:1:2	3:1:3	2:1:2
m	0	4.3	4.3	8.8	8.8
n	5.50	5.94	3.81	4.92	2.79
Predicted A.M.W. ^{*1}	1900	2202	1598	2452	1848
Actual A.M.W. ^{*2}	1979	2308	1691	2456	1890
Content of R (wt%)	0	10.8	15.6	20.8	27.6

^{*1} predicted A.M.W. = E.E.W. (calculated from reactant) X 2

^{*2} Actual A.M.W. : determined by GPC



IV



V

Throwing Power

Throwing power, how uniformly the electrodeposited film is developed and how deeply it penetrates and deposits inside hollow and complicated structures, is one of the most favorable characteristics of electrocoatings. Figures 3(A) and (B) show the effects of deposition time and applied voltage on the throwing power of resins IIIa-e. The throwing power has a tendency to increase with increasing voltage and deposition time. Under the same conditions of electrodeposition, the resin with higher molecular weight gives a lower throwing power (i.e., the throwing power order of resins III is IIIc > IIIe > IIIa > IIIb > IIId). This can be readily rationalized by taking

into account the decrease of colloidal weight per charged resin unit increasing the force of deeper penetration of the cationic resin into the shielded portions.

Properties of Mixtures of Cationic Resins (III) and Nonionic Crosslinker (V)

Gel Content of V/III Mixed Film

Figure 4 shows the effect of composition of V/III mixed film on its gel content. The optimum composition (V/V + III, by weight) of mixed film is at 0.4-0.5 (i.e., free —NCO of V/—OH of III molar ratio during curing is at about 0.5-0.65). The result

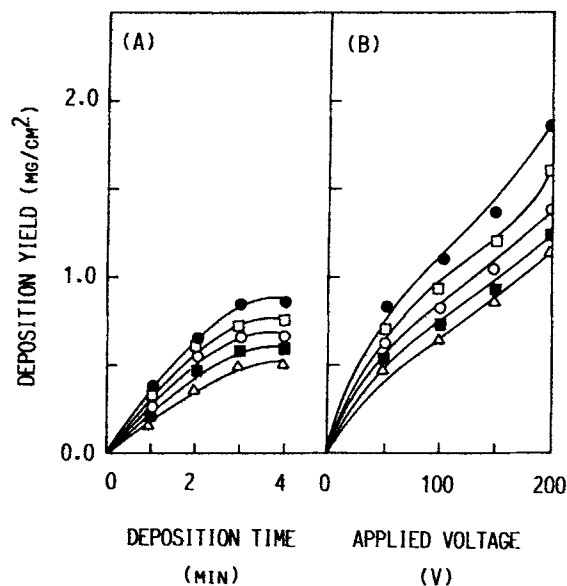


Figure 2 Effects of deposition time and applied voltage on deposition yield of resin III emulsions. (A) applied voltage, 50 V; (B) deposition time, 3 min; (○) III-a; (□) III-b; (△) III-c; (●) III-d; (■) III-e; resin concentration, 10 wt %; BCS content, 4 wt %; pH, 5.0–5.1.

suggests that some hydroxyl groups of III are not reacted with —NCO groups of V at this curing condition.

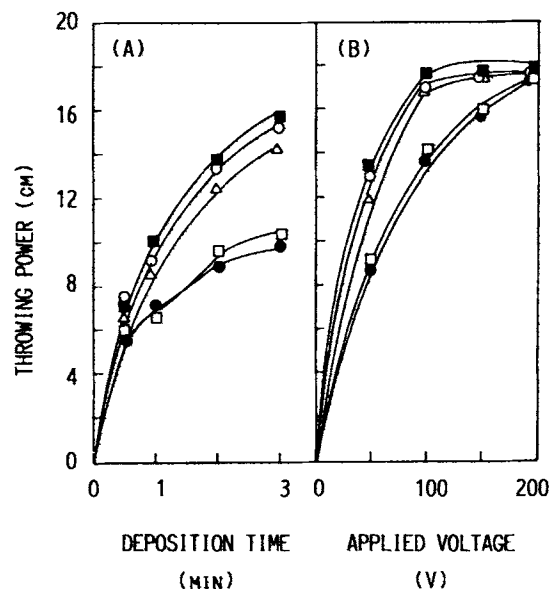


Figure 3 Effects of applied voltage and deposition time on the throwing power of resin III emulsions. (A) applied voltage, 50 V; (B) deposition time, 2 min; (○) III-a; (□) III-b; (△) III-c; (●) III-d; (■) III-e; resin concentration, 10 wt %; BCS content, 4 wt %; pH, 5.0–5.1.

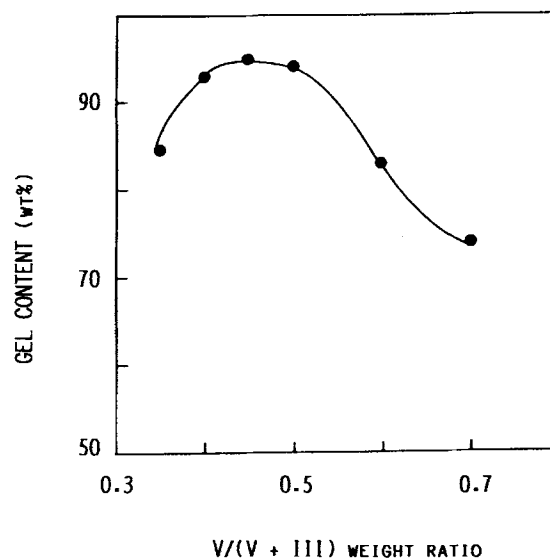


Figure 4 Effects of resin composition on gel content. Curing temperature, 190°C; curing time, 40 min.

Mechanical Properties of the V/III Crosslinked Film

The stress–strain curves of V/III crosslinked film are shown in Figure 5. The elongation at break of crosslinked film prepared from the mixture of resins V and IIIa is the worst. The elongation at break increases with increasing content of soft segment (oxypropylene groups) contained in the backbone

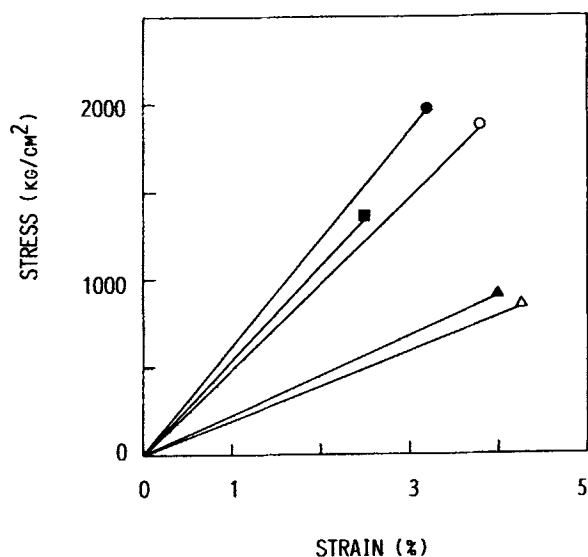


Figure 5 S–S curve of cured film. V/III weight ratio, 0.9; curing temperature, 190°C; curing time, 40 min; (■) V/III-a; (●) V/III-b; (○) V/III-c; (▲) V/III-d; (△) V/III-e.

of resins III, but the tensile strength of crosslinked films decreases with increasing the soft segment content.

Calibration Curve

Resins V 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 $[C=O]/[CH]$ ratios of absorbance areas were plotted against V/V + III weight ratios to give the calibration curve shown in Figure 6. It shows that the $[C=O]/[CH]$ Abs ratio increases with increasing V content.

Properties of V/III Coemulsion

Electrodeposition Yield

Effects of deposition time and applied voltage on deposition yield of V/III coemulsion are shown in Figures 7(A) and (B). The deposition yield increases with increasing deposition time and applied voltage. At the same conditions of electrodeposition, the order of deposition yields of V/III coemulsion is V/III-d > V/III-b > V/III-a > V/III-e > V/III-c. The result indicates that increasing molecular weight of resins III will increase the deposition yield of coemulsion. Moreover, from Figures 2 and 7, it can be seen that the deposition yield of coemulsion is greater than that of the individual III emulsion at the same resin concentration. This may be caused by the increase of colloidal weight per charged unit,

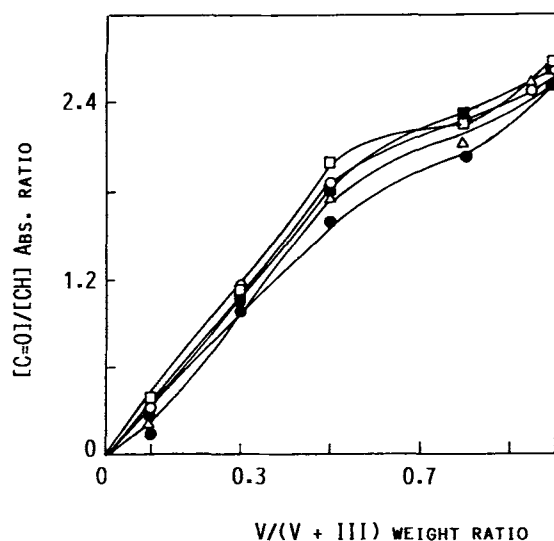


Figure 6 Calibration curve of V/III film. (■) V/III-a; (○) V/III-b; (△) V/III-c; (□) V/III-d; (●) V/III-e.

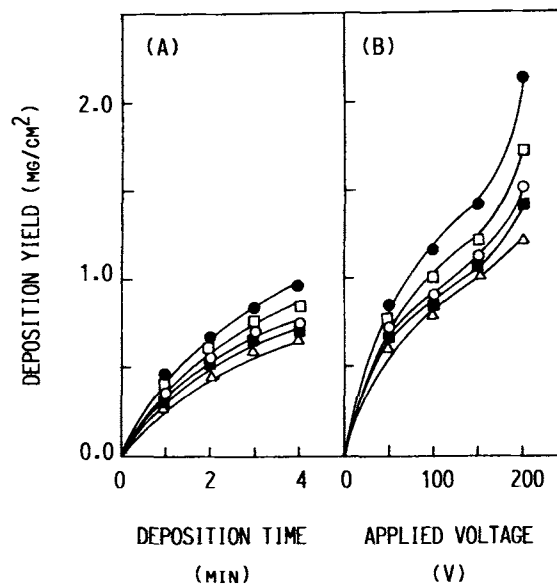


Figure 7 Effects of deposition time and applied voltage on the deposition yield of coemulsion. (A) applied voltage, 50 V; (B) deposition time, 3 min; (○) V/III-a; (□) V/III-b; (△) V/III-c; (●) V/III-d; (■) V/III-e; resin concentration, 10 wt %; BCS content, 4 wt %; pH, 4.9–5.0; resin composition of coemulsion, 0.4 (V/V + III, by weight).

which leads to higher efficiency when electrodeposited.

Throwing Power

Effects of deposition time and applied voltage on throwing power are shown in Figures 8(A) and (B). The throwing power has a tendency to increase with increasing voltage or deposition time. At the same conditions of electrodeposition, the order of throwing power of V/III coemulsions is V/III-e > V/III-d > V/III-c > V/III-b > V/III-a. This order is not the same as that of emulsion of III series (III-c > III-e > III-a > III-b > III-d, Fig. 3); that is, the throwing power of V/III coemulsion is not related to the molecular weight of resins III. It is, however, affected by soft-segment content of resin III. The higher soft segment content may assist the mixture of V/III to codisperse in the aqueous system, leading to the formation of smaller cationic particles and resulting in a deeper penetration of the cationic particles into the shielded portions.

The Composition of Film Deposited from Coemulsion

At a constant III concentration of 5 wt %, the effect of an additional amount of V on the composition of

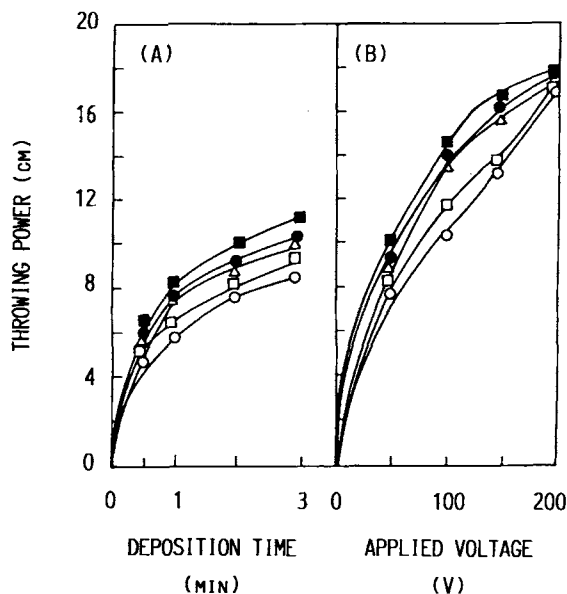


Figure 8 Effects of deposition time and applied voltage on the throwing power of coemulsion. (A) applied voltage, 50 V; (B) deposition time, 2 min; (○) V/III-a; (□) V/III-b; (△) V/III-c; (●) V/III-d; (■) V/III-e; resin concentration, 10 wt %; BCS content, 4 wt %; pH, 4.9–5.0; resin composition of coemulsion, 0.4 (V/V + III, by weight).

deposited film is shown in Figure 9. The level of V in electrodeposited film increases with the increasing amount of V in coemulsion, and gradually reaches

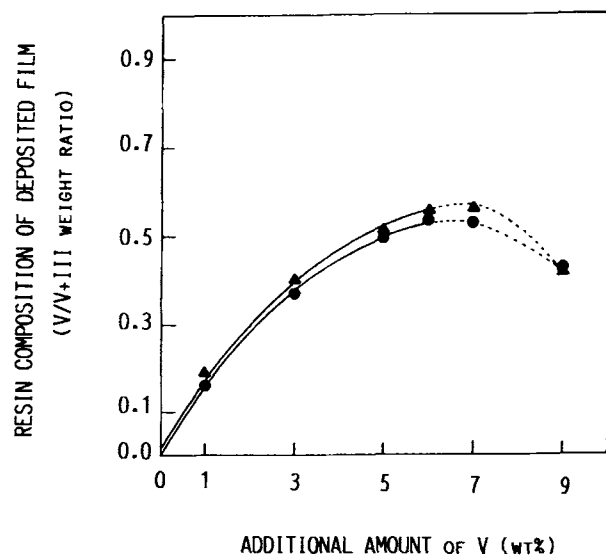


Figure 9 Effects of additional amount of V on resin composition of deposited film. Concentration of III, 5 wt %; deposition time, 3 min; applied voltage, 50 V; BCS content, 4 wt %; (●) V/III-b; (▲) V/III-d.

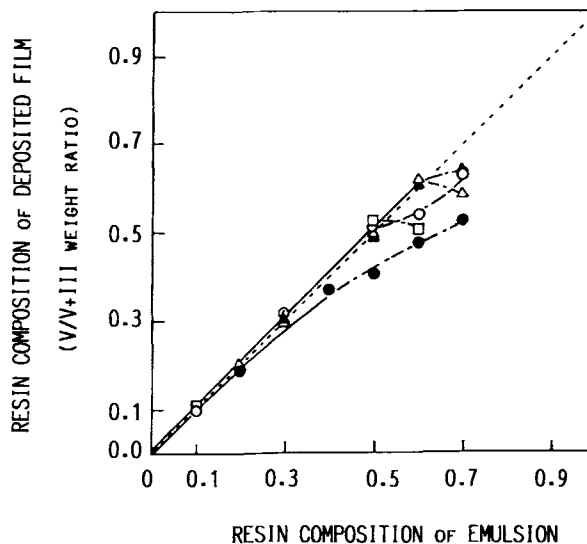


Figure 10 Effects of resin composition of coemulsion on resin composition of deposited film. Deposition time, 3 min; applied voltage, 50 V; resin concentration, 10 wt %; BCS content, 4 wt %; (●) V/III-a; (○) V/III-b; (△) V/III-c; (□) V/III-d; (▲) V/III-e.

a limit; however, an amount of V exceeding a particular limit causes coagulation and precipitation of V and lowers the level of V in the deposited film.

At a resin concentration of 10 wt %, the effects of resin concentration of coemulsion on the resin composition of deposited film are shown in Figure 10. It shows that at conditions providing stable coemulsions, the V content in the electrodeposited film increases with increasing V content in the coemulsion. The V content in the electrodeposited film is close to the value of ideal blending (the diagonal line of Figure 10, assuming that the resin composition of electrodeposited film is equal to the resin composition of coemulsion). However, too high a V content causes precipitation of V and makes the V content in the deposited film lower than that of coemulsion. According to the hydrophilic level of resins III for forming stable coemulsions, the maximum V contents in coemulsions of V/III series are different. The maximum V contents providing stable coemulsions for V/IIIa are 0.4 and for V/IIIb–e are 0.5–0.6 (V/V + III, by weight). This may be caused by the higher content of soft segment in IIIb–e, which leads to the attainment of aqueous codispersion with higher stability.

Physical and Chemical Properties of Cured Films

The zinc phosphate pretreated steel panels were cathodically electrocoated in the electrodeposition

Table I Physical and Chemical Properties of the Cured Film Deposited From V/III Coemulsions

Properties	V/III-a	V/III-b	V/III-c	V/III-d	V/III-e
Pencil hardness	3H	3H	3H	2H	2H
Adhesive strength	100/100	100/100	100/100	100/100	100/100
Alkali resistance ^a	99.1	99.5	99.6	99.6	99.3
Acidic resistance ^b	99.4	99.7	99.4	99.5	99.3

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

^b Tested by dipping in 0.2 N aqueous H₂SO₄ for 48 h; the value recorded as wt % as described in the preceding footnote.

baths at 50 V for 3 min at a bath temperature of 25°C. The wet electrodeposited films were cured by baking at 190°C for 40 min. The cured films were evaluated for adhesive strength, pencil hardness, alkali resistance, and acidic resistance. The results are shown in Table I. All cured films showed excellent adhesive strength, high alkali and acidic resistance, and good hardness up to 2–3 h.

CONCLUSIONS

- Both the deposition yield and throwing power of IIIa–e emulsions increase with increasing applied voltage. At the same condition of electrodeposition, the deposition yield and throwing power of IIIa–e are related to M_w of resins. Higher M_w gives higher deposition yield but lower throwing power.
- The deposition yield of coemulsion is greater than that of individual III emulsion at the same resin concentration. This may be because of the increase of colloidal weight per charged unit, which leads to higher efficiency when electrodeposited.
- The throwing power of V/III coemulsion is not related to the M_w of III but is affected by the soft segment in III. Increasing the soft segment content in III increases the throwing power of coemulsion.
- At the conditions providing stable coemulsion, the composition of electrodeposited film is almost equal to the resin composition of coemulsion.
- All V/III cured film shows excellent adhesive strength, high alkali and acidic resistance, and good hardness up to 2–3 h.

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