

Studies on Complex Multilayer Structure of Acrylic–Epoxy Resin

BIN ZHONG, DEBEN CHEN, ZONGHUA ZHOU, ANYONG ZHONG, ZONGYING DU

Department of Chemistry, Sichuan University, Chengdu, 610064, People's Republic of China

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ABSTRACT: In this article, a cationic acrylic resin and an epoxy resin which have certain surface tensions were prepared. The two resins were blended together, and after electro-deposition, a complex paint film can be obtained which is designed to comprise a couple of layers. The results of Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy showed that a layer-separation structure can be built in the paint film. The upper layer is mainly of acrylic resin, and the lower, chiefly of epoxy resin. Studies on the surface tension showed that the surface tensions of the component resins were the driving force of layer separation. Also, the greater the disparity of the two resins' surface tensions, the more striking the extent of the layer separation of the complex structure. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1855–1862, 1998

Key words: acrylic resin; epoxy resin; surface tension; layer-separation complex structure

INTRODUCTION

The concept of a polymer alloy has widely been infiltrated into every field of polymer material. Its infiltration in the coating field is the result of complex coating.^{1,2} As we know, acrylic resin is characterized by its high weathering resistance, and excellent corrosion resistance is characteristic of epoxy resin. The two resins are generally used in cathodic electrodeposition resin systems. There are many reports on mixing the two resins completely together or copolymerizing to modify the properties of the materials.^{3–5} However, to fully exert the properties of the two resins, the optimum structure of the complex film is that the acrylic resin is in the upper layer to decorate the steel substrate and to resist weathering, and the epoxy resin is in the lower layer to resist corrosion. The studies on how to achieve complex

multilayer coating film which has high weathering resistance as well as high corrosion resistance, in only one process by cathodic electrodeposition, are less reported. Also, particularly, there are few reports on the driving force of layer separation and how to make use of the difference of the surface tension of the resins to obtain a multilayer structure of the deposited film.

In the present article, a cationic acrylic resin and a modified epoxy resin were prepared. The former is a type of cationic resin with positively charged groups at a side chain, and the latter is a type of cationic resin with positively charged groups at the end of the polymer chain. It is the cationic groups and the hydrophilic nature of the main chain that allows emulsification in water. After these cationic resins were dissolved in a suitable solvent and mixed with deionized water to form a stable emulsion, a deposited film was achieved by the current application. Then, a layer-separation complex coating film was obtained during the curing process of the film in the drying oven.^{6–8} The upper layer, mainly of acrylic resin, can impart a superior weathering resistance, and

Correspondence to: D. Chen.

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the lower, chiefly of epoxy resin, excellent corrosion resistance. In this study, the forming of the multilayer structure and its driving force, connected with the surface tension, were studied and some interesting results were obtained.

EXPERIMENTAL

Materials

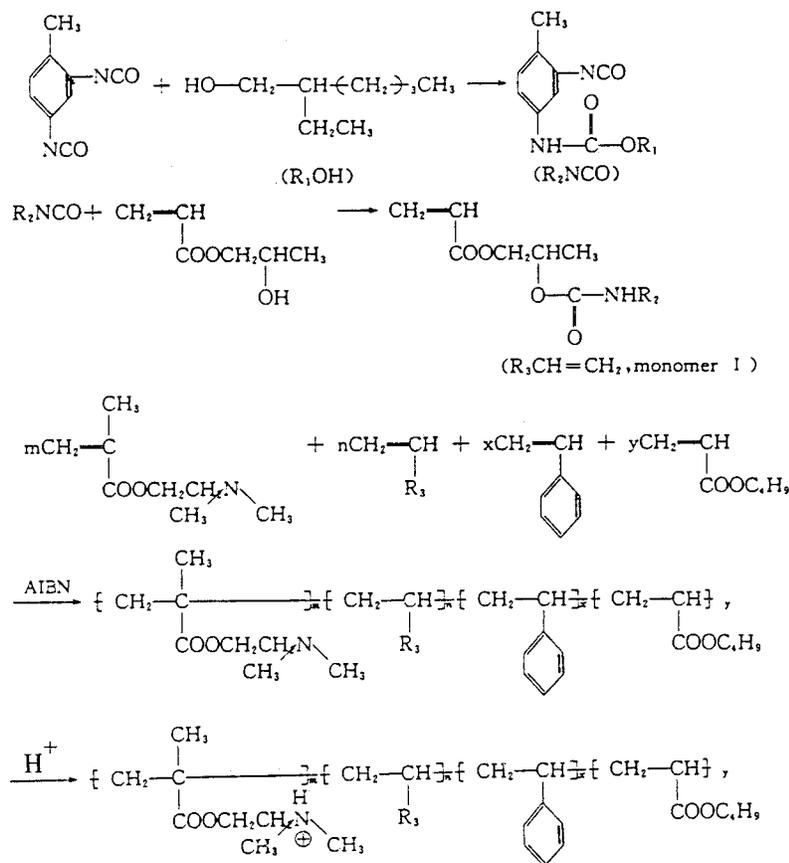
The monomers used in the preparation of the acrylic resin (A) include butyl acrylate (BA), *N,N*-dimethylaminoethyl methacrylate (DM), styrene (S), 2-hydroxypropyl methacrylate (HPA), 2-ethylhexanol (2EH), toluene-2,4-diisocyanate (TDI), *n*-butanol, and 2-2'-azobisisobutyronitrile (AIBN). Epox 601 (diglycidyl ether of bisphenol A, $M_n = 900$), Epox 604 (diglycidyl ether of bisphenol A, $M_n = 1400$), diethanolamine, and ethylene glycol monoethyl ether were employed in the preparation of the modified epoxy resin (E). All the chemicals above are chemical pure (Beijing Chemical Co., Beijing, China).

Synthesis

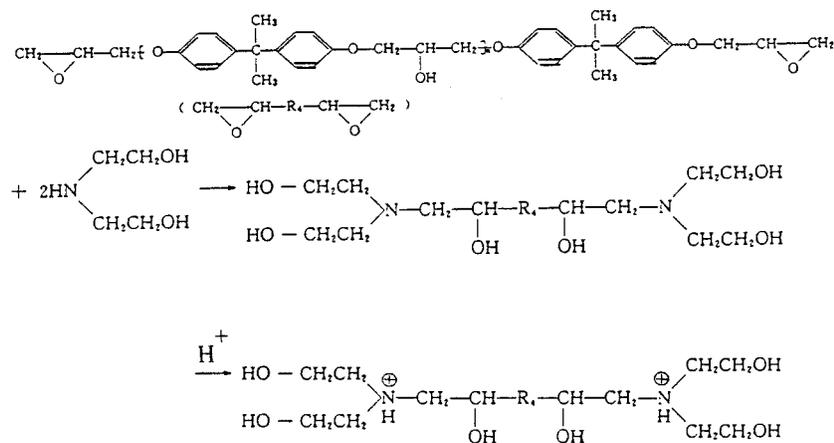
Acrylic Resin (A)

In a three-necked reaction vessel, a half-blocked TDI was prepared by slowly adding 2EH (12.6 g, 0.2 mol) to TDI (34.8 g, 0.2 mol) over a period of 40 min below 10°C. Then, the batch was kept below 20°C for an additional 40 min and after that heated to 40°C and held for 1 h. HPA (29 g, 0.2 mol) was then added into the flask. The whole mixture was kept at 40°C for about 1.5 h until no free isocyanate groups were evident to give the monomer (I) containing blocked TDI.

n-Butanol (50 g) was charged into another reactor equipped with a condenser, stirrer, thermometer, and dropping funnel. The monomer I, BA (76.8 g, 0.6 mol), DM (31.4 g, 0.2 mol), S (20.8 g, 0.2 mol), and AIBN (2 g) were well mixed in a flask. The reactor-charged *n*-butanol was heated to 100°C, and then the whole mixture of monomers was added using a dropping funnel over a 2 h period. At the completion of the addition, the reaction was allowed to continue at 110°C. Over



Scheme 1



Scheme 2

5 h was required to make the resultant product's conversion approach 100%. The synthesis route of A is shown in Scheme 1.

Modified Epoxy Resin (E_1 , E_2)

An epoxy resin Epox 604 (70 g, 0.05 mol) and ethylene glycol monoethyl ether (35 mL) were charged into a three-necked flask. The mixture was heated to 70°C to dissolve the epoxy resin. Diethanolamine (10.5 g, 0.1 mol) was then added into the flask. The whole mixture was kept at that temperature for about 3 h until no free epoxy groups were evident to give the modified epoxy resin E_1 .

Epoxy resin E_2 was obtained when Epox 604 (45 g, 0.05 mol) was used as above instead of Epox 601. The synthesis routes of E (E_1 , E_2) are shown in Scheme 2.

Preparation and Electrodeposition of the Complex Emulsion

The general process for the preparation of the emulsion was carried out as follows: In a reactor, the acrylic resin and epoxy resin were mixed in an equal ratio and dissolved in a certain amount of ethylene glycol ethyl ether. A desired amount of acetic acid was then added to prepare the cationic

resins. The mixture was heated to 50°C for 10 min to react completely. Then, deionized water was added dropwise into the solution with vigorous stirring to produce an emulsion.

An approximately 300-mL emulsion was placed in the glass vessel of the electrodeposition apparatus. The electrodes were immersed in the emulsion and electrodeposition was carried out at 40 V for 3 min. During the process, the cationic resins were deposited on the cathode, and then the cathode was removed from the emulsion, washed with water, and heated under a certain oven condition (170°C/10 min) to obtain the deposition yield.

Characterization of Multilayer Structure

Fourier Transform Infrared (FTIR) Spectroscopy

A Nicolet-170SX-FTIR was employed. The samples were analyzed in the absorption mode at a resolution of 4 cm^{-1} by signal averaging 15 scans. The analytical wavelength range was between 400 and 4000 cm^{-1} .

X-ray Photoelectron Spectroscopy (XPS)

XPS analysis of the treated samples was performed using an XSAM8000 photoelectron spectrometer, which employs a monochromatized

AlK α X-ray source. The X-ray gun was operated at 13 kV and 25 mA with the sample chamber at a pressure of approximately 10^{-9} Torr. The samples were of the coating film. The carrier was copper flake. Concentrated sulfuric acid was used as the corrosion material. After different extents of corrosion, X-ray photoelectron spectra of the film at different depths were collected.

C $_{1s}$ spectra were used to calculate the atomic percentage composition. All data were processed using the standard software provided with the instrument. C $_{1s}$ spectra were resolved using the assumption of Gaussian peak shapes. The value of 285.0 eV was used for the binding energy of the C $_{1s}$ core level photoemission of all peaks equivalent to saturated hydrocarbon. The binding energy data were reproducible to within ± 0.2 eV.

Surface Tension

The sample coating film was cleaned strictly. From a static contact angle measurer (ERMA Optical Works Co. Ltd.), the surface contact angle was determined.⁹ Then, the surface tension could be calculated by the Sell. Neumann test formula.¹⁰

RESULTS AND DISCUSSION

FTIR Spectroscopy

The synthesized acrylic resin and the modified epoxy resin were blended to prepare the complex emulsion. By electrodeposition, a thick coating film of about 40 μ m was obtained. To clarify the distribution of the component resins in the film, the top layer and the bottom layer were each then taken to be analyzed by FTIR spectroscopy. Figures 1 and 2 show the FTIR spectra of the acrylic

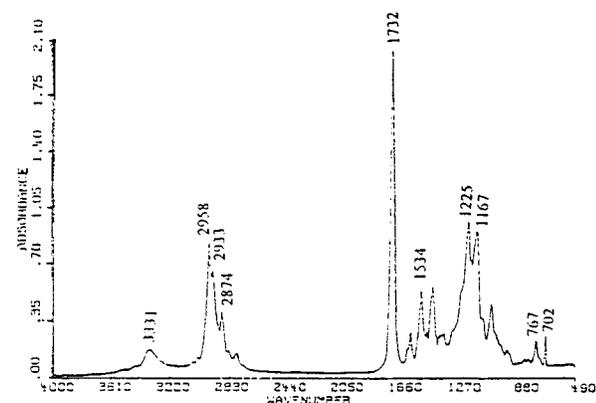


Figure 1 FTIR spectrum of the acrylic resin (A).

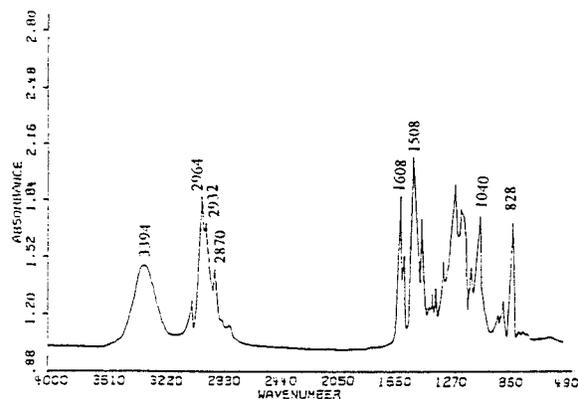


Figure 2 FTIR spectrum of the modified resin epoxy (E).

resin and the modified epoxy resin. Figure 3 displays the spectra of the top and bottom layers of the AE $_1$ system. The attribution of the IR characteristic vibration peaks are shown in Table I.¹¹

From the molecular structure, we know that acrylic resin has carbonyl groups at about 1732 cm^{-1} on the FTIR spectrum which cannot be found on the spectrum of the epoxy resin. It was also found that the two resins both had CH groups at about 2900 cm^{-1} , which had no change during the process and could be chosen as the reference group. In the case of the complex coating film, the greater the epoxy resin content or the smaller the acrylic resin content, the smaller the ratio of the absorbance areas of the peaks at 1732 and 2900 cm^{-1} (S_{1732}/S_{2900}). So, the change of the relative composition of the film could be obtained by investigating the change of S_{1732}/S_{2900} . We chose the

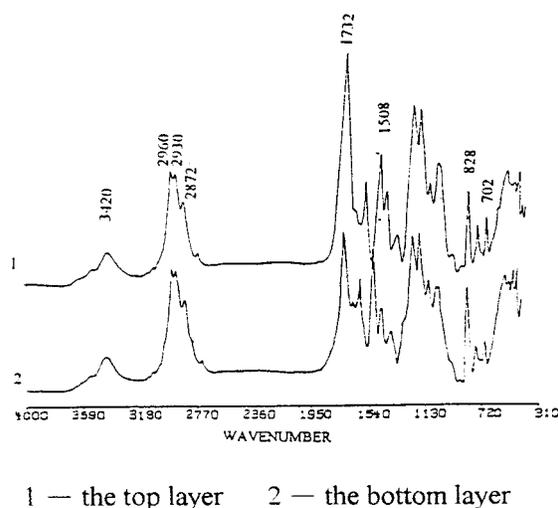


Figure 3 FTIR spectra of coating film for AE $_1$ system.

Table I Attribution of the IR Vibration Peaks

Acrylic Resin A (cm ⁻¹)	Modified Epoxy Resin E (cm ⁻¹)	Vibration mode
	3394	ν (O—H)
3331		ν (N—H)
2958, 2933, 2874	2964, 2932, 2870	ν (C—H)
1732		ν (C=O)
	1608	δ (N—H) (amide I band)
1534		δ (N—H) (amide II band)
	1508	δ (C—H) (<i>para</i> -substituted benzene)
1225		δ (N—H) (amide III band)
1167		ν (C—O) (fatty ester)
	828	δ (C—H) (<i>para</i> -substituted benzene)
702		δ (C—H) (monosubstituted benzene)

ranges 1681–1800 and 2817–3020 cm⁻¹ in the calculation of the absorbance areas of the C=O and C—H groups, respectively. In this way, the complex film of the AE₁ system was analyzed. The results are collected in Table II.

From Table II we know that there was more acrylic resin in the top layer than in the bottom layer in the AE₁ system, indicating that a layer-separation structure, not a homogeneous blended film, was built. In the double-layer film, the top layer is mainly acrylic resin and the bottom layer is chiefly epoxy resin.

X-ray Photoelectron Spectroscopy (XPS)

To confirm the layer-separation structure, the complex coating film was further analyzed by XPS. From the molecular structure of the acrylic resin and the epoxy resin, we know that acrylic resin has carbonyl groups which the epoxy resin does not have. So, the acrylic resin can be distinguished from the epoxy resin by the carbonyl group which is identified as a small shoulder at 289 eV on the C_{1s} region of the XPS spectra. Figures 4 and 5 show the XPS spectra (C_{1s} region) of the acrylic resin and the modified epoxy resin,

respectively. The major C_{1s} peak located at 285.0 eV corresponds to the aliphatic carbon (C—C). The small peak at 289 eV corresponds to the carbonyl carbon (C=O) derived from the acrylic resin.^{3,12}

In the study, corrosion handling was adopted to achieve samples at different depths of the complex coating film. Concentrated sulfuric acid was used as corrosion material. Since for a thick film the longer the corrosion time, the deeper the corrosion depth of film, the samples of different depths of the coating film can be obtained by corroding a thick complex film about 40 μ m for different times. Also, then the sectional XPS spectra were collected as shown as Figure 6. From the XPS spectra, it is evident that the section of the complex film caused a slant in the concentration of the acrylic resin component and that the nearer the film constituent comes to the top layer the greater the acrylic resin content.

The sensitive C_{1s} peak can be accurately resolved into contributions from C—C, C—O, and C=O by a Gaussian fit. This analysis, shown as Figure 7, gave consistent relative decreases in the C=O peak, indicating that the nearer the film constituent comes to the bottom layer the lower

Table II Changes of the Ratio S_{1732}/S_{2900} at Different Depths of the Complex Film for the Two Systems

System	AE ₁			AE ₂		
	2900 cm ⁻¹ (2817–3019)	1932 cm ⁻¹ (1681–1800)	S_{1732}/S_{2900}	2900 cm ⁻¹ (2817–3019)	1932 cm ⁻¹ (1681–1800)	S_{1732}/S_{2900}
Top layer	2.670	3.193	1.196	2.570	2.796	1.088
Bottom layer	2.550	1.949	0.764	2.460	2.219	0.902

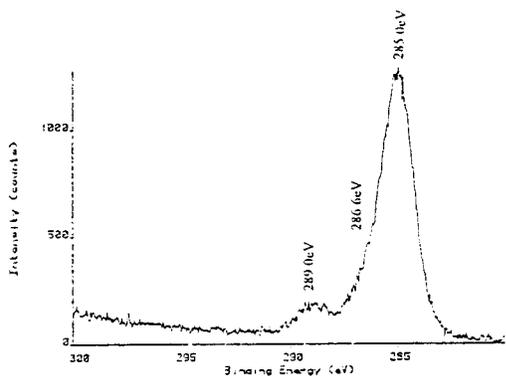


Figure 4 XPS spectrum of the acrylic resin A (C_{1s} region).

is the acrylic resin component content. This change is illustrated in Table III. Obviously, the above XPS analysis results were accordant with the FTIR results.

Surface Tension

The analytical results showed that a layer-separation complex film was obtained. But they did not show the driving force of such a layer separation. After many factors have been studied, the surface tension is assumed to be the main point. It is supposed that the complex film deposited by the current application undergoes a thermal flow before the film solidifies in the drying oven; in this stage, a layer-separation structure can be built, based on the difference in surface tension between the two types of resins. To verify the supposition, another modified epoxy resin E_2 with a lower surface tension was prepared, and surface tensions of all the three types of resins were determined.

After changing the resins into smooth films,

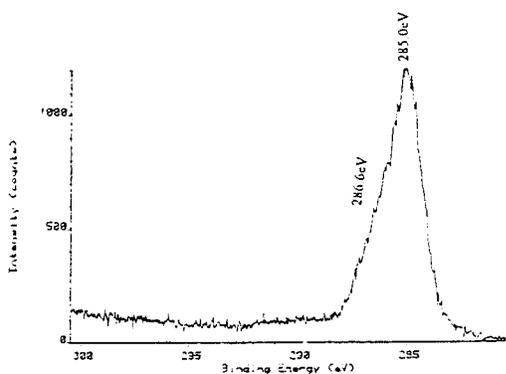
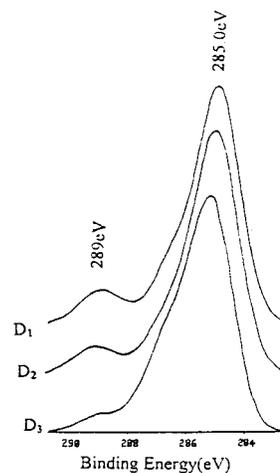


Figure 5 XPS spectrum of the modified epoxy resin E (C_{1s} region).



D-depth $D_1 < D_2 < D_3$

Figure 6 XPS spectra at different depths of the coating film for AE_1 system.

the surface contact angle of each film could be determined by the static surface contact angle measurement as below:

$$\theta_A = 80.5^\circ; \quad \theta_{E_1} = 50.5^\circ; \quad \theta_{E_2} = 68.0^\circ$$

From the Sell. Neumann test formula,¹⁰

$$\cos \theta = \frac{(0.015\gamma_S - 2)\sqrt{\gamma_S\gamma_L} + \gamma_L}{\gamma_L(0.015\sqrt{\gamma_S\gamma_L} - 1)}$$

where γ_L is the surface tension of water (72.8 dyne/cm); γ_S , the surface tension of the resin (dyne/cm); and θ , the surface contact angle. The surface tension of the resin (γ_S) could be calculated as below:

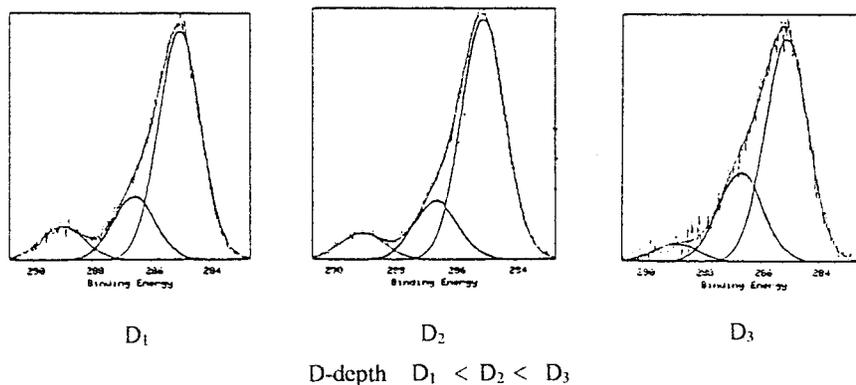
$$\gamma_A = 38.4 \text{ dyn/cm}; \quad \gamma_{E_1} = 60.5 \text{ dyn/cm};$$

$$\gamma_{E_2} = 49.7 \text{ dyn/cm}$$

Table III Relative Concentration of Acrylic Resin at Different Depths of the Complex Film for the Two Systems

Depth ^a	AE_1	AE_2
D_1	10.7	9.7
D_2	8.0	9.2
D_3	5.1	8.1

^a $D_1 < D_2 < D_3$.



D₁ D₂ D₃
D-depth D₁ < D₂ < D₃

Figure 7 Gaussian-fitted XPS spectra of AE₁ system.

Obviously, there is a relationship among the above data: $\gamma_A < \gamma_{E_2} < \gamma_{E_1}$.

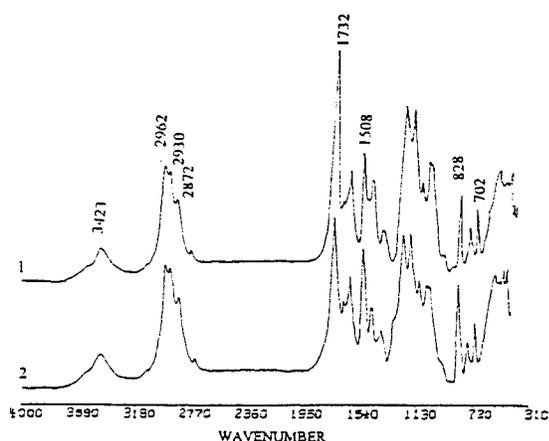
From the surface tensions of resins A and E₁, it is shown that their surface tensions were indeed different. Also, it is this disparity that was supposed to be the driving force of the layer separation. To do further study, another complex system AE₂ was prepared and the deposited film was analyzed by FTIR and XPS as the AE₁ system. The analytical results are shown as Figures 8–10. Also, the relative concentrations of the acrylic resin in different depths of the complex film were calculated from FTIR and XPS and are shown in Tables II and III, respectively, in contrast to the AE₁ system.

From the results of the FTIR and XPS analyses, three interesting points could be inferred:

1. Due to the disparity of surface tensions of the

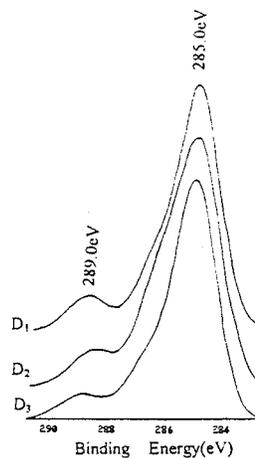
two resins, a layer-separation complex structure can be built in the complex films of both the AE₁ and AE₂ systems. The upper layer, mainly of acrylic resin, can impart a superior weathering resistance, and the lower layer, chiefly of epoxy resin, excellent corrosion resistance. This was accordant with the above supposition.

2. The extent of layer separation in the AE₁ system is more striking than in the AE₂ system. It should be noted that the acrylic resin (A) and the epoxy resin E (E₁, E₂) had a definite surface tension. Their relationship is $\gamma_A < \gamma_{E_2} < \gamma_{E_1}$, which means that $\gamma_{E_2} - \gamma_A < \gamma_{E_1} - \gamma_A$. It follows that the surface tension has an effect on the layer-separation structure. Also, the layer-separation structures of the films are not similar if the disparities of the two



1 — the top layer 2 — the bottom layer

Figure 8 FTIR spectra of coating film for AE₂ system.



D₁ D₂ D₃
D-depth D₁ < D₂ < D₃

Figure 9 XPS spectra at different depths of the coating film for AE₂ system.

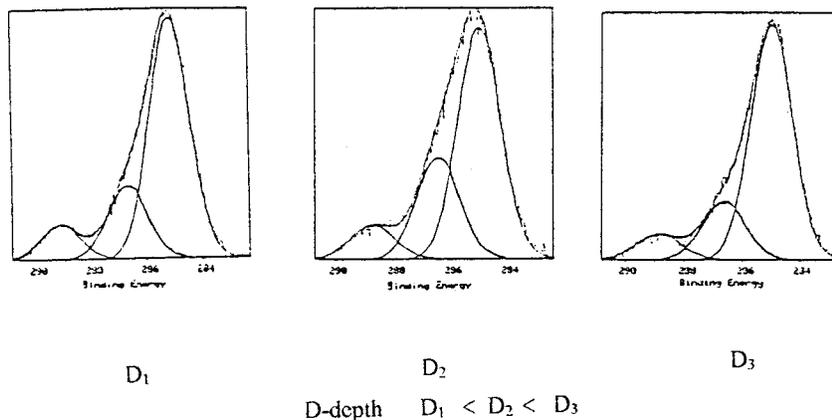


Figure 10 Gaussian-fitted XPS spectra of AE_2 system.

component resins' surface tensions are different. The greater the disparity of surface tension, the more striking the extent of layer separation. Furthermore, this result verified the reasonability of the supposition. The surface tension was proved to be the main factor that influenced the extent of layer separation.

- So, based on the difference in surface tension between the two types of resins, various complex films with different degrees of a layer-separation structure can be obtained. This is a very interesting and valuable result. But it does not follow that the greater the disparity of the surface tension the better the film quality is, because many tests have shown that a too great disparity of the surface tension led to a worse compatibility of the two component resins and made it difficult to prepare a stable complex emulsion which is necessary for the cathodic electrodeposition.

CONCLUSION

- Two complex coating systems were prepared. An acrylic resin was incorporated into the coating in addition to an epoxy resin. The deposited complex film undergoes a thermal flow before the film cures in the drying oven, and then a layer-separation structure can be built based on the difference in the surface tension between the two component resins.
- The results of the FTIR and XPS analyses confirmed that the complex film had a layer-separation structure. The nearer the film con-

stituent comes to the top layer, the greater the acrylic resin component content.

- The FTIR and XPS analyses also showed that the greater the disparity of the surface tension of the two resins the more striking is the extent of the layer separation of the complex film. The result proved that the disparity of the resins' surface tensions determined the layer-separation complex structure.

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