

Syntheses and Properties of Cationic Amine–Epoxy Adducts and Their Use in Electrodeposition: I. Diethanolamine/Diethylamine Terminated Cationic Epoxy with Pendant 2-Ethylhexanol-Blocked TDI Groups

CHIN-PING YANG* and YAHN-HAUR CHEN

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

SYNOPSIS

Alkyl partially blocked toluene diisocyanate (PBTDI) and hydroxyl group-containing polyepoxide were mixed to produce a blocked TDI–epoxy resin and then reacted with secondary amine and treated with acetic acid to give a cationic resin. In this study, six cationic resins (IV-A and IV-B, two series) were synthesized from three diglycidyl ethers of bisphenol A with different epoxy equivalent weights of 508, 650, and 950, and two secondary amines (diethylamine and diethanolamine). Acetic acid was used as the neutralization agent and ethylene glycol mono-*n*-butyl ether (butyl cellosolve, BCS) and deionized water were utilized as the emulsion solvents. Some properties of electrodeposition, such as throwing power and rupture voltage, and some physical and chemical properties of the deposited films were investigated.

It was found that the appearance of emulsion, deposition yields, and quality of the deposited films are strongly dependent on pH, BCS, and resin contents. To obtain suitable deposition properties and stable emulsions from IV-A and IV-B systems, the aqueous dispersion should meet the following conditions: pH, 5.5–6.0; BCS contents, 3.0–5.0 wt %; and resin concentration, 7.0–9.0 wt %. For both systems, the deposited films had good appearance, adhesion, hardness, and alkali reagent resistance. The salt spray resistance and acid resistance of films deposited from series III-A (epoxy resin formulations containing diethylamine) are superior to films deposited from series III-B (epoxy resin formulations containing diethanolamine).

INTRODUCTION

Electrodeposition has become increasingly important in the coating industry because it offers higher paint utilization, stronger throwing power, better outstanding corrosion protection, lower environmental contamination, definitely smoother coverage, and more susceptibility 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 highly valued coating

operations as priming motor cars, electrical appliances, and many other commercial articles.

In fact, electrodeposition consists of anionic^{1,2} and cationic^{3–16} processes. In the former case, metal ions are evolved at the anode, which may discolor the deposited films and reduce the surface corrosion resistance. As a result, particular interest has recently arisen in electrodepositable coatings that deposit on the cathode.

On the other hand, cationic resins involved in the latter case generally include one-^{3–13} and two-component^{14–16} systems. To take advantage of controllable self-curing properties of one-component cationic resin, toluene-2,4-diisocyanate was first half-blocked and three diglycidyl ethers of bisphenol A with different equivalent weights were added to

* To whom correspondence should be addressed.

produce blocked TDI-epoxy resins. Then, two secondary amines were individually added to react with the epoxy group to produce six cationic resins. Subsequently, suitable solvents and acetic acid were used to investigate the emulsion and electrodeposition properties.

EXPERIMENTAL

Materials

Three diglycidyl ethers of bisphenol A (DGEBA, possessing an equivalent weight per epoxide group of 508, 650, and 950), toluene-2,4-diisocyanate (TDI), 2-ethylhexanol (Wako extra pure grade), diethylamine, and diethanolamine (Hanawa extra pure grade) were used in the preparation of cationic resins. The DGEBAs were mixed with toluene to remove water by azeotropic distillation before use, but the other chemicals were used without further purification. Toluene was dried by refluxing for several days over sodium, followed by slow distillation. Ethylene glycol mono-*n*-butyl ether (butyl cellosolve, BCS) (Wako EP grade) and acetic acid (Wako first grade) were used as received.

Synthesis of Polyepoxide-Amine Adduct

In a three-necked reaction vessel, a half-blocked TDI was prepared by slowly adding 28.3 g (0.21 mol) 2-ethylhexanol to 37.9 g (0.21 mol) TDI over a period of about 40 min; while mixing, the batch was externally cooled to maintain the reaction temperature below 20°C. At the completion of addition, the batch was mixed at 20°C for an additional 40 min and then heated to 40°C and held for 1 h.

Into another reaction vessel, 100 g DGEBA possessing an epoxy equivalent weight of 950 and 80 g toluene were charged and the mixture was heated to reflux at 120°C with agitation to remove any water product by use of a Dean-Stark trap. When cooled to 60°C, the contents of the first reaction vessel were introduced and 5 drops of dibutyl tin dilaurate catalyst were added. The reaction mixture was then heated to 100°C and held approximately 2 h to give the blocked TDI-epoxy resins (II-a) with a ratio of about two urethane groups for each hydroxyl group. After cooling to 80°C, 11.06 g (0.1 mol) diethanolamine (essentially stoichiometrically equivalent to the reaction mixture) was reheated to 100°C and held for 2 h to give a tertiary amine adduct (III-B-a). This adduct was thinned with 50 mL BCS and distilled at 80°C under reduced pressure to remove

toluene as possible. The resultant resin had a solid content of about 80 wt %. The other resins having different molecular weight and terminated with another amine, diethylamine, were synthesized by a similar procedure.

Preparation of Electrodeposition Emulsion

The general process for the preparation of emulsions of IV-A and IV-B series involved the dilution of the resinous reaction product prepared as described above with a solvent (like BCS) to a solution with solid content of 70 wt %. The mixture was solubilized with a calculated quantity of acid (80 mol % of the total theoretical neutralization) and dispersed in deionized water to form a cationic resin emulsion of 8 wt % solid content.

Electrodeposition

The electrodeposition apparatus included a glass reaction vessel with a cover in which the copper electrode (used as anode) and a phosphated iron plate (cathode) with a surface area of about 50 cm² were hanged. A schematic illustration of the apparatus connected to a DC power supply (0-500 V) is shown in Figure 1. In electrodeposition processes employing

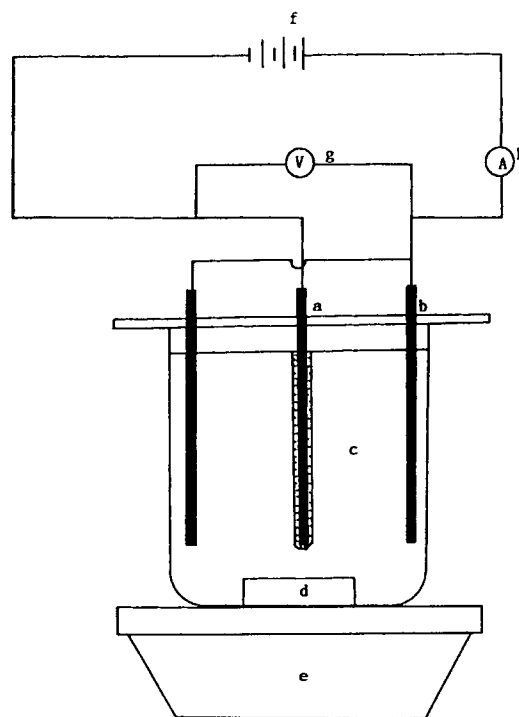


Figure 1 Cathodic electrodeposition apparatus. a, cathode; b, anode; c, emulsion; d, stirred bar; e, stirred plate; f, voltage source; g, volt. meter; h, amp. meter.

the aqueous coating emulsions described above, approximately 350 mL emulsion was placed in the glass vessel, in contact with the anode and cathode. Upon passage of electric current between the anode and cathode, while in contact with the bath containing the coating composition, an adherent film of the coating composition was deposited on the cathode. After deposition, the iron plate was rinsed to remove any nonadhering material and the coating was cured at 185–190°C.

Measurement

Throwing Power

The tube penetration test was used to measure the throwing power of the cationic resins, and the test apparatus is illustrated in Figure 2. In measurement processes, the cationic resin emulsion was poured into a stainless cylindrical vessel up to 20.5 cm from the bottom, and the bath was maintained at 25°C with uniform stirring. The test strip (8 × 205 × 0.8 mm) and the hollow glass tube were inserted in a holder and this assembly was immersed to a depth of 17.5 cm. The coating time is 3 min, and the voltage used ranges from 100–200 V. The distance up from the bottom of the strip measured in cm is the throwing power of the resin.

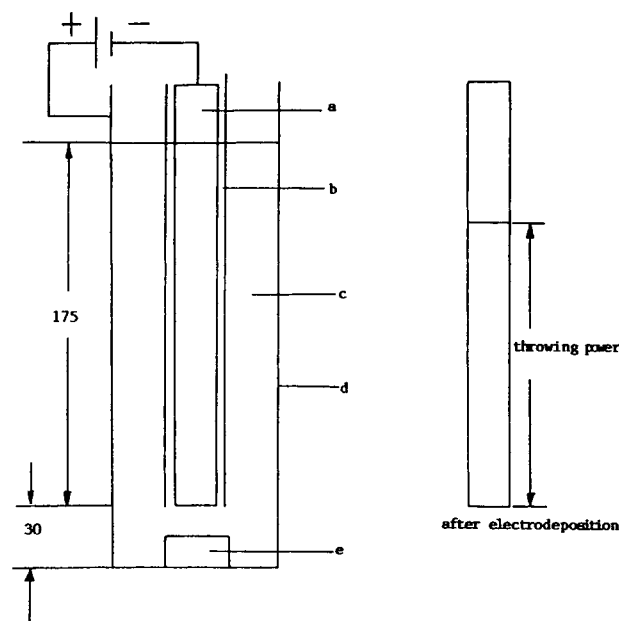


Figure 2 Throwing power apparatus (tube penetration method). a, stainless strip (205 × 8 × 0.8 mm); hollow glass tube (10 × 200 mm); c, emulsion; d, stainless tube; e, stirred bar.

Rupture Voltage

The rupture voltage was determined by the constant voltage method. The voltage was increased at 10 V of intervals from the lower one (at which normal film was obtained) until the change of current value during electrodeposition coating became abnormal (such as increasing) (at which the film became suddenly to show remarkable defects). This operation was repeated twice.

RESULTS AND DISCUSSION

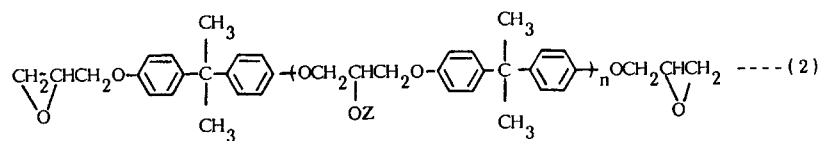
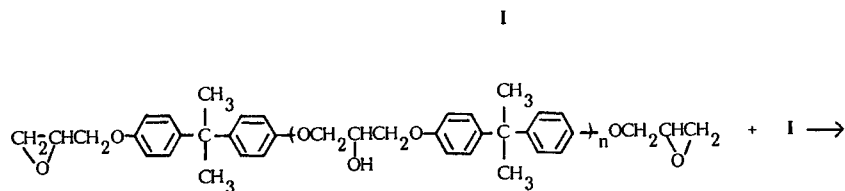
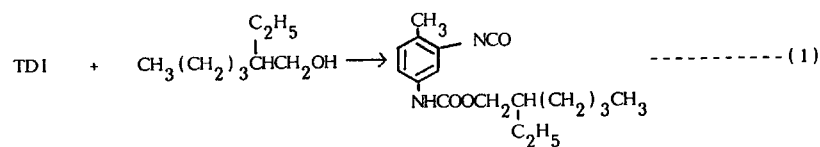
Synthesis of Cationic Epoxy Resins

The synthetic procedure of the cationic epoxy resins are shown in Scheme 1. First, the half-blocked 2,4-toluene diisocyanate (I) was obtained by reacting a sufficient quantity of 2-ethylhexanol (as the blocking agent) with 2,4-toluene diisocyanate (TDI) to provide a product having one free isocyanate group remaining. The reaction between TDI and the blocking agent is generally exothermic and is preferably carried out at low temperature to promote isocyanate group selectivity. Usually, temperature of 10°C or even lower can be employed.

Further, the epoxy group-containing materials also contains hydroxyl groups and pendant urethane linkages were prepared by reacting the DGEBA's possessing different epoxy equivalent weights of 508, 650, and 950 with the half-blocked TDI. The portion is not very critical. Preferably sufficient half-blocked TDI was employed to provide an adequate number of crosslinking sites to provide a cured film. Usually, less than 120°C was required to preserve the capped isocyanate groups to avoid gelation and to retain latent crosslinking sites. The reaction is generally conducted in the presence of a catalyst such as dibutyl tin dilaurate for urethane formation at a temperature between about 60°C and about 120°C. Temperatures of about 100°C are commonly employed. The completion of reaction can be confirmed by disappearance of the IR absorption peak at 2250 cm⁻¹ of isocyanate groups, as shown in Figure 3.

After the completion of the above reaction, the resulting product was then reacted with the amine. The reaction of the amine with the epoxy-containing material took place upon admixing then. In fact, the reaction is frequently exothermic. The reaction mixture may be heated to moderate temperature like 100°C to accelerate the reaction. It is frequently desirable to elevate the temperature at least slightly for a sufficient time to ensure complete reaction. The amount of amine reacted with the epoxy-con-

Scheme 1

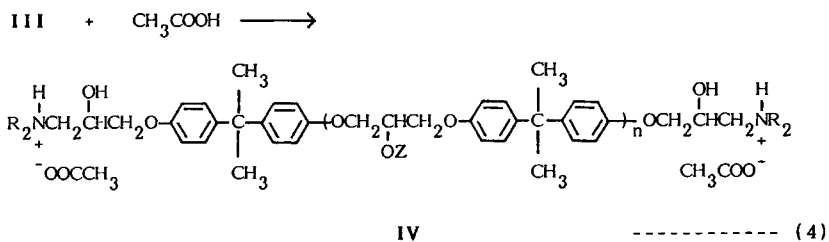
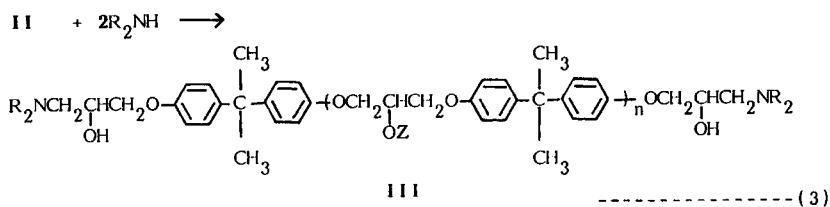


II

Z	Average number of Z
-H	x
or	
-CHNH- 	y

$$x = n/2 - 1, \quad y = n/2 + 1$$

- II-a: n=2
- II-b: n=4
- II-c: n=5.5



Resin	n	R
III-, IV-A-a	2	-C ₂ H ₅
III-, IV-A-b	4	-C ₂ H ₅
III-, IV-A-c	5.5	-C ₂ H ₅
III-, IV-B-a	2	-C ₂ H ₄ OH
III-, IV-B-b	4	-C ₂ H ₄ OH
III-, IV-B-c	5.5	-C ₂ H ₄ OH

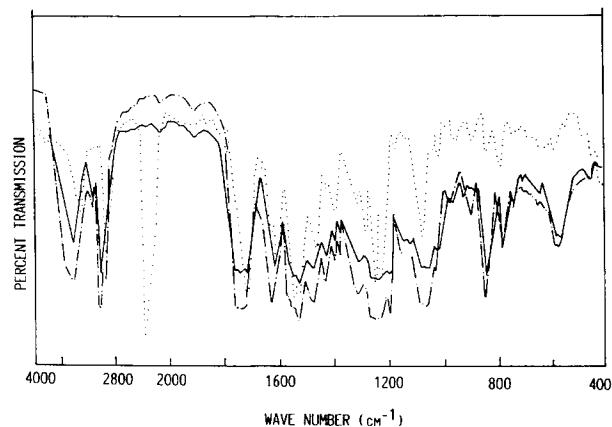


Figure 3 Infrared spectra of 2-ethylhexanol half-blocked TDI (I) (-----), resin II-A (- · - · -), and resin III-A-a (—).

taining material is at least that amount sufficient to render the resin cationic in character, i.e., transportable to the cathode when acid solubilized. In this work, all epoxy groups in the resin were reacted with amines. Two amines were used in the present work. They are diethylamine and diethanolamine.

Finally, the obtained epoxy-amine adducts (III) were neutralized with acetic acid and dispersed in deionized water, yielding a electrodepositable emulsion. The formation of a stable emulsion is affected by such factors as the pH value, the organic solvent content, and the resin content.

Preparation of Electrodeposition Emulsion

The polyepoxide-amine adducts III were readily soluble in various organic solvents, such as acetone, toluene, DMF, and BCS, whereas they were insoluble in water. It is necessary to add a neutralizing agent to obtain a suitable aqueous composition for electrodeposition. Neutralization of these adducts is accomplished by all or part of the amino groups with a water-soluble acid such as acetic acid. The extent of neutralization depends upon the particular resin system, and it is only necessary that sufficient acid is added to solubilize or disperse the resin. Thus, the pH value of resin solution plays an important role on the attainment of a stable emulsion. Moreover, the state of the aqueous dispersion was also affected by the contents of resin and organic solvent. Lower resin concentration and higher organic solvent content make the resins easier to be solubilized or dispersed in water. When the resin concentration exceeded a certain limit or the organic solvent content was too low, precipitation occurred.

Figure 4 shows the states of solution at different

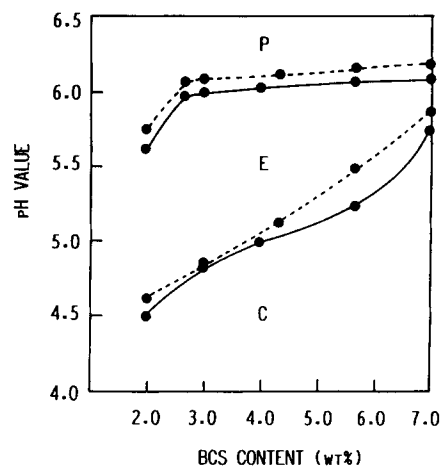


Figure 4 The effects of BCS content and pH value on the formation of stable emulsion of resin III-A-a and III-B-a. Resin concentration 7 wt %, resin III-A-a (—), and resin III-B-a (-----); P, precipitation; E, emulsion; C, clear solution.

pH values and BCS contents for the resins III-A-a and III-B-a at a resin concentration of 7 wt %. For both systems, when the BCS content ranged from 2–7 wt % and pH value was higher than 6.0, some polymer precipitated in the solution. If the pH value is lower than 4.5, the resins are almost completely neutralized and dissolve in the medium of water and BCS to form a clear solution. A stable, milky emulsion state was obtained when the pH value of so-

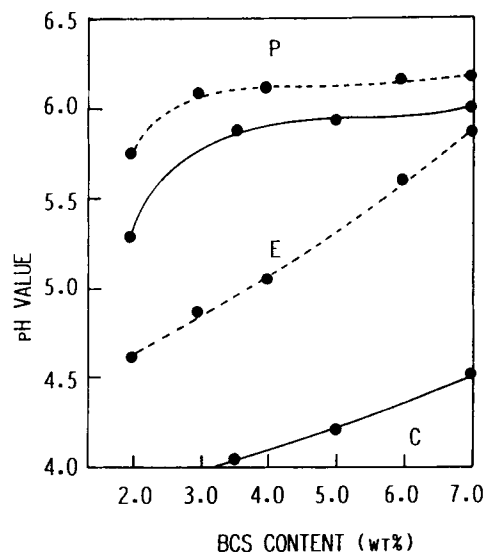


Figure 5 The effects of BCS content and pH value on the formation of stable emulsion of resin III-A-c and III-B-c. Resin concentration 8 wt %, resin III-A-c (—), and resin III-B-c (-----); P, precipitation; E, emulsion; C, clear solution.

lution was kept in a suitable range, as shown in Figure 4. Figure 5 shows the effects of pH value and BCS content on the formation of stable emulsions for resins III-A-c and III-B-c at a resin concentration of 8 wt %. In comparison with the conditions of III-A-a and III-B-a, it needs higher acidity (i.e., lower pH value) and BCS content to form a stable emulsion for these two resin systems. This is reasonable because resins III-A-a and III-B-a have higher molecular weights and, thus, lower solubility. Moreover, from Figures 4 and 5, it can be seen that III-B series require lower acidity and BCS content than III-A series to form stable emulsions or clear solutions. It may be explained as being due to an increase of hydrophilicity of diethanolamine-terminated III-B resins.

Electrodeposition of Resin Emulsions

Stable emulsions of the cationic epoxy resins could be obtained by the choice of suitable pH range, organic solvent content, and resin concentration. Proper quantity of emulsion was placed into the glass vessel of electrodeposition apparatus shown in Figure 1. When supplied with conductive electrodes and direct current, an adherent film of the resinous composition was deposited on the cathode (a phosphated steel panel). Following electrodeposition, the steel panel was rinsed to remove any nonadhering material and then baked to dry and crosslink the film. Some factors, such as the pH value, the organic

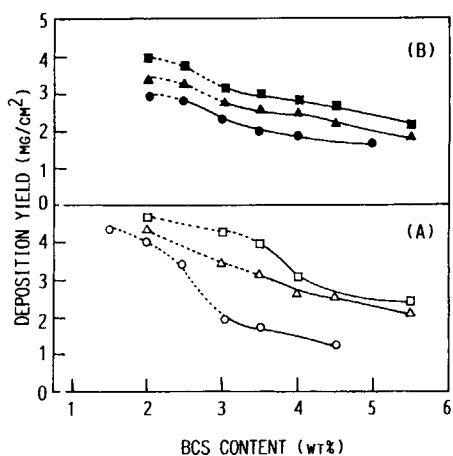


Figure 6 Effect of BCS content on deposition yield. (A), III-A system, pH 5.9, resin concentration 7.0 wt %; (B), III-B system, pH 5.9, resin concentration 8.0 wt %; ○, III-A-a; △, III-A-b; □, III-A-c; ●, III-B-a; ▲, III-B-b; ■, III-B-c; deposition time 3 min; applied voltage 150 V (----- uneven deposited coverage, — uniform deposited coverages).

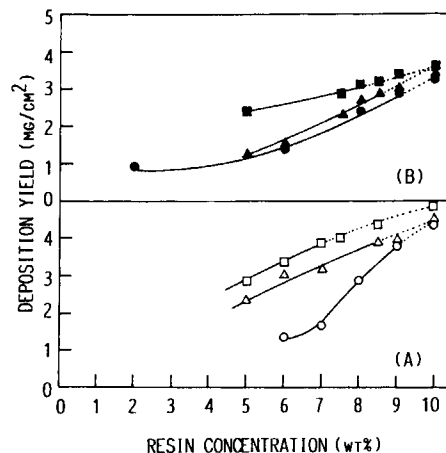


Figure 7 Effect of resin concentration on deposition yield. (A), III-A system, BCS content 3.5 wt %, pH 5.9; (B), III-B system, BCS content 3.0 wt %, pH 5.9; ○, III-A-a; △, III-A-b; □, III-A-c; ●, III-B-a; ▲, III-B-b; ■, III-B-c; deposition time 3 min; applied voltage 150 V (----- uneven deposited coverage, — uniform deposited coverage).

solvent content, and the resin content of the electrodeposition bath, affecting the yield of the deposited film after baking were investigated. The throwing power of the cationic resins and the rupture voltage of the wet electrodeposited film were also discussed.

Electrodeposition Yield

Figures 6(A) and (B) show the effects of BCS content on the deposition yield of resins III-A series and III-B series, respectively. Lower organic solvent contents might cause precipitation of the resin emulsions, and the suspended precipitated particles might migrate with the dispersed macrocations onto the cathode, leading to deposited films with rough surface. Higher BCS contents give deposited films with a pleasing appearance while lower deposition yields. The lower yields may account for the redissolution of the deposited resin particles on the cathode during electrodeposition at higher BCS contents.

Figure 7 shows the relationships between deposition yield and resin concentration when the BCS content and pH value of the emulsions were kept at a constant value. As expected, the deposition yield increases with the increase of resin concentration; however, too high a concentration (e.g., 10 wt %) causes precipitation of emulsion and gives deposited films with rough surface when electrodeposited.

The pH value of emulsion determines the dispersibility of the resins and hence it will affect the

electrodeposition yield. As shown in Figure 8, the deposition yield decreases with decreasing pH value. This is reasonable because higher acidity enhances the solubility of the deposited resin, lowering the yield. As the pH value exceeds 6.0, precipitation occurs and a uniform film cannot be obtained. Moreover, from Figures 6–8 it can be seen that the resin with higher molecular weight gives a higher deposition yield at the same conditions of electrodeposition. This may be attributable to the increase of molecular weight per charged resin unit, which leads to higher efficiency when electrodeposited. From the results shown in Figures 6–8, it can be concluded that the following conditions of electrodeposition emulsions are preferred for the attainment of deposited films with higher deposition yield and better appearance: pH of 5.5–6.0, BCS content between 3.0 and 5.0 wt %, and resin concentration in the range of 7.0 and 9.0 wt %.

Throwing Power

Throwing power is the one of most favorable characteristics of electrocoatings, meaning how uniformly electrodeposited film is built and how deeply it penetrates and deposits inside hollow and duplicated structures. The test apparatus and method were described in the experimental section. Figure 9 shows the effect of applied voltage on the throwing power of all cationic resins. The throwing power has a tendency to increase with increasing voltage, in

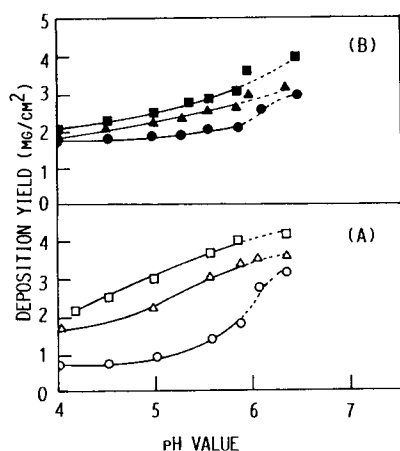


Figure 8 Effect of pH on deposition yield. (A), III-A system, BCS content 3.5 wt %, resin concentration 7 wt %; (B), III-B system, BCS content 3.0 wt %, resin concentration 8 wt %; ○, III-A-a; △, III-A-b; □, III-A-c; ●, III-B-a; ▲, III-B-b; ■, III-B-c; deposition time 3 min; applied voltage 150 V (----- uneven deposited coverage; ——— uniform deposited coverages).

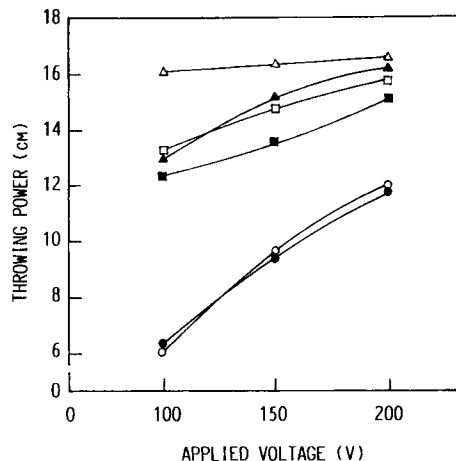


Figure 9 Effect of applied voltage on throwing power. Resin concentration 8 wt %; deposition time 3 min; ○, III-A-a; △, III-A-b; □, III-A-c; ●, III-B-a; ▲, III-B-b; ■, III-B-c.

particular for resins III-A-a and III-B-a. 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 result suggests that operation at the highest voltage possible, short of film rupture, will give the highest throwing power for a specific system. The effect of resin concentration on the throwing power is shown in Figure 10. Particularly for resins III-A-a and III-B-a of lower molecular weight, the throwing power decreases with the resin concentration. The decrease may be explained by the higher force of resistance of the migration of the macrocation during electrodeposition in an emulsion of higher resin content.

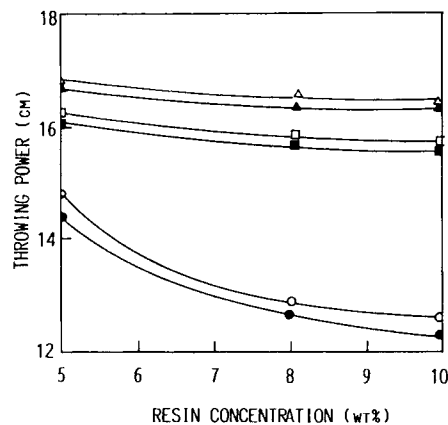


Figure 10 Effect of resin concentration on throwing power. Applied voltage 200 V; deposition time 3 min; ○, III-A-a; △, III-A-b; □, III-A-c; ●, III-B-a; ▲, III-B-b; ■, III-B-c.

Table I Rupture Voltage of Emulsions of Resin IV

Resin	Resin Content (wt %)	Rupture Voltage
IV-A-a	7	250
IV-A-b	7	300
IV-A-c	7	320
IV-B-a	8	250
IV-B-b	8	300
IV-B-c	8	320

Furthermore, Figures 9 and 10 also reveal that the resin with mediate molecular weight, such as III-A-b and III-B-b, showed the highest throwing power among each series of resins. However, the reason is not quite clear and it needs more detailed investigation.

Rupture Voltage

The rupture voltage means the electrocoating voltage at which the film, being so far in the normal conditions at the lower, begins suddenly to show remarkable defects like keloid, pit, etc. due to insulation rupture of film. During electrodeposition reaction, partially concentrated current due to the maldistribution of electroresistivity deposits excess resin film along with heat generation, leading to abnormal film formation that will be brought into film rupture as the final situation. Table I shows the rupture voltage of emulsions of resins IV-A series of 7 wt % and IV-B series of 8 wt %. All resins show a high rupture voltage above 250 V. This is expected because it needs higher energy to break the deposited

film from a resin of higher molecular weight due to a higher melting point.

Physical and Chemical Properties of Cured Films

The zinc phosphate pretreated steel panels were cathodically electrocoated in the electrodeposition baths at 150 V for 3 min at a bath temperature of 25°C. The bath conditions are: for III-A series, pH 5.7, BCS content 3 wt %, and resin concentration 7 wt %; for III-B series, pH 5.7, BCS content 3.5 wt %, and resin concentration 8 wt %. The wet deposited films were cured by baking at 185°C for 30 min. The mechanism is the formation of urethane linkage between interpolymers by deblocking (i.e., elimination of 2-ethylhexanol) the half-blocked TDI groups and subsequently being reacted with the hydroxyl groups pendant on the polymer backbones. The cured films were evaluated for adhesive strength, pencil hardness, salt-resistance, and alkali and acid resistance. The results are shown in Table II. All cured films showed excellent adhesive strength, good hardness up to 1 h, and high salt- and alkali-resistance. However, the cured deposited films derived from III-B resins showed less salt spray and acid resistance when compared to those derived from III-A series. This may be attributable to the fact that the terminal hydroxyl groups ($-C_2H_4OH$) of the III-B resins possibly reacted with the blocked TDI groups at elevated temperatures, thus leading to a lower degree of crosslinking of the cured films. These can be improved by increasing the content of the pendant-blocked TDI groups on the polymer backbone. As shown in the last column of Table II, the salt spray- and acid-resistance were significantly

Table II Physical and Chemical Properties of the Cured Film

Properties	III-A-a	III-A-b	III-A-c	III-B-a	III-B-b	III-B-c ^a	III-B-d ^b
Adhesive strength ^c	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Pencil hardness ^d	1H	1H	1H	1H	1H	1H	1H
Salt spray test (mm) ^e	2	2	2	4	4	4	2
Alkali resistance ^f	99.0	99.7	99.6	99.0	99.3	99.1	99.5
Acidic resistance ^g	98.7	99.2	99.5	— ^h	—	—	99.2

^a Total -OH group/-PBTDI mole ratio = 3.5.

^b Total -OH group/-PBTDI mole ratio = 1.0.

^c Determined by the standard method of JIS D-0202 (1 mm² × 100).

^d Measured with Mitsubishi pencils by using a Bravive-Instruments B-4000.

^e Evaluated by the standard method of JIS Z-2371, sprayed with 5% aqueous NaOH for 24 h.

^f 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 corresponding to the one before dipping.

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

^h The film was broken down completely.

enhanced by increasing the blocked TDI/hydroxyl group ratio to 1.0.

CONCLUSIONS

Self-crosslinking cationic electrodepositable resins can be prepared by first reacting diglycidyl ethers of bisphenol A having different epoxide equivalents with half-blocked 2,4-toluene diisocyanate, then ring-opening the epoxide groups with a secondary amine such as diethylamine or diethanolamine, and finally being neutralized with acetic acid. The resulting resins can be easily dispersed in deionized water, forming stable, milky emulsions by proper control of the pH value, BCS content of 3.0–5.0, and resin concentration of 7.0–9.0 wt %, and can be used in the cathodic electrodeposition process, producing resin films with favorable deposition yield and pleasing appearance after being cured at elevated temperatures. The throwing power of the cationic resins increases with the increase of applied voltage, and the resins with moderate molecular weight such as III-A-b and III-B-b showed the highest throwing power among each series. The rupture voltage of the deposited films was related to the molecular weight of resinous polymers. The film derived from the resin with higher molecular weight exhibited a higher rupture voltage during electrocoating. All cured deposited films from the resins of III-A and III-B series showed good appearance and adhesive strength, as well as high hardness and alkali-resistance; however, the ones derived from III-B series showed less salt

spray- and acid-resistance. Incorporating more crosslinking sites into III-B resins could enhance the salt spray- and acid-resistance of their deposited films after being cured.

REFERENCES

1. W. M. Alvino and L. C. Scala, *J. Appl. Polym. Sci.*, **27**, 341 (1982).
2. W. A. Alvino, T. J. Fuller, and L. C. Scala, *J. Appl. Polym. Sci.*, **28**, 267 (1983).
3. T. Matsumoto, E. Ushioda, M. Kono, and T. Uehara, *Kobunshi Ronbunshu*, **32**, 610 (1975).
4. Y. Fujimura, K. Nakamae, I. Sakai, and T. Matsumoto, *Kobunshi Ronbunshu*, **39**, 777 (1982).
5. K. Sekmakeeas and R. Shah, U.S. Pat. 4,263,189 (1981).
6. J. F. Bosso, U.S. Pat. 4,294,741 (1981).
7. E. L. Jozwiak, U.S. Pat. 4,297,261 (1981).
8. K. Sekmakas, U.S. Pat. 3,891,527 (1975).
9. D. Suryya, U.S. Pat. 304,703 (1981).
10. E. H. Wagener and R. A. Wessling, U.S. Pat. 4,225,407 (1980).
11. N. Hiso, H. Michisuke, and Y. Seij, *Jpn. Kokai* 80,05,933 (1980).
12. J. F. Bosso, U.S. Pat. 4,294,741 (1981).
13. S. K. Das, U.S. Pat. 4,304,703 (1981).
14. K. F. Schimmel, U.S. Pat. 4,069,210 (1978).
15. J. F. Bosso, R. M. Nugent, and J. E. Plasynski, U.S. Pat. 4,260,720 (1981).
16. H. P. Patzschke and A. Gobel, U.S. Pat. 4,252,703 (1981).

Received February 28, 1990

Accepted April 23, 1990