

# Preparation and Cationic Electrodeposition of Amine-Functional Epoxy Resins

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## Synopsis

2-Ethylhexanol-blocked toluene diisocyanate (2-EH-blocked TDI) modified resin was first prepared from epoxy resin and 2-EH partially blocked TDI and subsequently reacted with di(2-methylisobutylketiminoethyl)amine to obtain ketimine-terminated resins. These ketimine-terminated resins were hydrolyzed and partially neutralized with acetic acid to give macrocations. The resulting cationic resins were dissolved in suitable solvents and mixed with deionized water to form various emulsions. The formation of a stable emulsion is strongly dependent on the pH value of the emulsion and the amount of solvent added. Electrodeposition of the emulsion produced films of amine-terminated and 2-EH-blocked TDI modified epoxy resins on the surface of a cathode. Factors such as the pH value of the emulsion, the content of organic solvents, the amount of 2-EH-blocked TDI, applied voltage, and electrodeposition time on the electrodeposition properties (such as deposition yield and throwing power of the resins) were investigated. Moreover, the deposited film could be thermally cured to have a crosslinked structure. It was found that a temperature above 160°C is required to crosslink the deposited resins.

## INTRODUCTION

The process of electrodeposition has been developed to provide uniform, highly adhesive, corrosion-resistant primer coats, particularly for the automobile industry. A cationic deposition process has recently been introduced commercially. Theoretically, it offers the best potential for rust resistance. In the most common form of the process, polymers that contain amine functionality are produced.<sup>1-5</sup> These polymers are then "solubilized" in an aqueous medium by partial neutralization with an acid to give macrocations. Several other types of macrocations have been described in the patent literature, such as quaternary ammonium acid salts,<sup>6,7</sup> quaternary ammonium hydroxides,<sup>8</sup> quaternary phosphonium acid salts,<sup>9</sup> tertiary sulfonium acid salts,<sup>10,11</sup> and quaternary ammonium carboxylate.<sup>12,13</sup> The polymers generally used for the backbone of cathodic electrodeposition resins are acrylic copolymers,<sup>14-16</sup> epoxy resins and their copolymers,<sup>6,8-10</sup> and polyurethanes.<sup>17-19</sup>

The part to be coated is made a cathode (-) and immersed in a tank containing the macrocation solution plus pigment, plasticizer, curing agent, and other ingredients. The applied electric field draws the macrocations to the surface where they are deposited as a film. Following electrodeposition, objects are usually rinsed to remove any nonadhering material and then baked to dry and fuse the film, and perhaps crosslink it. From the standpoint of forming a continuous, uniform, and therefore highly corrosion-resistant film, this process has significant advantages. The electric field draws the articles into all the

nooks and crannies of the part (good "throwing power"). Furthermore, pollution and fire hazards are minimized, and the process wastes very little material (unlike spraying) and so offers economic advantages.

In the present work, our purpose was to prepare thermally crosslinkable amine-functional epoxy resins starting from an epoxy resin of diglycidyl ether of bisphenol A (with epoxy equivalent of 950), 2-ethylhexanol-blocked TDI, and di(2-methylisobutyl)ketimine of diethylene triamine. The resins obtained are then solubilized in organic solvents such as butyl cellosolve (BCS) or hexyl cellosolve (HCS) by neutralization with acetic acid to give the macrocation solutions and to which the proper quantity of deionized water is added to form emulsions used for electrodeposition. The effects of pH value and the amount of organic solvent added on the preparation of emulsion will be investigated. The nature of electrodeposition of the cationic resins and the crosslinking behavior of the deposited films will also be discussed.

## EXPERIMENTAL

### Materials

Reagents used in the preparation of di(2-methylisobutylketiminoethyl)amine included the reagent-pure grade of diethylene triamine (DETA), methyl isobutyl ketone (MIBK) (Hayashi Pure Chemicals, Ltd., Japan), and 50w-x8 ion exchange resin (Merck).

A diglycidyl ether of bisphenol A (DGEBA) epoxy resin (epoxy equivalent 950), toluene diisocyanate (TDI), 2-ethylhexanol (2-EH) (WAKO Extra Pure Grade), and di(2-methylisobutylketiminoethyl)amine were used in the preparation of thermally crosslinkable cationic electrodeposition resins. The epoxy resin was dried by toluene-water azeotropic distillation before use.

### Apparatus

An IR spectrometer (JASCO IRA-2), a thermal analyzer (DuPont 951 analysis unit), a conductivity meter, a pH meter, an electrodeposition apparatus, and a throwing power testing vessel were employed. The electrodeposition apparatus included a glass vessel with a cover. On the cover were suspended a clean plated iron pretreated with zinc phosphate (used as the cathode) and a copper electrode (as the anode), which contained a surface area of approximately 20 cm<sup>2</sup>. The electrodes were connected to a dc power supply (PHI Hong Instrumental Co.; 0-500 V, 0-6 A). The throwing power testing vessel included a stainless steel vessel (used as the anode) with a height of 23 cm and an inner diameter of 6 cm and a stainless steel strip (as the cathode) with a length of 20.5 cm, a width of 0.8 cm, and a thickness of 0.08 cm. The stainless steel strip was suspended in a hollow glass vessel with a height of 20 cm and a diameter of 1 cm.

### Synthesis

#### *Di(2-methylisobutylketiminoethyl)amine (1)*

DETA (47.7 g, 0.463 mol), MIBK (112 g, 1.12 mol), Dowex 50w-x8 ion exchange resin (0.25 g), and benzene (300 g) were added to a 500-mL three-

necked flask equipped with an electric stirrer and a Dean-Stark reflux condenser. The mixture was heated to boil. The generated water was distilled off azeotropically. The azeotropic distillation was continued until no further evolution of water was observed. After cooling, the ion exchange resin was removed by filtration. Then, benzene was distilled under reduced pressure. The di(2-methylisobutylketiminoethyl)amine obtained was purified by distillation at 116–118°C under 0.8 torr. The product was a colorless liquid (sp. gr. 1.17) at room temperature.

### *2-Ethylhexanol-blocked TDI (2)*

A given quantity of TDI was added to a four-necked flask equipped with an electric stirrer, a reflux condenser, a dropping funnel, and an inert nitrogen blanket. A calculated quantity of 2-ethylhexanol was added dropwise into the flask under an ice bath. The mixture was kept at room temperature for 1 h and was gradually heated to 40°C for an additional 30 min to give 2-ethylhexanol half-blocked TDI (2-EH-blocked TDI) (**2**).

### *Synthesis of Resin 5a–d*

An epoxy resin (95 g) and toluene (300 mL) were added to a five-necked flask equipped with an electric stirrer, a Dean-Stark trap, a dropping funnel, and inert nitrogen blanket. The mixture was heated to 110–120°C to remove any water in the epoxy resin by azeotropic distillation. The azeotropic distillation was continued until no further evolution of water was observed. After cooling to 40–50°C, a calculated quantity of **2** was added into the flask. The whole mixture was gradually heated to 90°C and kept at that temperature for 3 h. After cooling the product to 60°C, 26.7 g (0.1 mol) of **1** was added to the flask. The mixture was heated to 90°C and kept at that temperature for 3 h for the completion of the reaction. Finally, toluene was distilled off under reduced pressure. When cooled to room temperature, a golden, brittle solid of resin **5a–d** was obtained.

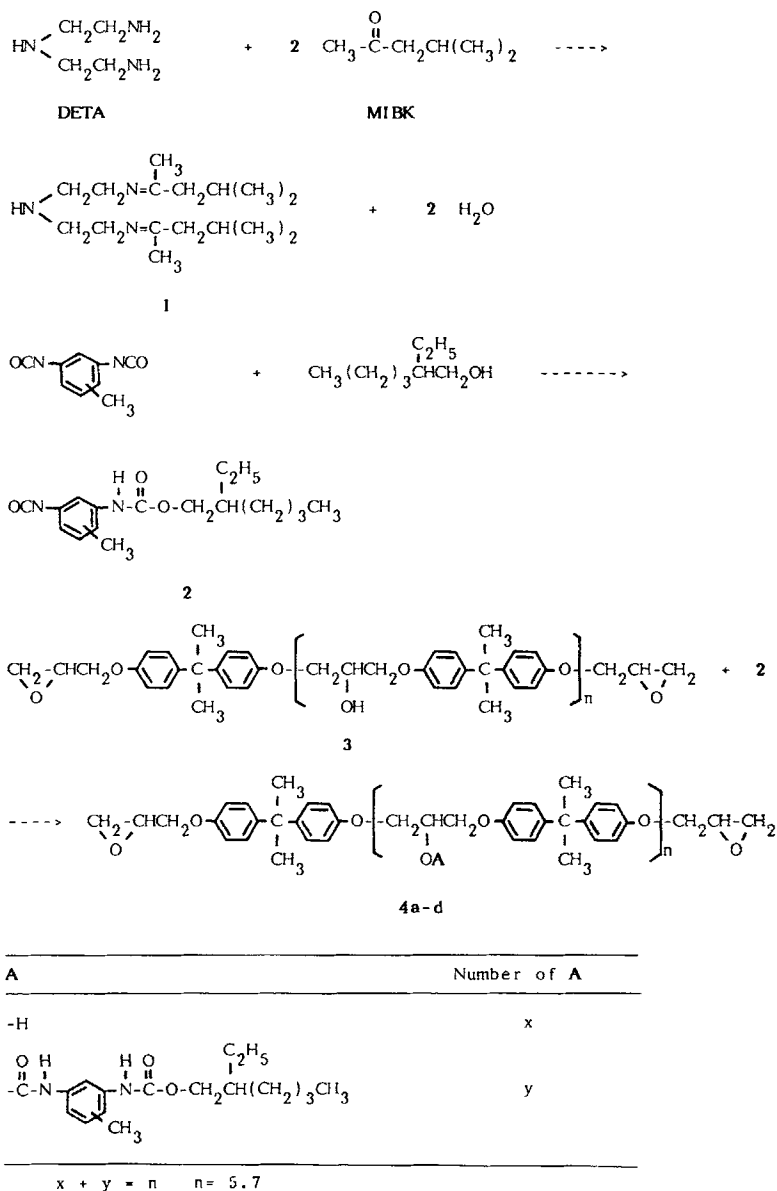
### *Preparation of Emulsions*

The general process for the preparation of the emulsion is as follows. In a reactor 17.5 g of resin **5a–d** were dissolved in various amount of HCS or BCS. Into the solution a desired amount of acetic acid was added, and the mixture was heated at 60°C for 10 min. Then, 330 mL of deionized water was added dropwise into the solution with vigorous stirring to produce an emulsion.

## **Characterization**

### *Thermogravimetric Analysis*

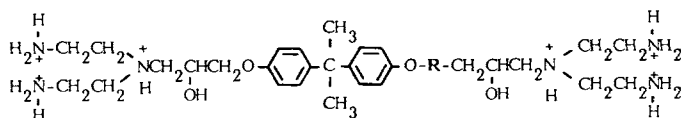
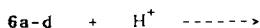
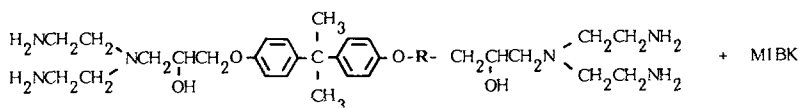
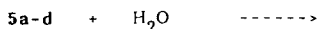
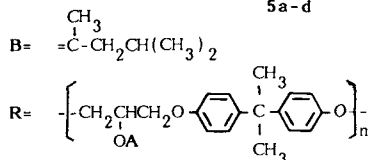
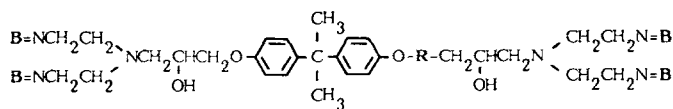
The thermogravimetric (TG) analysis was performed on a DuPont 951 thermogravimetric analyzer coupled to a DuPont 1090 thermal analyzer in flowing nitrogen (50 cm<sup>3</sup>/min) at a heating rate of 10°C/min.



Scheme 1

### Gel Content

A 40 wt % resin solution, prepared by mixing the resin and toluene, was spread on aluminum foil and baked at various temperatures for 20 min to form crosslinked film. The crosslinked film of the resin obtained 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 crosslinked film.



4-7	4-7a	4-7b	4-7c	4-7d
y	3	4	5	5.7

Scheme 1 (Continued from the previous page.)

*Bath Conductivity*

The conductivity and pH value of the emulsion was measured by adding acetic acid dropwise into the emulsion at room temperature.

*Electrodeposition*

Approximately 350 mL of emulsion was placed in the glass vessel of the electrodeposition apparatus as described in a previous publication.<sup>20</sup> The electrodes were immersed in the emulsion and electrodeposition was carried out at various voltages for different deposition times. The cathode was removed from the emulsion, washed with water, and successively heated to 180°C to obtain the deposition yield.

*Throwing Power*

The throwing power of the emulsion was measured by a tube penetration test, which includes a stainless vessel connected to the cathode and a stainless

strip connected to the anode. The stainless strip and a hollow cylinder was immersed into the emulsion contained in the vessel. After a constant dc voltage was applied for 1 min, the strip was rinsed off with water. The height (in cm) of polymer deposited is defined as the throwing power.

## RESULTS AND DISCUSSION

### Synthesis

Cationic resins (**7a–d**) were synthesized by reacting the secondary amine of ketimine blocked diethylene triamine (**1**) with 2-EH-blocked-TDI-modified epoxy resin (**4a–d**) and subsequent hydrolysis of the resulting resin and further neutralization with acetic acid. As shown in Scheme 1, diethylene triamine first reacts with MIBK to form the primary amine-protected triamine **1**, which subsequently reacts with 2-EH-blocked-TDI-modified resin (**4**) to give ketimine-terminated resin **5**. Resin **5** can be easily hydrolyzed to primary amine-containing resin **6**.

There are two procedures for producing resin **5a–d**. One is to first react the epoxy resin (**3**) with secondary amine (**1**). The resulting resins are then reacted with 2-EH-blocked TDI (**2**). The secondary is to first react epoxy resin with 2-EH-blocked TDI, followed by the reaction with secondary amine to give resin **5a–d**. The latter procedure is adopted in this study.

Resin **6** was treated with acetic acid to give cationic resin **7**. The quantity of acetic acid added decided the amount of cation formed, and thus, the solubility of these cationic resins.

### Crosslinking Reaction and Crosslinking Properties of Resin **6**

When resin **6** was heated at elevated temperature, the pendant-blocked isocyanate will release the blocking agent, 2-ethyl hexanol, to generate free isocyanate. These free isocyanates react with the secondary hydroxyl groups or primary amine groups of other molecules to form new urethane linkages or urea linkages and produce a crosslinked structure. Figure 1 shows that the rate of weight loss increases at temperatures above 160°C. This indicates that the pendant-blocked isocyanate deblocks the 2-EH at temperatures higher than 160°C. The initial pyrolysis temperature of the resins is about 300°C and the resins decompose completely at about 500°C.

The effects of curing temperature on the gel content of crosslinked films prepared from resin **6** are shown in Figure 2. When the curing temperatures are lower than 160°C, all the gel contents are lower than 50%. The gel content of the crosslinked film increases with curing temperature when the curing temperature is above 160°C and then the gel content reaches a constant value at temperatures higher than 180°C. This shows that the crosslinking reaction takes place at temperatures above 160°C. Figure 3 reveals that the gel content of the crosslinked film also increases with increasing amounts of 2-EH-blocked TDI added (i.e., **6d** > **6c** > **6b** > **6a**).

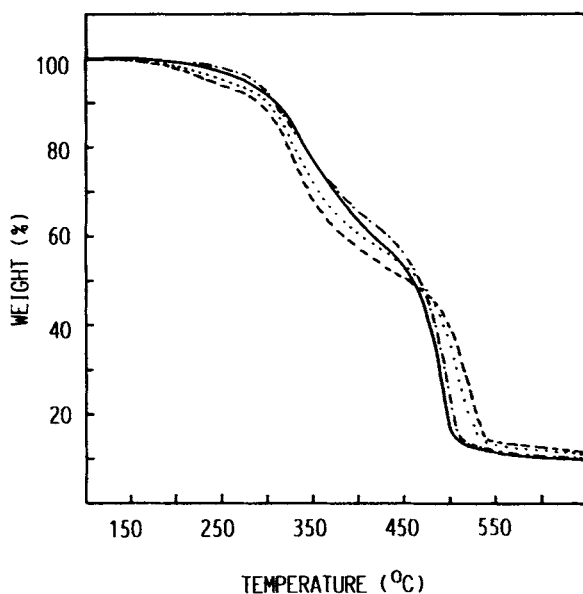


Fig. 1. TGA curves of resins **6a–d** with a heating rate of 10°C/min in N<sub>2</sub>: (---) **6a**; (—) **6b**; (· · · ·) **6c**; (- · - ·) **6d**.

## PROPERTIES OF CATIONIC RESINS

### Effects of pH Value and Amount of Organic Solvents on the Formation of Emulsion

Resin **6** contains tertiary amine and primary amine groups and can be converted to cationic resin **7** when treated with acetic acid. The aqueous solution of cationic resin can form stable emulsions when mixed with proper amounts of organic solvent such as BCS and HCS. Resin **6** is readily dissolved in organic solvents, such as BCS and HCS, but difficult to dissolve in water. In the presence of ammonium salts, resin **7** is readily soluble in hydrophilic solvents and polar solvents but is insoluble in hydrophobic solvents. The water solubility of resin **6** is significantly affected by the pH value of the emulsion. The conversion of resin **6** to **7** is reversible. For high pH solutions, resin **6** is predominant, and the solubility of resin is reduced. Lower pH value, i.e., higher acidity, favors the formation of cationic resin **7**. For example, at 5 wt % of solid content of resin **6a**, the solution with little or no BCS content (less than 5 wt % on the basis of resin) will precipitate quickly. When the BCS content is over 45 wt %, the emulsion is almost clear if the pH value is lower than 8.2 (Fig. 4). The resin solution forms a stable emulsion state at 5–45% of BCS content and 5.0–8.2 of pH value. When using HCS as the solvent, the mixed solution appears homogeneous and clear at pH values lower than 5.6. Precipitation occurs when the HCS content is below 10 wt % or the pH value is higher than 8.7. As shown in Figure 4, the solution shows a stable emulsion state if pH is at 5.6–8.7 and with higher than 10 wt % of HCS content.

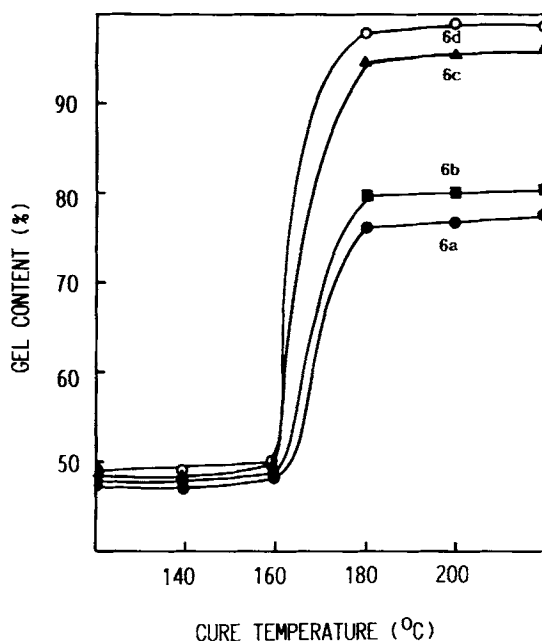


Fig. 2. Effects of curing temperature on the gel content of the crosslinked films prepared from resin **6a-d**.

### Bath Conductivity

The bath conductivity of the emulsion is dependent on the pH values of the emulsion. Figures 5, 6, and 7 show the relationship between the bath conductivity and pH values of the emulsions of **7a-d** for different solvent systems. It can be seen that the conductivity of the emulsions decrease with increasing pH.

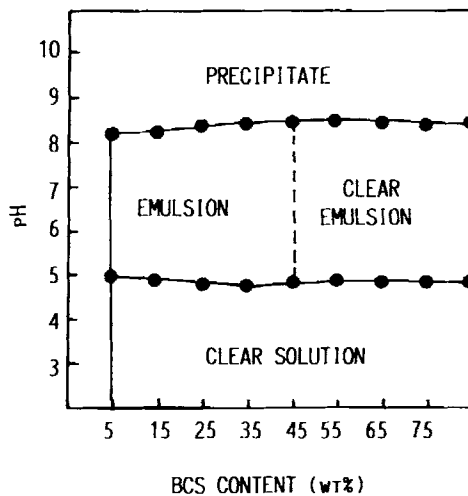


Fig. 3. Effects of BCS content and pH value on the solubility of resin **6a**.



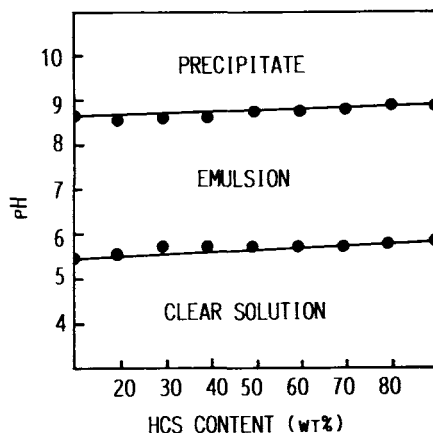


Fig. 4. Effects of HCS content and pH value on the solubility of resin **6a**.

Comparisons of curves in Figures 5 and 6 reveal that the conductivity of the emulsions also decrease with the increase of the amount of 2-EH-blocked TDI (i.e., **7a** > **7b** > **7c** > **7d**). This is due to the fact that the emulsion prepared from the resin with smaller molecular weight contains more conductive ions. Figure 7 shows that the conductivity of the emulsion increases with the increase of BCS content.

### Electrodeposition Properties

The principle of electrodeposition is that of emulsion solution electrolysis when the voltage is applied. Hydroxyl anions are generated at the cathode, and

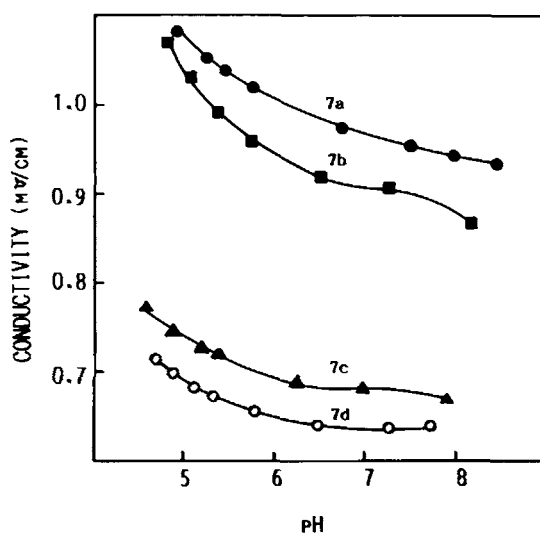


Fig. 5. Effects of pH value on the conductivity of emulsion prepared from resin **7a-d**: BCS content = 10 wt %; resin concentration = 5 wt %.

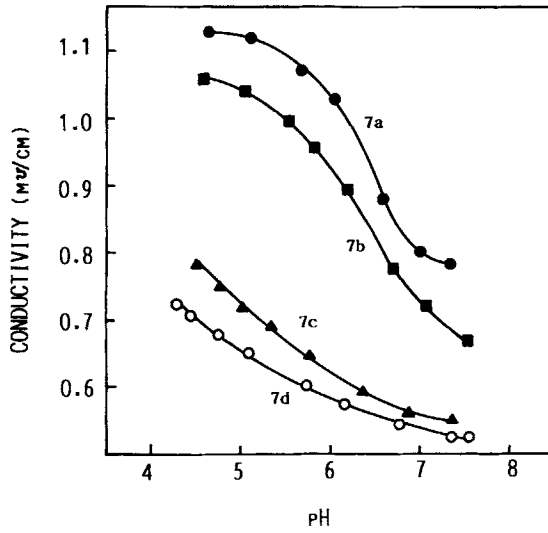


Fig. 6. Effects of pH value on the conductivity of emulsion prepared from resin 7a-d: HCS content = 10 wt %; resin concentration = 5 wt %.

the cationic resin (7) is deposited on the cathode to form an insoluble resin 6. The cathodic reactions are as follows:

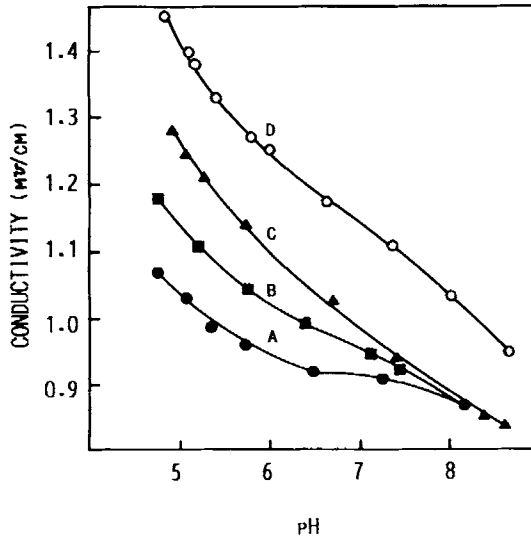
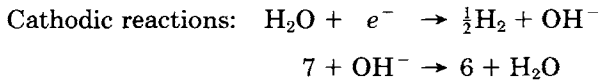


Fig. 7. Effects of pH value on the conductivity of emulsion prepared from resin 7b: resin concentration = 5 wt %. BCS content = (A) 10 wt %, (B) 20 wt %, (C) 30 wt %, and (D) 40 wt %.

*Throwing Power*

The throwing power of a paint is a term used to describe the ability of the paint to coat recessed and shielded areas. It depends on the electrical conductivity of the liquid paint and the resistance of the deposited films. The throwing power of the synthetic resins is dependent on the pH values of emulsions, the content of solvent, and the applied voltages, as shown in Figures 8, 9, and 10. The throwing power increases with decreasing pH values, as shown in Figure 8. This is due to the fact that at lower emulsion pH the ionic resin **7** predominates and increases the emulsion conductivity. It can be observed that the throwing power also increases as the applied voltage increases, as shown in Figures 9 and 10. This can be explained by the fact that the increase of applied voltage accelerates the migration rate of the resin. The amount of solvent added in the emulsion also affects the throwing power. Increasing the amount of solvent in the emulsion increases the solubility of the resin and reduces the resistance to motion of macrocations, leading to increasing throwing power. At higher solvent content, the throwing power reaches a limiting value at higher applied voltages (Fig. 9). Meanwhile, the throwing power also depends on the amount of 2-EH-blocked TDI in the pendant resin side chain. More 2-EH-blocked-TDI-modified resin shows a higher throwing power. For the same resin, the throwing power of HCS-containing emulsion is higher than that of BCS-containing emulsion. This can be explained by the higher solvating power of BCS, which can redissolve the deposited resin.

*Electrodeposition Yield*

The electrodeposition yields are dependent on the deposition time, pH value of the emulsion, the applied voltage, the kind and the amount of solvent added,

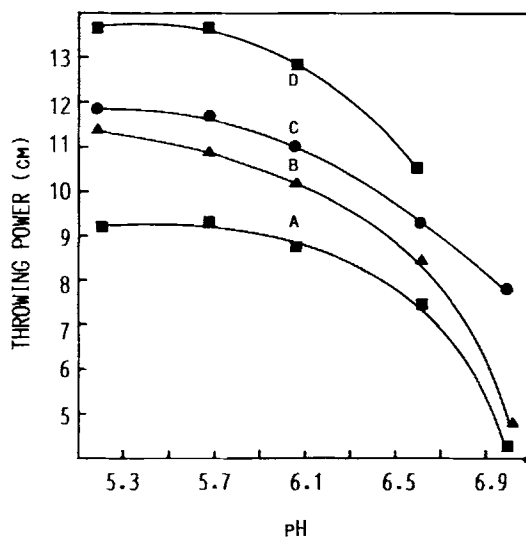


Fig. 8. Effects of pH value on the throwing power of emulsion prepared from resin **7a**: HCS content = 10 wt %; resin concentration = 5 wt %; applied voltage = (A) 90 V, (B) 120 V, (C) 150 V, and (D) 200 V.

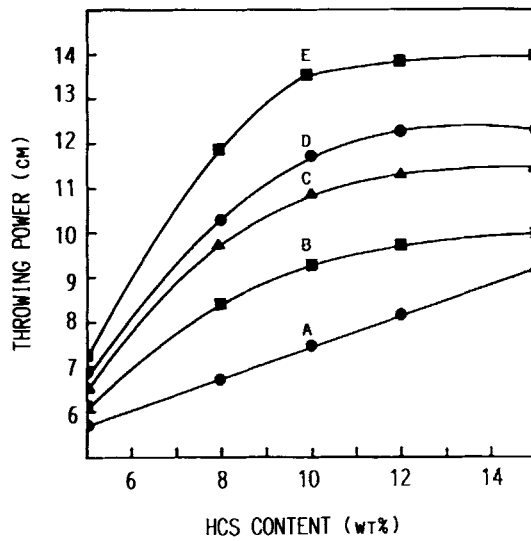


Fig. 9. Effects of HCS content on the throwing power of emulsion prepared from resin **7a**: resin concentration = 5 wt %; applied voltage = (A) 70 V, (B) 90 V, (C) 120 V, (D) 150 V, and (E) 200 V.

and the kind and molecular weight of the resins. Figure 11 shows the effects of electrodeposition time and pH value on the deposition yield of resin **7a**. The electrodeposition yield increases with the deposition time and levels off after about 3 min of electrodeposition. Emulsions having a higher pH value give a higher deposition yield (Figures 11 and 12). This can be attributed to the fact

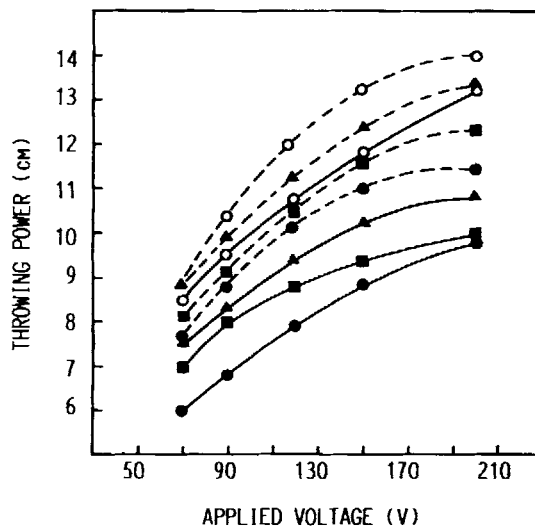


Fig. 10. Effects of applied voltage on the throwing power of emulsion prepared from resin **7a-d**: ■ **7a**; ● **7b**; ▲ **7c**; ○ **7d**. pH = 6.29 (—) BCS content = 10 wt %; (---) HCS content = 10 wt %.

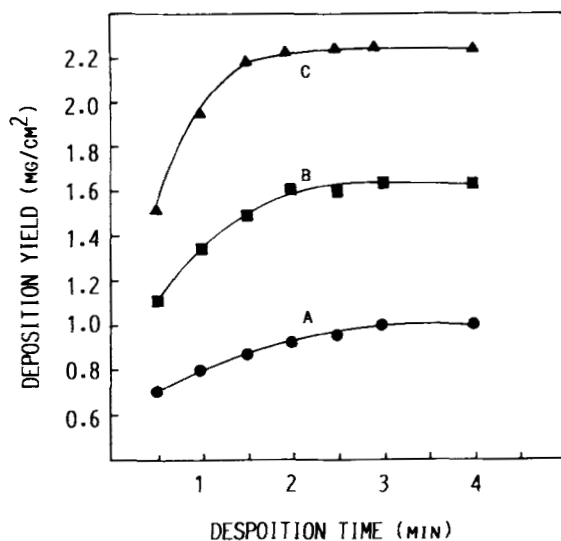


Fig. 11. Effects of deposition time and pH value of the emulsion on the deposition yield of emulsion prepared from resin **7a**. HCS content = 10 wt %; resin concentration = 5 wt %; applied voltage = 150 V; (A) pH = 5.18; (B) pH = 5.56; (C) pH = 6.06.

that the low pH value (i.e., high acidity) of the emulsion increases the solubility of deposited films. From Figures 13–15, it can be observed that the deposition yield increases as the applied voltage increases. The deposition yield of the emulsion is also dependent on the kind and the quantity of solvent added. In the case of adding BCS as solvent, a higher BCS content leads to a lower deposition yield (Fig. 13). This phenomenon also can be explained by the higher

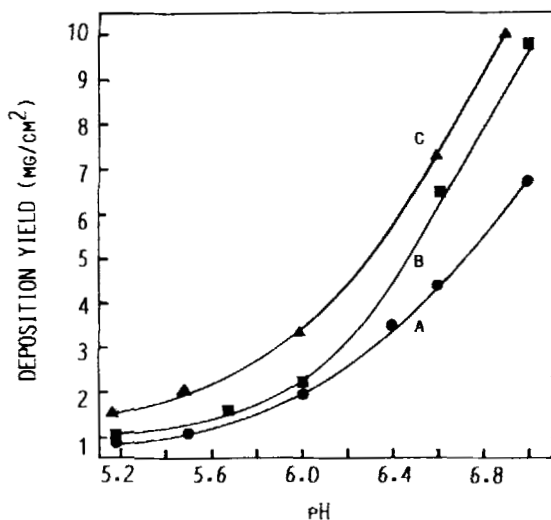


Fig. 12. Effects of pH value on deposition yield of emulsion prepared from resin **7a**: HCS content = 10 wt %; resin concentration = 5 wt %; applied voltage = 150 V; deposition time = 3 min.

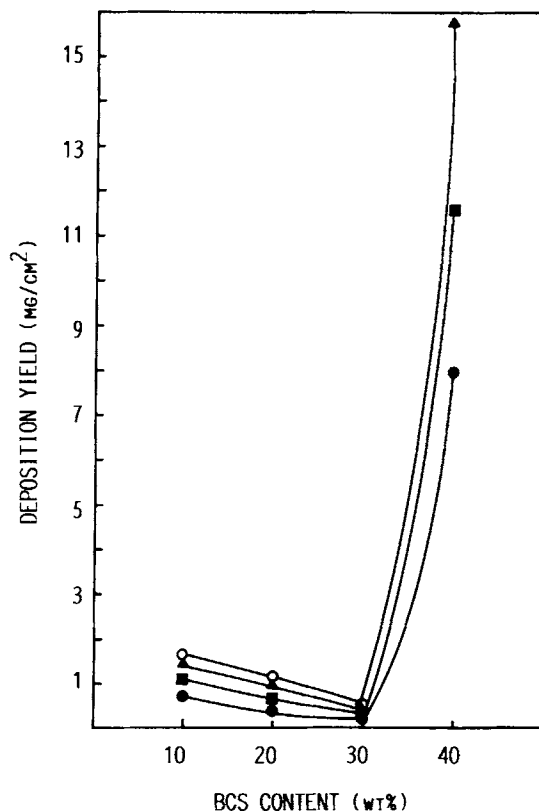


Fig. 13. Plot of the deposition yield of emulsion prepared from resin **7a** vs. BCS content under different applied voltage: resin concentration = 5 wt %; deposition time = 3 min; applied voltage = ● 50 V, ■ 100 V, ▲ 150 V, and ○ 200 V.

solvating power of BCS, as already described. When the BCS content is beyond 40 wt %, a large amount of rough and porous resin deposits on the cathode. From the examination of deposition current, it can be found that deposition current keeps a constant value during the deposition. This indicates that the rough and porous resin cannot form an isolation film on the cathode, so the electrolysis continues and a large amount of resin neutralizes on the cathode. When HCS is used as solvent, higher levels give a higher deposited yield (Fig. 14). Because HCS is more hydrophobic than BCS, the deposited film on the cathode is not easily redissolved during electrodeposition. Figure 15 shows that the deposition yield decreases with increasing amounts of the 2-EH-blocked TDI contained in the pendant chain of resin **7** (i.e., **7a** > **7b** > **7c** > **7d**).

## CONCLUSIONS

1. 2-EH-blocked-TDI-modified resin will deblock 2-EH to regenerate free isocyanate above 160°C and then react with hydroxyl groups or amino groups to form urethane or urea linkages.

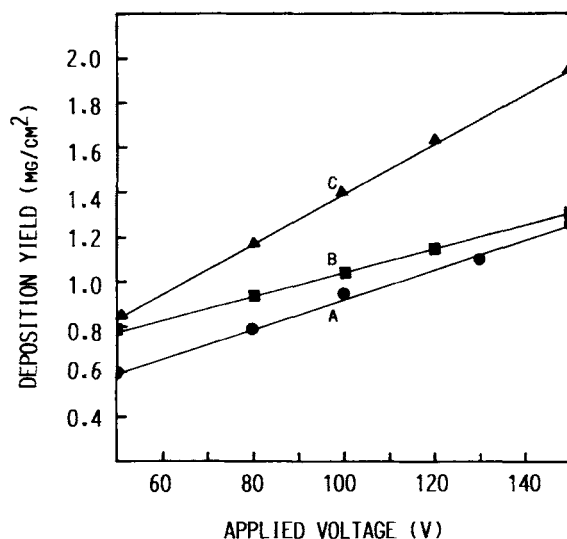


Fig. 14. Relationships of the deposition yield of the emulsion of resin **7b** with various HCS contents and applied voltage: pH = 4.48; deposition time = 3 min; resin concentration = 5 wt %; HCS content = (A) 5 wt %, (B) 10 wt %, and (C) 15 wt %.

2. The emulsion properties are strongly dependent on the pH value of emulsion and the amount of solvent added. The resin solution forms a stable emulsion state when the BCS content is between 5 and 45 wt % and the pH value is between 5.0 and 8.2. When using HCS as the solvent, the solution shows a

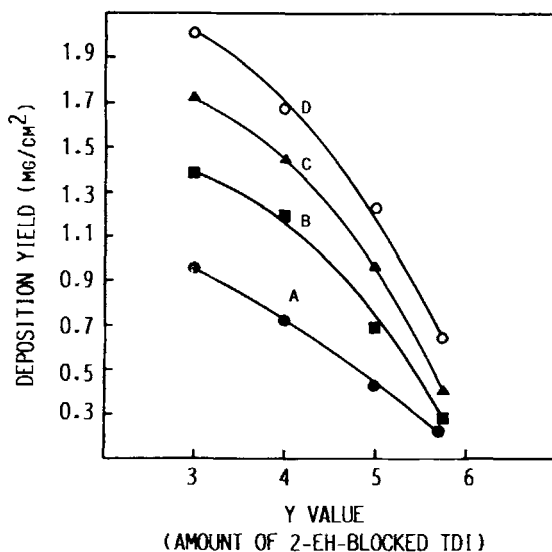


Fig. 15. Effects of the amount of 2-EH-blocked TDI (y value) on deposition yield of emulsion prepared from resin **7** under different applied voltage: BCS content = 10 wt %; deposition time = 3 min; pH = 6.3; resin concentration 10 wt %; applied voltage = (A) 50 V, (B) 100 V, (C) 150 V, and (D) 200 V.

stable emulsion state when pH value is between 5.6 and 8.7 and the HCS content is beyond 10 wt %.

3. The bath conductivity of the emulsion decreases with the increase in pH value of the emulsion. It also decreases with increasing amounts of 2-EH-blocked TDI of cationic resins.

4. The throwing power of the emulsion decreases with increasing pH and increases with increasing HCS content and applied voltage.

5. For stable emulsion, the higher HCS content gives a higher deposition yield. But the deposition yield decreases with increasing BCS content. The thickness of deposited films can be controlled by adjusting the solvent content.

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