

Preparation and Electrodeposition Properties of Trimethylolpropane-Toluene Diisocyanate-Dimethylaminoethanol/2-Ethylhexanol Resins

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SYNOPSIS

2,4-Toluene diisocyanate (TDI) was partially blocked with equimolar mixtures of dimethylaminoethanol (DMAE) and 2-ethylhexanol (2EH) of different ratios to form the DMAE/2EH half-blocked TDIs, which were subsequently reacted with 1/3 mol trimethylolpropane (TMP) to yield the trimethylolpropane-toluene diisocyanate-dimethylaminoethanol/2-ethylhexanol (TMP-TDI-DMAE/2EH) resins having various content of tertiary amine groups. These resins were neutralized with acetic acid and then dispersed in deionized water, resulting in the milky emulsions used for cationic electrodeposition. Some electrodeposition properties, such as deposition yield, conductivity, rupture voltage, and throwing power, of the resins were investigated. In addition, one of the obtained resins (added as a crosslinker) and an amine-epoxy adduct were codispersed in deionized water, and the nature of electrodeposition of the two-component emulsion is discussed.

INTRODUCTION

A large and diverse class of polymers has been developed for cathodic electrodeposited coatings. The most frequently used ones included acrylic copolymers,¹⁻⁹ epoxy resins and their copolymers,¹⁰⁻¹⁴ and polyurethanes.¹⁵⁻¹⁸ Epoxy resins and their copolymers offer higher levels of corrosion resistance and hence have been adopted to provide the first or prime coat to a variety of products such as automotive bodies. Acrylic copolymers provide better weather resistance and outstanding gloss, suitable for applications as topcoats.

According to the type of crosslinking, the cationic electrodeposition coatings can be divided into one-component (self-crosslinking type)^{1-4,10-11,15} and two-component systems.^{5-9,12-14,16-18} In the former system, the binder polymer contains latent crosslinking sites in the backbone that are thermosetting without addition of additional crosslinking component. The amounts of latent crosslinking groups can

be easily controlled to give the desired crosslinking density of the electrodeposited films. However, due to the presence of latent curing groups, gelation may occur when the preparation of the binder polymer is carried out at elevated temperature. In the latter system, a crosslinking agent is mixed with a binder polymer and then codispersed in an aqueous solution. This avoids possible gelation during the preparation of the binder polymer. It also imparts better storage stability to the electrodeposition emulsions. However, the difference in electrophoretic velocities between the resin and the crosslinker molecules may cause a deleterious effect on the electrodeposition.

In the reported papers, the crosslinkers of two-component cationic resin system were commonly noncharged resins such as blocked isocyanates; therefore, the electrodeposition mechanism is not quite clear. It is presumed that the noncharged crosslinkers are entangled by the positively charged resin during the dispersion process and comigrate with the resin to the cathode during electrodeposition. However, crosslinkers without hydrophilic groups will render the emulsions unstable, and precipitation may occur when they are dispersed in the aqueous solutions. The ratio of the crosslinker to the charged resin in the emulsion will vary after

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successive depositions, so that the deposition amounts of the crosslinker and the charged resin are not easy to control. These factors will affect the properties of the deposited films. In this study, in order to reduce these defects, a tertiary amine group was introduced into the crosslinkers and then treated with acetic acid and dispersed in deionized water to form positively charged crosslinker dispersions. For example, mixtures of DMAE/2EH was first reacted with 2,4-toluene diisocyanate (TDI) to yield partially blocked TDI, which was then reacted with a stoichiometric amount of trimethylolpropane (TMP) giving rise to TMP-TDI-DMAE/2EH resin, which contains tertiary amine groups. These resins were neutralized with acetic acid and dispersed in deionized water, and some parameters involved in the optimization of electrodeposition were investigated. In addition, an amine-epoxy adduct prepared from diethylamine and Epikote 1004 is codispersed with the crosslinkers, TMP-TDI-DMAE/2EH resins, to form the two-component electrodeposition coatings and their electrodeposition properties are also discussed.

EXPERIMENTAL

Materials

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

Epikote 1004 [poly(glycidyl ether) of bisphenol A, commercially available from Shell Chemical Co. and possessing an epoxy equivalent weight of about 950] and diethylamine (Hanawan extra pure grade) were used in the preparation of amine-epoxy adduct.

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

A conductivity meter, a pH meter, an electrodeposition apparatus and a throwing power testing vessel were employed. 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. The electrodes were connected to a dc power supply (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 (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

TMP-TDI-DMAE/2EH Resin

In a three-necked reaction vessel, a half-blocked TDI was prepared by slowly adding the mixture of 2-ethylhexanol (49.92 g, 0.384 mol) and dimethylaminoethanol (17.11 g, 0.192 mol) to TDI (100 g, 0.576 mol) over a period of about 40 min, while mixing external cooling the batch to maintain the reaction temperature below 20°C. At the completion of addition, the batch was kept at 20°C for additional 40 min and then heated to 40°C and held for 1 h. The solution of trimethylolpropane (25.7 g, 0.192 mol) in DMAc (50 g) was added dropwise in the reaction product after the reaction temperature was heated to 60°C. In the meantime, an external cooling was held to maintain the reaction temperature below 100°C. At the completion of addition, an additional 1 h was held at 100°C to give the TMP-TDI-DMAE/2EH resin (IId) solution in DMAc. Finally, the obtained resin solution was distilled at 80°C under reduced pressure to remove DMAc.

Amine-Epoxy Adduct (III)

An epoxy resin (Epikote 1004, 100 g) and toluene (100 mL) were charged into a three-necked flask. The mixture was heated to 80°C to dissolve the epoxy resin. Diethylamine [7.70 g (0.105 mol)] was added into the flask. The whole mixture was kept at that temperature for about 2.5 h to give the resin solution of amine-epoxy adduct (III) in toluene. Finally, toluene was distilled off under reduced pressure. When cooled to room temperature, a golden, brittle solid of amine-epoxy adduct (III) was obtained.

Preparation of Electrodeposition Emulsion

The general process for the preparation of emulsions of resins II and III involved the dilution of the resinous reaction product prepared as described above

with a solvent (like BCS) to a solution with a calculated quantity of acid (80 mol % of the total theoretical neutralization) and dispersed in deionized water to form a cationic emulsion of 10 wt % solid content.

Characterization

Bath Conductivity

The conductivity and pH value of the emulsions were measured at room temperature.

Electrodeposition Yield

Approximately 350 mL of emulsion was placed in the glass vessel of the electrodeposition apparatus as described in the previous publication.¹⁹ The electrodes were immersed in the emulsion and electrodeposition was carried out at 100 V for different deposition time intervals. The cathode was removed from the emulsion, washed with water, and successively heated to 100°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 2 min, the strip was rinsed off with water. The height (in cm) of polymer deposited is defined as the throwing power.

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 became abnormal (such as increasing) (at which time the film suddenly had remarkable defects). This operation was repeated twice.

Gel Content

The electrodeposited films were baked at 80°C for various time periods to form the crosslinked films. The crosslinked films were immersed in acetone to reflux for 24 h. After drying, the gel content was calculated by dividing the residual weight by the initial weight of the crosslinked film.

RESULTS AND DISCUSSION

Synthesis of TMP-TDI-DMAE/2EH Resins and Amine-Epoxy Adduct

The synthetic procedure of the TMP-TDI-DMAE/2EH resins containing various contents of tertiary amine group is shown in Scheme 1.

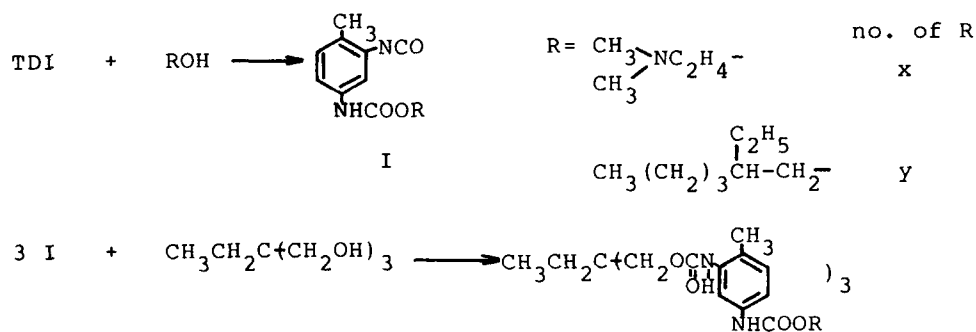
First, the half-blocked 2,4-toluene diisocyanate (I) was obtained by reacting TDI and the mixtures of *N,N*-dimethylaminoethanol (DMAE) and 2-ethylhexanol (2EH) (as the blocking agent) with different molar ratios. The reaction between TDI and the blocking agent was exothermic and preferably carried out at temperature below 10°C. Then a sufficient quantity of trimethylolpropane (TMP) was added slowly over 2 h at the temperature of 50–60°C. After the addition, an advanced reaction time was proceeded at the same temperature to give the TMP-TDI-DMAE/2EH resins (IIa–f). Furthermore, an amine-epoxy adduct was prepared by reacting diethylamine and Epikote 1004 through the ring-opening reaction of epoxy groups.

Preparation of Electrodeposition Emulsion

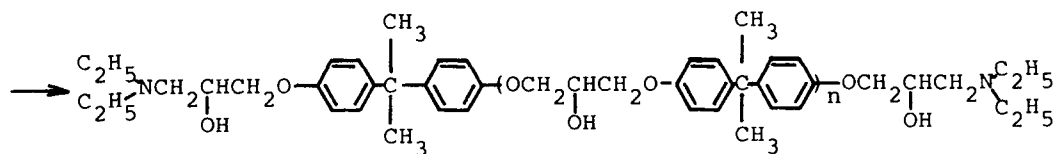
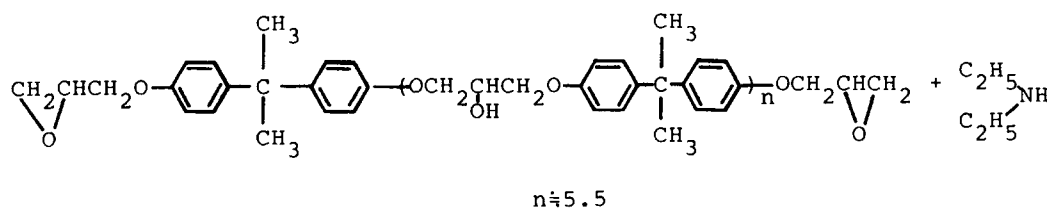
The obtained resins IIa–f contain tertiary amine groups in their molecules, which can be neutralized with the organic acid to form the amine salts to increase the hydrophilicity of resin. Neutralization of the resins is accomplished by all or part of the amino groups. The extent of neutralization depends upon the particular resin system, and it is only necessary that sufficient acid be added to solubilize or disperse the resin. Thus, the pH value of the resin solution plays an important role on the attainment of a stable emulsion. Moreover, the state of the aqueous dispersion is also affected by the contents of resin and organic solvent.

Table I shows the properties of aqueous dispersions prepared from resin II with 10 wt % of resin concentration and 3 wt % of BCS content. From the table, the pH value and the state of the dispersed bath were quite affected by the added amount of acetic acid. Resin IIa having the highest amino group content in the series of resin II gave a stable emulsion with a pH value higher than 7 if the resin was neutralized to an extent lower than 80% of the total theoretical neutralization. As shown in Table I, the dispersion numbered 2 shows a pH of 7.04, when the degree of neutralization of the theoretical neutralization of the resin is 70%. However, the basic emulsions are not suitable for cationic electrode-

Scheme 1



	IIa	b	c	d	e	f
x/x+y	1	0.5	0.45	0.34	0.17	0



III

Scheme 1

position. With the same degree of neutralization, the pH values of the dispersions decreased in the order: IIa > IIb > IIc > IId > IIe, due to the decrease of amino group contents in their polymer backbones. Resins IIb and IIc formed stable emulsions with pH values lower than 7.0 if the degree of neutralization of the resins ranged from 70 to 80%. However, for the lower amine contents containing resins IId and IIe, too low a degree of neutralization, such as 70%, caused precipitation of the dispersions. Moreover,

in the absence of amino group, II f was not easily formed stable emulsion when dispersed in deionized water even though the BCS content was increased to 10 wt %.

Bath Conductivity

Bath conductivity is an important parameter influencing electrodeposition process. It has been found that the higher the bath conductivity, the more ef-

Table I Properties of the Aqueous Dispersions Prepared from Resins IIa to IIf^a

No.	Resin	Neutralized Extent of Theoretical Neutralization (%)	pH	State of Dispersion
1	IIa	60	7.28	Milky emulsion
2	IIa	70	7.04	Milky emulsion
3	IIa	80	6.21	Milky emulsion
4	IIb	70	6.33	Milky emulsion
5	IIb	80	6.02	Milky emulsion
6	IIc	70	6.21	Milky emulsion
7	IIc	80	5.90	Milky emulsion
8	IId	70	5.91	Precipitation
9	IId	80	5.65	Milky emulsion
10	IIe	70	5.87	Precipitation
11	IIe	80	5.60	Milky emulsion
12	IIf		6.04	Precipitation
13 ^b	IIf		5.79	Precipitation

^a The dispersions contain 10 wt % resin concentration and 3 wt % BCS, with the exception as indicated.

^b Resin concentration = 10 wt %; BCS content = 10 wt %.

efficient will be the coating process. Moreover, higher bath conductivity leads to higher throwing power but lower rupture voltage.^{20,21}

Figure 1 shows the effect of the content of amino group on the bath conductivity of the emulsions prepared from resin II. At the same extent of neutralization, the resins with higher content of tertiary

amine group carry a larger number of unit charges on the surfaces of their particles, and thus, their dispersions showed higher electrically conductive.

Rupture Voltage

Figure 2 shows the effect of the amino group content of resin II on the rupture voltage of the deposited

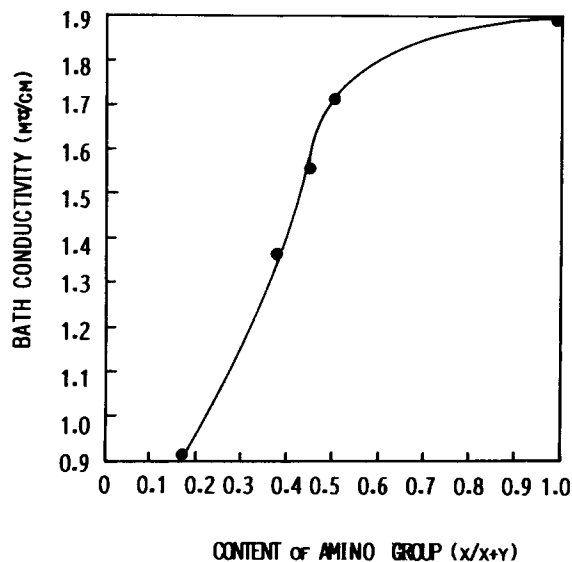


Figure 1 The effect of the amino group content on the conductivity of emulsions prepared from resins IIa-e. Resin concentration 10 wt %; BCS content 3 wt %; degree of neutralization 80% (pH = 5.6-6.2).

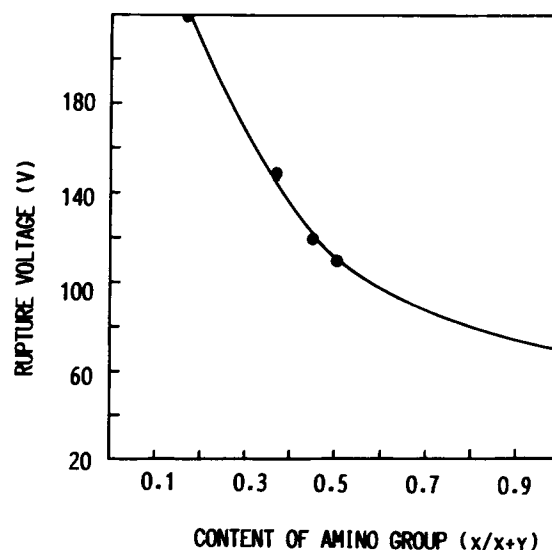


Figure 2 The effect of the amino group content on the rupture voltage of the deposited film from the emulsions of resins IIa-e. Resin concentration 10 wt %; BCS content 3 wt %; degree of neutralization 80% (pH = 5.6-6.2).

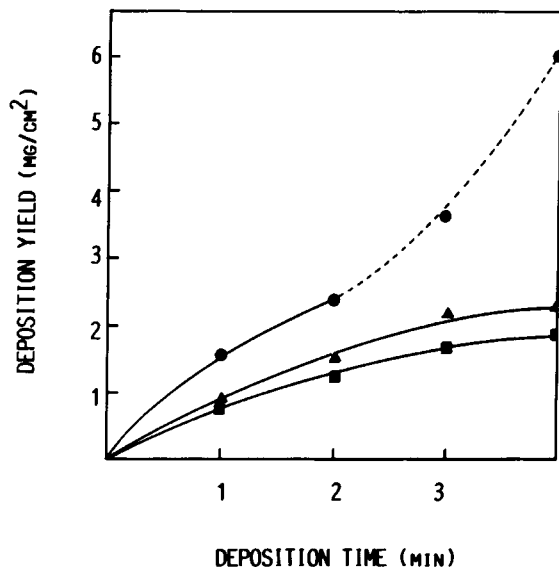


Figure 3 The effect of deposition time on deposition yield of emulsions prepared from IIC, IID, and IIE. Resin concentration 10 wt %; BCS content 3 wt %; applied voltage 100 V; (●) IIC, pH 5.85; (▲) IID, pH 5.78; (■) IIE, pH 5.51; (---) rough coverages; (—) uniform coverages.

film. The rupture voltages of resins IIA–IIE increased from 70 to 220 V as their amino group contents, in terms of $x/(x + y)$, decreased from 1.0 to 0.17. It might be explained by the fact that the higher amino group content gave the higher conductivity favoring the formation of hydrogen (reduction of water) at the surface of cathodic substrate than the diffusion of it from the cathodic substrate through the electrodeposited film; thus the polymer particle cannot be uniformly deposited onto the substrate to result in the rupture of the polymer emulsion, where the current value became abnormal (such as increasing).

Deposition Yield

The deposition yield is affected by the applied voltage, deposition time, pH value, BCS content and resin concentration of the bath. The relationships between deposition time and deposition yield for IIC, IID, and IIE are shown in Figure 3. For IID and IIE, the deposition yield increased with the deposition time in the initial 3 min and reached to a limit being an insulating film formed. However, for IIC, a limit yield cannot be obtained and a rough deposited coverage was formed after the initial 3 min. It may be caused by the lower rupture voltage of IIC (about 100 V). The resin having a higher amino group con-

tent gave a higher deposition yield, i.e., IIC > IID > IIE.

Figure 4 shows the effect of resin concentration on deposition yield. It appears that the deposition yield increased with the increase of resin concentration.

The effect of BCS content on deposition yield of IID and IIE are shown in Figure 5. Higher BCS contents give deposited films with a pleasing appearance and a lower deposition yield. The lower yields may be accounted for the redissolving of the deposited resin on the cathode during electrodeposition at higher BCS contents. Lower BCS contents might cause precipitation of the resin emulsion, and the suspended precipitated particles might migrate with the dispersed marocations onto the cathode leading to deposited film with a rough appearance. In conclusion, in order to obtain better deposition yield and pleasing appearance from IID and IIE, the BCS contents of the emulsions have to be kept between 2.5 and 3.0 wt %.

The pH value of emulsion determines the dispersibility of the resins and hence it will affect the deposition yield. As shown in Figure 6, the deposition yields of IID and IIE decrease with the decrease of pH value. This is reasonable because higher acidity of the emulsion enhances the amino group of the deposited resin converting into amine salt and increases the solubility of deposited resin leading to the decrease of deposition yield. As the pH value

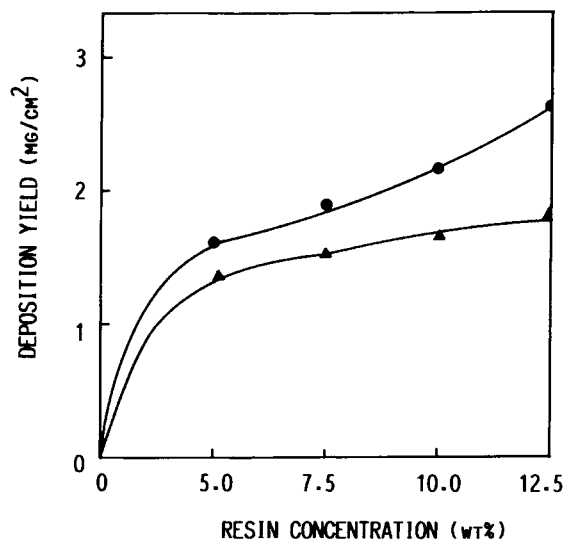


Figure 4 The effect of resin concentration on deposition yield of emulsions prepared from IID and IIE. Applied voltage 100 V; deposition time 3 min; BCS content 3 wt %; (●) IID, pH 5.7–5.8; (▲) IIE, pH 5.5–5.6.

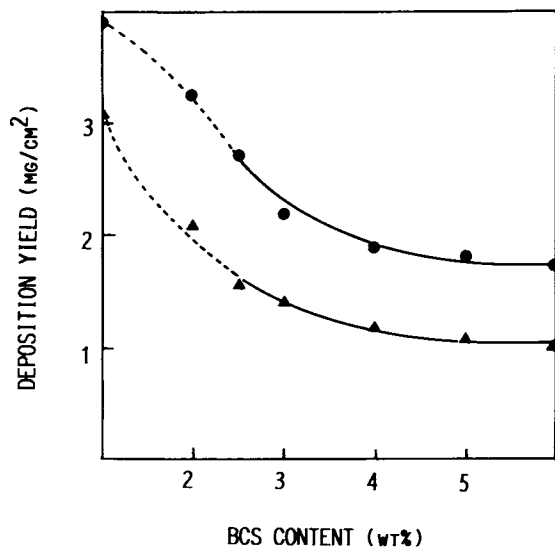


Figure 5 The effect of BCS content on deposition yield of emulsions prepared from IID and IIE. Applied voltage 100 V; deposition time 3 min; resin concentration 10 wt %; (●) IID, pH 5.6–5.7; (▲) IIE, pH 5.4–5.5; (---) rough coverages; (—) uniform coverages.

exceeds 5.7, precipitation occurs and a rough appearance is obtained. In order to get better deposition yield and pleasing appearance of deposited coatings from IID and IIE, the pH value of the emulsions is preferably kept at 5.5–5.7.

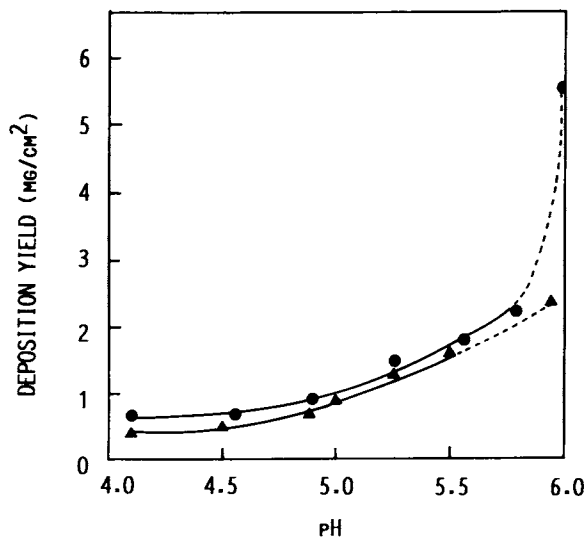


Figure 6 The effect of pH value on deposition yield of emulsions prepared from IID and IIE. Resin concentration 10 wt %; BCS content 3 wt %; applied voltage 100 V; deposition time 3 min; (●) IID; (▲) IIE; (---) rough coverages; (—) uniform coverages.

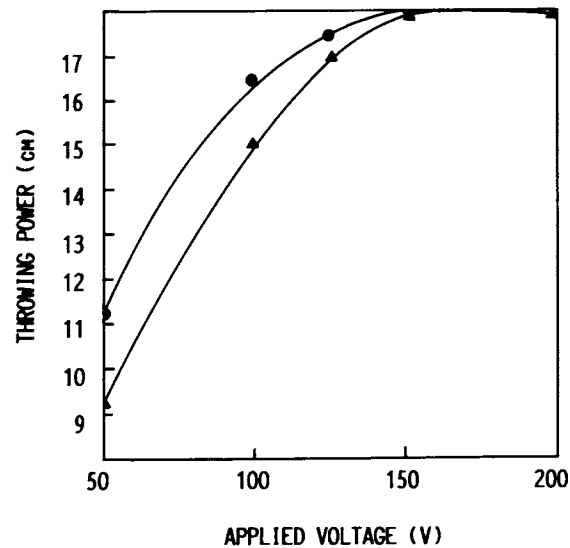


Figure 7 The effect of applied voltage on throwing power of emulsions prepared from IID and IIE. Resin concentration 10 wt %; BCS content 3 wt %; (●) IID, pH 5.7; (▲) IIE, pH 5.5; deposition time 2 min.

Throwing Power

Figure 7 shows the effect of applied voltage on the throwing power of the emulsions prepared from IID and IIE. Higher applied voltage gives higher throwing power. The throwing power of IID is higher than that of IIE. It is due to the fact that the bath conductivity of IID emulsion is higher than that of IIE.

Electrodeposition Properties of III/II Codispersed Emulsion

The deposited coatings from cationic resins IIA–e are not self-curable by heating. However, the cationic resins IIA–e can be used as the crosslinkers when mixed with a hydroxyl group-containing resin. Figures 8–10 show the electrodeposition properties of III/II codispersed emulsions. Figure 8 shows the relationship between deposition time and deposition yield. The deposition yield increases with the deposition time and levels off after 3 min. Moreover, the deposition yields of the emulsions are IID > III + IID > III.

Figure 9 shows the effect of applied voltage on the throwing power of emulsions of IID, III, and IID + III. Increasing the applied voltage increases with the throwing power. The throwing power of the emulsions are IID + III = IID > III. It might be explained by the fact that the throwing power of the codispersed emulsion of IID and III was affected more

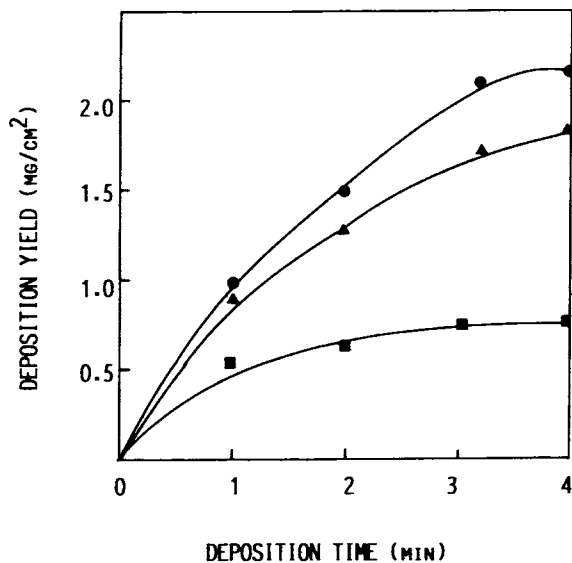


Figure 8 The effect of deposition time on deposition yield of emulsions prepared from III, IId, and III + IId. Applied voltage 100 V; BCS content 3 wt %; (■) III, resin concentration 10 wt %; (●) IId, resin concentration 8 wt %; (▲) III + IId, resin concentration 18 wt % (IId/III weight ratio = 4/5).

significantly by IId because of its smaller particle size favoring migration.

The relationship between the baking time and the gel content of the film deposited from the IId/

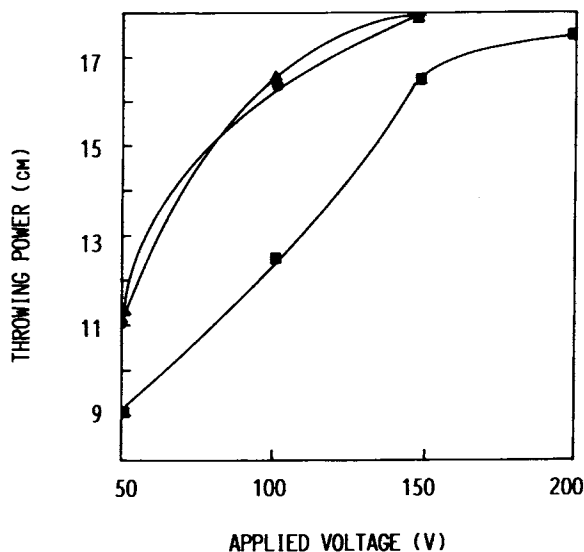


Figure 9 The effect of applied voltage on the throwing power of the emulsions prepared from III, IId, and III + IId. Resin concentration 10 wt %; BCS content 3 wt %; deposition time 2 min; (■) III, conductivity = 1.01 mv/cm, pH 5.21; (▲) IId, conductivity 1.38 mv/cm, pH 5.7; (●) III + IId, conductivity 1.23 mv/cm, pH 5.46.

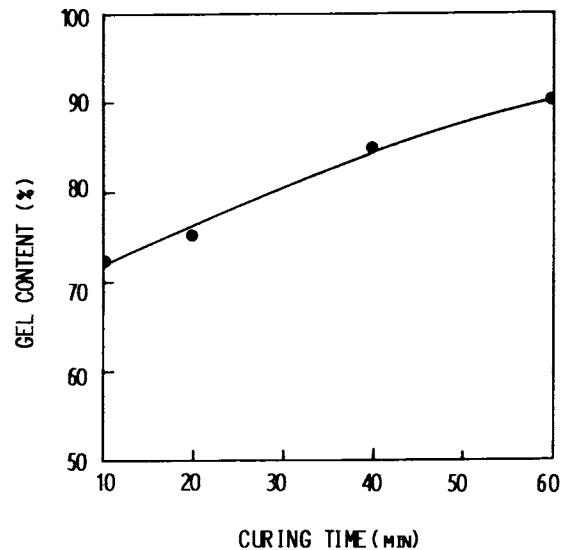


Figure 10 The effect of curing time on gel content of the film electrodeposited from the emulsion of III + IId. Curing temperature 180°C.

III emulsion are shown in Figure 10. The gel content of the deposited film reaches 90% at a baking temperature of 180°C for 40–60 min. As a result, combining IId (a crosslinker) with adduct III (a polyol) can give a superior two-component electrodepositable cationic resins.

CONCLUSION

1. The TMP-TDI-DMAE/2EH resin prepared by reacting TMP, TDI, and the mixture of DMAE and 2EH with a proper molar ratio can be used as a superior crosslinker for the formation of urethane linkages in the two-component cationic resin system.
2. The electrodeposition properties were quite affected by the pH value, BCS content, and resin concentration. In order to obtain better deposition yield and pleasing appearance from TMP-TDI-DMAE/2EH resins, the aqueous dispersion should meet the following conditions: pH 5.5–5.7, BCS contents 2.5–3.0 wt %, and resin concentration 10–12.5 wt %.
3. The gel content of the crosslinked deposited film derived from the codispersed bath of amine-epoxy adduct (III) and TMP-TDI-DMAE/2EH can reach to 90%.

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