

Synthesis and Properties of Cationic Resins Derived from Urethane-Modified Epoxy Resins and Methylethanolamine

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SYNOPSIS

Six urethane-modified cationic resins were synthesized by reacting half-blocked polyglycol-toluene diisocyanate-urethane (half-blocked-PG-TDI-urethane) and 2-ethylhexanol-blocked toluene diisocyanate (2-EH-blocked-TDI) modified epoxy resins with methylethanolamine and subsequent neutralization with acetic acid. Three different polyglycols were used to react with toluene diisocyanate to form isocyanate-terminated urethanes (**1a-c**) and subsequently two different monoalcohols were added to react with **1a-c** to give half-blocked-PG-TDI-urethanes (**2a-f**). These cationic resins were then dissolved in suitable solvents and mixed with deionized water to form emulsions. The crosslinking properties, emulsion, and electrodeposition properties of these resins were studied in some detail. The deposition yields of emulsions prepared from urethane-modified epoxy resins were higher than those of other emulsions. The pencil hardness of the crosslinked films of urethane-modified resins were lower than that of non-urethane-modified resin. The emulsion and electrodeposition properties of the cationic resins were also deeply affected by the nature of the pendant positively charged group contained in the resins.

INTRODUCTION

Recently, major emphasis has been placed on converting all automotive paint facilities to cathodic electrocoating systems due to the superior corrosion protection provided, compared to earlier anodic and spray primer systems. The advantages of electrodeposition are high levels of coating utilization, automation, low levels of pollution, and high throwing power, i.e., the ability to coat the recessed portions of complex shaped metal parts.

Cathodic electrodeposition resin systems generally consist of epoxy¹⁻⁷ or acrylic^{8,9} polymer backbones with cationic groups being provided by protonated salt groups. It is the cationic or ionizable group and its hydrophilic nature which allows emulsification in water. Curing may be accomplished by crosslinking of hydroxyl and epoxy groups with isocyanate, phenolic, melamine, or similar reactive groups. The preferred resin for electrodeposition is the DGEBA type epoxy resin obtained by reacting

epichlorohydrin with bisphenol A in the presence of sodium hydroxide. The deposition yields of the cationic resins directly prepared by DGEBA epoxy resins with secondary amine are low, that is, the deposited films are thin. In this study, isocyanate-terminated urethanes (**1a-c**) were first prepared from three different polyglycols (PG) and toluene diisocyanate (TDI), and subsequently reacted with two different monoalcohols to obtain half-blocked PG-TDI-urethanes (**2a-f**). Half-blocked PG-TDI-urethanes and 2-ethylhexanol-blocked TDI (**3**) prepared from 2-ethylhexanol and TDI were used to modify DGEBA epoxy resin to give urethane-modified epoxy resins (**4a-g**), which contain urethane as a side chain. These modified epoxy resins were reacted with methylethanolamine and subsequently neutralized with acetic acid to give urethane-modified cationic resins. The monoalcohol used to prepare half-blocked PG-TDI-urethane included 2-ethylhexanol and dimethylethanolamine. The latter contains tertiary amine, so that the synthetic cationic resins can be divided into two series. One is a type of cationic resin with positively charged groups at the end of the polymer chain. The other is a type of cationic resin containing the positively charged

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groups not only at the end of polymer chain but also as a side chain. These cationic resins can be dissolved in suitable solvents and mixed with deionized water to form stable emulsions. The properties of these emulsions were studied in some detail to compare the properties of cationic resins prepared from different modified epoxy resins. The results show that the deposition yields of the emulsions prepared from urethane-modified epoxy resins are higher than those of the emulsions prepared from nonmodified epoxy resins. In addition, the electrodeposition properties of the emulsion were deeply affected by the content of cationic groups in the pendant polymer chain.

EXPERIMENTAL

Materials

Reagents used in the preparation of thermal cross-linkable cationic resins included diglycidyl ether of bisphenol A epoxy resin (epoxy equivalent 650), 2-ethylhexanol (2-EH) (Hayashi Extra Pure Grade), 2-dimethylaminoethanol (2-DMAE) (Hayashi Extra Pure Grade), toluene diisocyanate (TDI), polyglycol (PG), 2-methylaminoethane (2-MAE) (Fluka agent grade), and acetic acid. Three polyglycols were used in this study: poly(ethylene glycol)s [PEG(#400) and PEG(#600)] and poly(propylene glycol) [PPG(#1000)]. All of them are Hayashi Extra Pure Grade.

Organic solvents used in this study were toluene and ethylene glycol mono-*n*-butyl ether (butyl cellosolve) (BCS).

Apparatus

A Braive Instrument (B-4000), 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. From the cover, a clean plated strip of iron pretreated with zinc phosphate (used as the cathode) and a copper electrode (as the anode) were suspended. The copper electrode contains a surface area of approximately 20 cm². 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

Isocyanate-Terminated Urethane (1a–c)

A given quantity of TDI was added to a 500 mL four-necked flask equipped with an electric stirrer, a reflux condenser, a dropping funnel, and an inert nitrogen blanket. A calculated quantity of PG [PEG(#400), PEG(#600), or PPG(#1000)] was added dropwise into the flask. The mixture was kept at room temperature for 30 min, and gradually heated to 70°C for 2 h for completion. The resultant product was isocyanate-terminated urethane.

Half-Blocked PG-TDI-Urethane (2a–f)

A calculated quantity of 2-EH or 2-DMAE was added dropwise into the flask containing the isocyanate-terminated urethane (1a–c) under an ice bath. The mixture was kept at room temperature for 1 h, and was gradually heated to 50°C for an additional 1 h to give 2-ethylhexanol half-blocked PG-TDI-urethane (2-EH-blocked-PG-TDI-urethane) (2a–c) or 2-dimethylaminoethanol half-blocked PG-TDI-Urethane (2-DMAE-blocked-PG-TDI-Urethane) (2d–f).

2-Ethylhexanol-Blocked TDI (3)

A given quantity of TDI was added under an inert nitrogen blanket to a four-necked flask equipped with an electric stirrer, a reflux condenser, and a dropping funnel. 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-toluene-diisocyanate (2-EH-blocked TDI) (3).

Synthesis of Resins 5a–g

Epoxy resin (epoxy equivalent weight 650) (130 g, 0.1 mol) and toluene (100 mL) were added under an inert nitrogen blanket to a five-necked flask equipped with an electric stirrer, a Dean-Stark trap, and a dropping funnel. The mixture was heated to 110–120°C to remove any water in the epoxy resin by azeotropic distillation. After cooling to 40–50°C, a calculated quantity of 2 and 3 (Scheme 1) was added into the flask. The whole mixture was gradually heated to 90°C and kept at that temperature for 4 h. After cooling the product to 60°C, 0.2 mol methylethanolamine was added. The mixture was

heated to 90°C and kept at that temperature for 3 h for the completion of reaction. Finally, toluene was distilled off under reduced pressure.

Preparation of Emulsions

The general process for the preparation of the emulsion was as follows. In a reactor 17.5 g of resin **5a–g** (Scheme 1) were dissolved in various amounts of BCS. A desired amount of acetic acid was then added, and the mixture was heated at 60°C for 10 min. Then, about 330 mL of deionized water was added dropwise into the solution with vigorous stirring to produce an emulsion.

Characterization

Gel Content

A 40% resin solution, prepared by mixing the resin and toluene, was spread on aluminum foil and baked at various temperature for different times to form cured crosslinked film. The latter was immersed in acetone and brought to reflux for 24 h. After drying, the gel content was calculated by dividing the residual weight by the initial weight of crosslinked film.

Bath Conductivity

The conductivity and pH value of the emulsion were measured by adding acetic acid dropwise into the emulsion at room temperature using the appropriate instruments.

Electrodeposition

Approximately 350 mL of emulsion was placed in the glass vessel of the electrodeposition apparatus as described in the previous publication.¹⁰ 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 heated to 200°C to obtain the deposition yield.

Throwing Power

The throwing power of the emulsion was measured by a tube penetration test,¹¹ which includes a stainless vessel connected to the cathode and a stainless strip connected to the anode. The stainless strip and a hollow cylinder were immersed into the emulsion contained in the vessel. After the constant dc voltage was applied for 1 min, the strip was taken out and rinsed with water. The height (in cm) of polymer deposited is defined as the throwing power.

Rupture Voltage

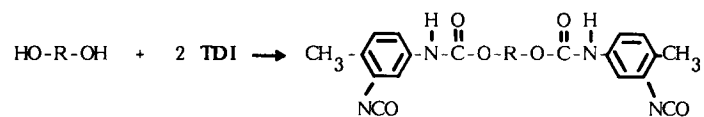
The rupture voltage was determined by the constant voltage method.¹¹ The voltage was increased (in steps of 10 V from that at which normal film was obtained) until the change of current value during electrodeposition coating became abnormal (such as increasing).

RESULTS AND DISCUSSION

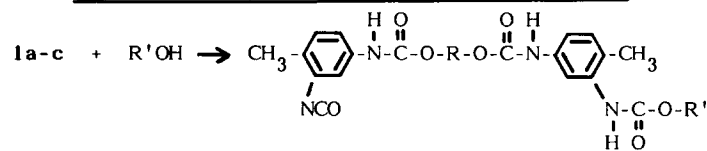
Synthesis

Cationic resins (**6a–g**) (Scheme 1) were synthesized by reacting methylethanolamine with half-blocked-PG-TDI-urethane (**2a–f**) and 2-EH-blocked-TDI (**3**) modified epoxy resins and subsequent neutralization with acetic acid.

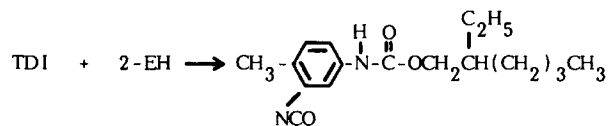
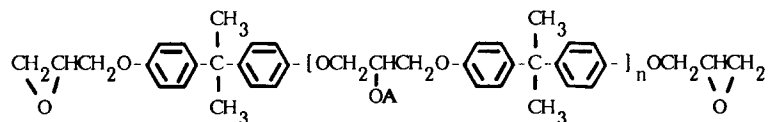
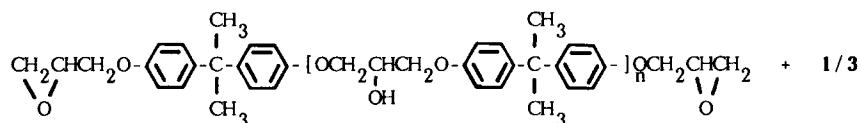
As shown in Scheme 1, three different polyglycols were reacted with toluene diisocyanate to form isocyanate-terminated urethane (**1a–c**) and subsequently two different blocking agents such as 2-ethylhexanol or 2-dimethylamino ethanol, were added to react **1a–c** to give half-blocked-PG-TDI-urethane (**2a–f**). 2-EH-blocked TDI (**3**) was synthesized by reacting 2-ethylhexanol (2-EH) with the isocyanate group of TDI in the para position at low temperature. Both **2a–f** and **3** contain one free isocyanate group, so they can react with the hydroxyl groups of epoxy resins to obtain thermally crosslinkable epoxy resins (**4a–g**). The extent of reaction of epoxy resin with **2a–f** and **3** can be evaluated by the change of characteristic absorption of isocyanate group in infrared spectra. The end of the reaction, judging from the disappearance of the isocyanate absorption, is reached in about 4 h at 90°C. These thermally crosslinkable epoxy resins (**4a–g**) react with methylethanolamine, through the ring-opening reaction of epoxy groups, to give tertiary amine-terminated resins **5a–c** and **5g** or resins **5d–f** containing tertiary amine groups in the terminal and side polymer chain. Resins **5a–g** were treated with acetic acid to give thermally crosslinkable urethane-modified cationic resins **6a–g**. The amount of cation formed and the solubility of these resins were determined by the quantity of acid added. Thermally crosslinkable cationic resin **6g** was directly prepared from epoxy resin to compare the properties of urethane-modified cationic resins **6a–f**, which contain long polyglycol segments in the side chain. Resins **6a–c** contain cationic groups at the end of the polymer chain, whereas resins **6d–f** contain cationic groups not only at the end of the polymer chain but also in the side chain.

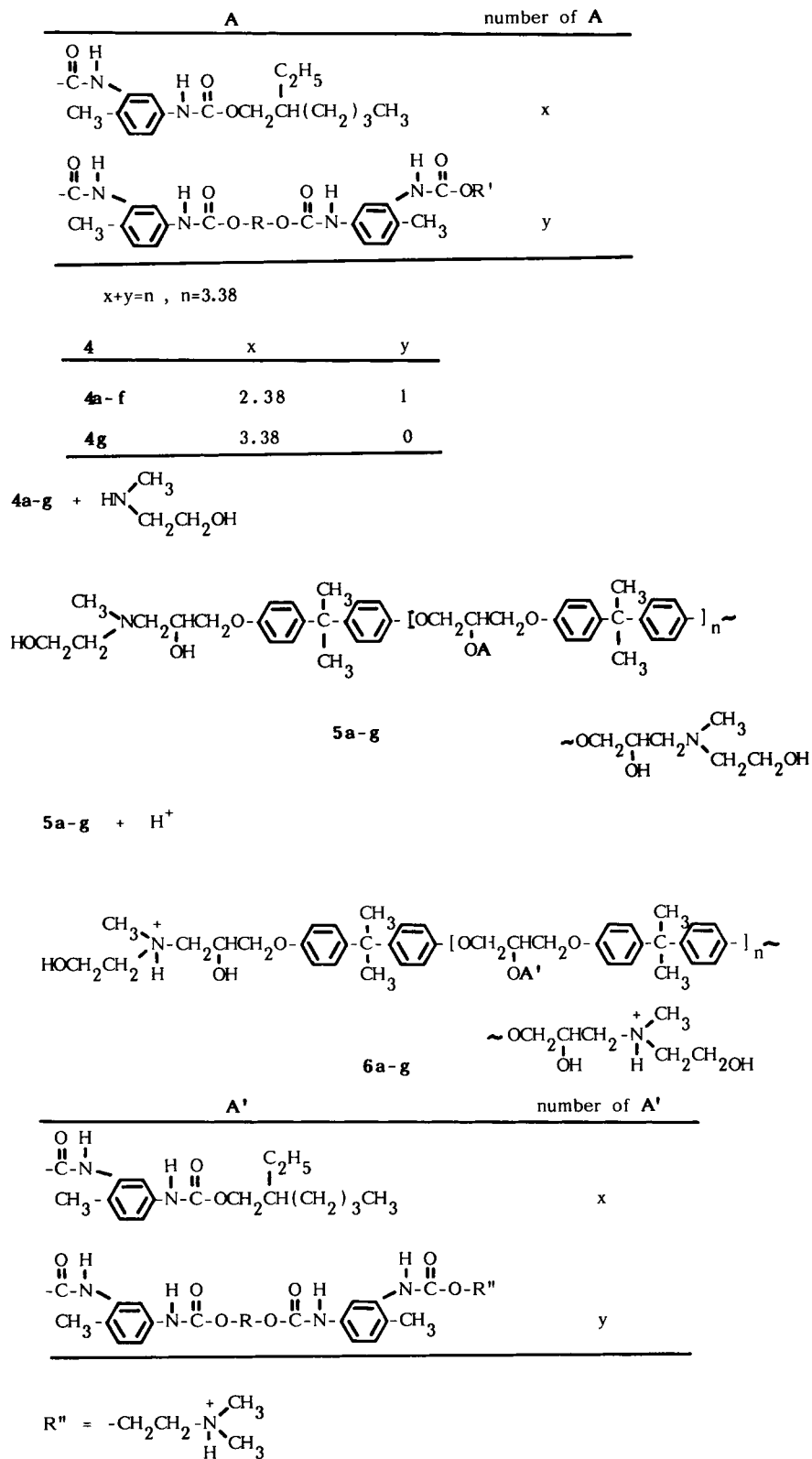
**1a-c**

1	R	Mn
1a	$-(\text{-CH}_2\text{CH}_2\text{O})_m\text{CH}_2\text{CH}_2-$	400
1b	$-(\text{-CH}_2\text{CH}_2\text{O})_m\text{CH}_2\text{CH}_2-$	600
1c	$-(\text{-CH}_2\underset{\text{CH}_3}{\text{CHO}})_m\text{CH}_2\underset{\text{CH}_3}{\text{CH}}-$	1000

**2a-f**

2	1	R'
2a	1a	$\text{CH}_3(\text{CH}_2)_3\text{C}(\text{C}_2\text{H}_5)\text{HCH}_2-$
2b	1b	"
2c	1c	"
2d	1a	$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2-$
2e	1b	"
2f	1c	"

**3****4a-g****Scheme 1**



Scheme 1 (continued from the previous page)

Crosslinking Properties of Resins 5a-g

When resins 5a-g were heated at elevated temperature, the pendant blocked isocyanate will release the blocking agent, 2-ethylhexanol or 2-dimethylaminoethanol, to generate free isocyanate. These free isocyanates react with the secondary hydroxyl groups of other molecules to form new urethane linkages and produce a crosslinked structure. The extent of crosslinkability was significantly affected by curing temperatures and curing time. The effects of curing temperature on the gel content of the crosslinked films prepared from resins 5a-g are shown in Figure 1. When the curing temperatures are lower than 150°C, the gel contents of the crosslinked films are low. The gel content of resin 5g increases quickly with curing temperature when the curing temperature is above 150°C, and reaches a constant value at temperatures higher than 200°C. For resins 5a and 5d, the gel contents increase significantly with the increase of curing temperature when the curing temperatures are higher than 160°C. It requires 170°C to increase the gel content of resins 5b-c and 5e-f. The gel contents of all resins reach a constant value at temperatures higher than 200°C. Figure 1 also reveals that the gel contents of 5g is higher than that of other resins. The lower molecular weight of the polyglycol contained in the resin gives a higher gel content of the crosslinked film. The effects of curing time on the gel contents of resins are shown in Figure 2. The gel

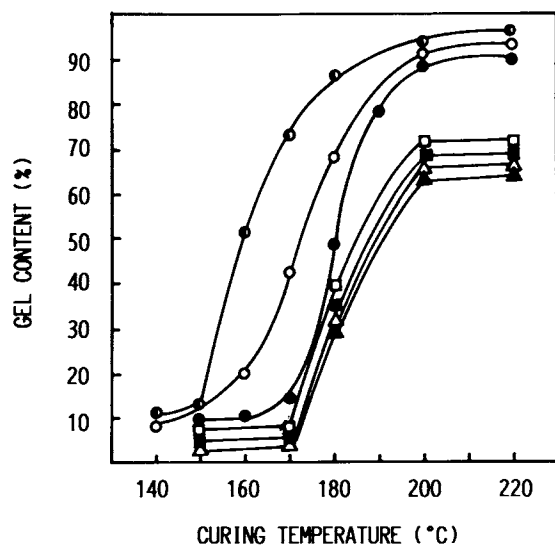


Figure 1 Effects of curing temperature on the gel content of the crosslinked films: (○) 5a; (□) 5b; (△) 5c; (●) 5d; (■) 5e; (▲) 5f; (●) 5g. Curing time = 20 min.

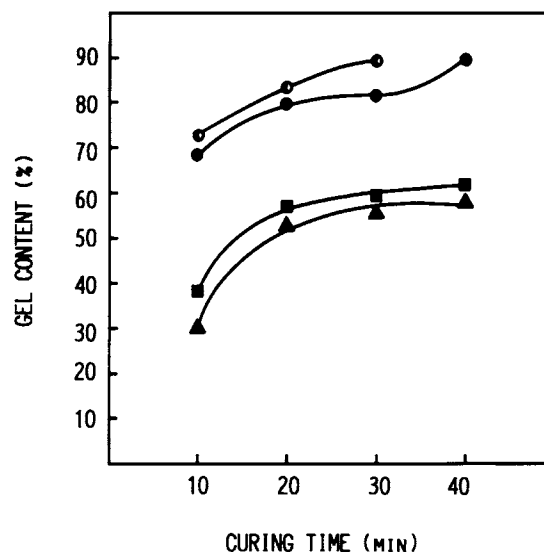


Figure 2 Effects of curing time on the gel content of the crosslinked films prepared from 5d-f: (●) 5d; (■) 5e; (▲) 5f; (●) 5g. Curing temperature = 200°C.

content of resin increases with curing time up to 20 min and then no longer changes significantly.

Properties of Cationic Resins

Effects of pH value and Amount of Organic Solvent on the Formation of Emulsion

Resins 5a-c and 5g contain tertiary amine at the end of the polymer chain and resins 5d-f contain tertiary amine at the end and on the side chain, so they can be converted to cationic resins 6a-g when treated with acetic acid. Such cationic resins dissolved in suitable solvents and mixed with deionized water can form stable emulsions. Resins 5a-g are readily dissolved in organic solvents, but difficult to dissolve in water. In the form of ammonium salts, resins 6a-g are readily soluble in hydrophilic solvents or polar solvents, but are insoluble in hydrophobic solvents. The water solubility of resins 5a-g is significantly affected by the pH value of the emulsion. In low-pH solutions, resins 6a-g are predominant and the solubility of resins is increased. The critical solvent content and pH range for the preparation of stable emulsions of resins 6a-g are shown in Table I. The lowest amount of the critical solvent content to form stable emulsions is required for cationic resins 6d-f, which contain a positively charged group in the side chain. Stable emulsions can be obtained when the critical solvent content is higher than 0.5 wt %. For resins 6a-c, it can also be seen that the higher molecular weight of poly-

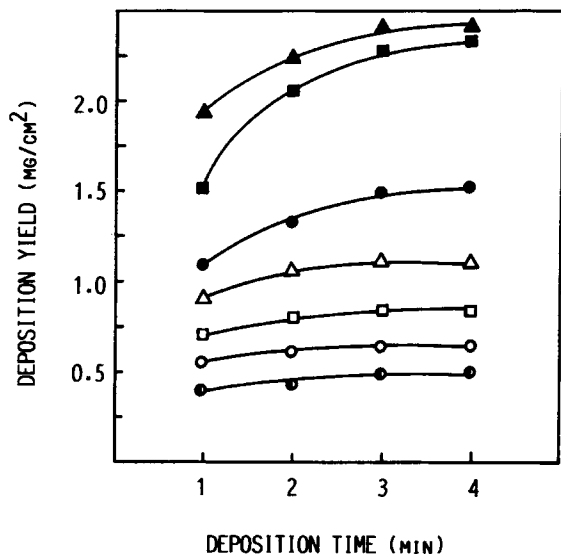


Figure 4 Effects of deposition time on the deposition yield of the emulsions prepared from **6a–g**: (○) **6a**; (□) **6b**; (△) **6c**; (●) **6d**; (■) **6e**; (▲) **6f**; (◐) **6g**. Applied voltage = 200 V, BCS content = 1.5 wt %, resin concentration = 5 wt %, pH = 4.98.

tralized and coagulated in the alkaline boundary layer around the cathode. At the same time, water is electrolyzed at the anode, and the hydrogen ions generated at the anode drive out the residual acetic ion.

Factors Affecting Electrodeposition Yield

The electrodeposition yields of emulsions are dependent on the deposition time, the applied voltage, the pH value of the emulsion, and the molecular weight of the resins. When the emulsion of cationic resin is coated at constant voltage, the deposition yield increases with deposition time as shown in Figure 4. Deposition appears to start instantaneously, within a fraction of a second. Until the isolation film is formed on the cathode or the deposition film redissolves at a rate comparable to the rate of electrodeposition, the deposition yield no longer increases with the deposition time, that is, the deposited film will tend to a limiting film thickness. Figure 5 shows the effect of applied voltage on the deposition yield of the emulsions. For resins **6a–c** and **6f–g**, it can be observed that the deposition yield increases as the applied voltage increases. But the deposition yield of resins **6d** and **6e** decreases as the applied voltage increases. This phenomenon is contrary to the deposition yield of cationic resins, in general, which increases with an increase of ap-

plied voltage. An explanation is that when a higher voltage is applied, the isolation film is quickly formed on the cathode and prevents the cationic resin from continuing to deposit on the cathode. When a lower voltage is applied, the isolation film forms slowly and the resin continues to deposit on the cathode. Under constant voltage (200 V) electrodeposition conditions, the effects of pH value on the deposition yield of the emulsions are shown in Figure 6. Emulsions having a higher pH value give a higher deposition yield. This can be attributed to the fact that the low pH value (i.e., high acidity) of the emulsion increases the solubility of deposited films. Figures 4–6 also show that the deposition yield increases with increasing molecular weight of cationic resin. It can also be observed that resins having pendant cationic groups give a higher deposition yield. It is likely that the increase of conductive groups accelerates the migration rate of the resin.

Factors Affecting Throwing Power

A major advantage of the electrodeposition process for coating metal parts is its ability to coat recessed areas, cavities, or channels in fabricated products. This ability of a coating system to deposit films in recessed areas is called throwing power. The throwing power of synthetic resins is dependent on the applied voltages, the content of solvent, the pH of

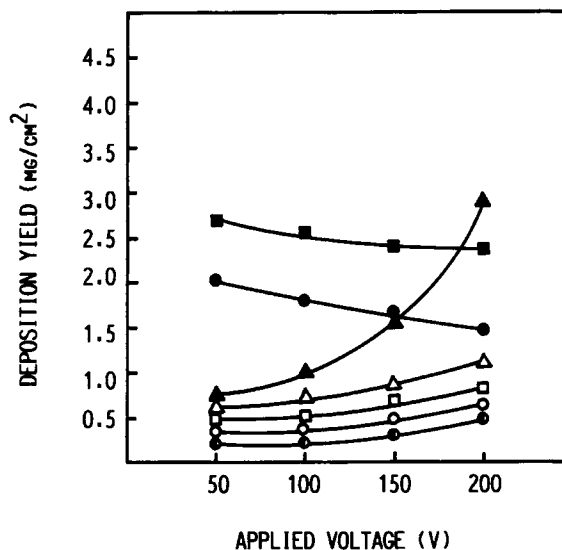


Figure 5 Effects of applied voltage on the deposition yield of the emulsions prepared from **6a–g**: (○) **6a**; (□) **6b**; (△) **6c**; (●) **6d**; (■) **6e**; (▲) **6f**; (◐) **6g**. Resin concentration = 5 wt %, BCS content = 1.5 wt %, deposition time = 3 min, pH = 5.04.

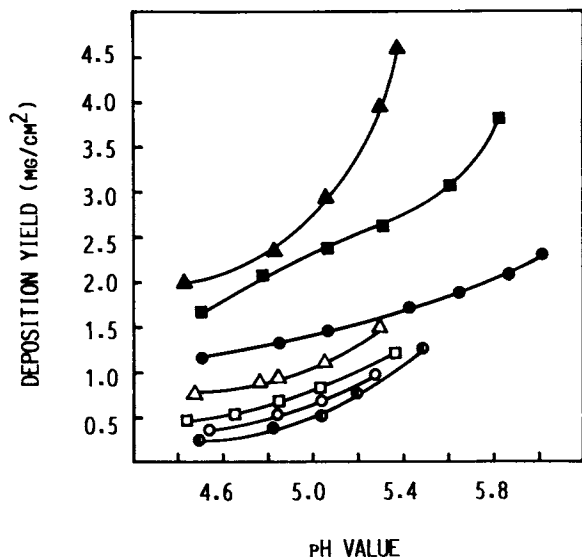


Figure 6 Effects of pH value on the deposition yield of the emulsions prepared from 6a-g: (○) 6a; (□) 6b; (△) 6c; (●) 6d; (■) 6e; (▲) 6f; (◐) 6g. Resin concentration = 5 wt %, BCS content = 1.5 wt %, deposition time = 3 min.

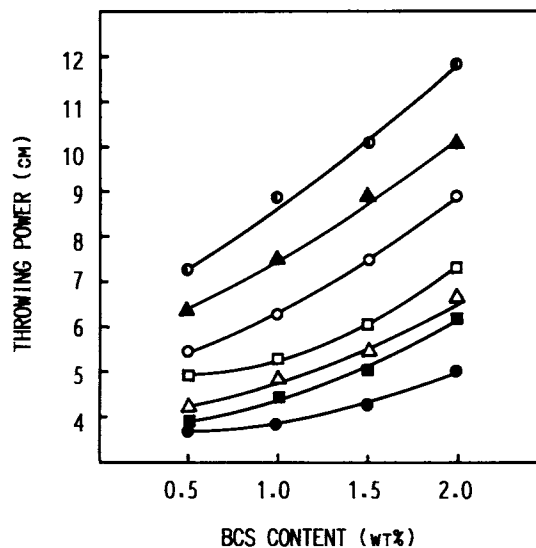


Figure 8 Effects of BCS content on the throwing power of emulsions prepared from 6a-g: (○) 6a; (□) 6b; (△) 6c; (●) 6d; (■) 6e; (▲) 6f; (◐) 6g. Resin concentration = 5 wt %, applied voltage = 200 V, deposition time = 1 min, pH = 5.04.

emulsions, and the nature of the cationic resin. Figure 7 shows that the throwing power increases by raising the applied voltage. This is due to the fact that the increase of applied voltage accelerates the migration rate of the resin. Increasing the amount of solvent in the emulsion increases the solubility

of the resin and reduces the resistance to motion of macrocations, leading to increase throwing power, as shown in Figure 8. The pH values of emulsions also affect the throwing power, as shown in Figure 9. It can be seen that the throwing power of resins 6a-c and 6g decreases with increasing pH values

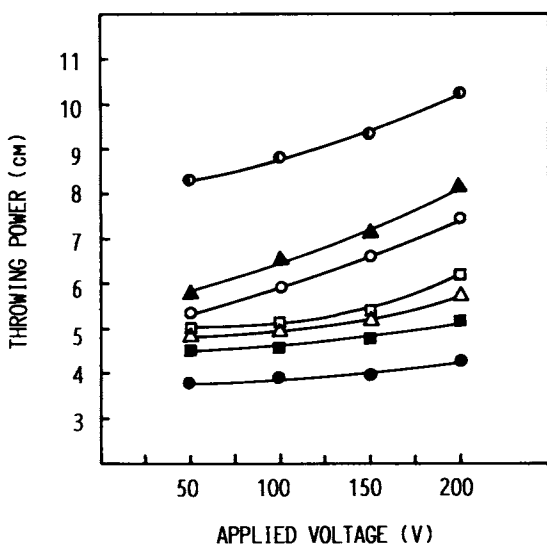


Figure 7 Effects of applied voltage on the throwing power of emulsions prepared from 6a-g: (○) 6a; (□) 6b; (△) 6c; (●) 6d; (■) 6e; (▲) 6f; (◐) 6g. Resin concentration = 5 wt %, BCS content = 1.5 wt %, deposition time = 1 min, pH = 4.83.

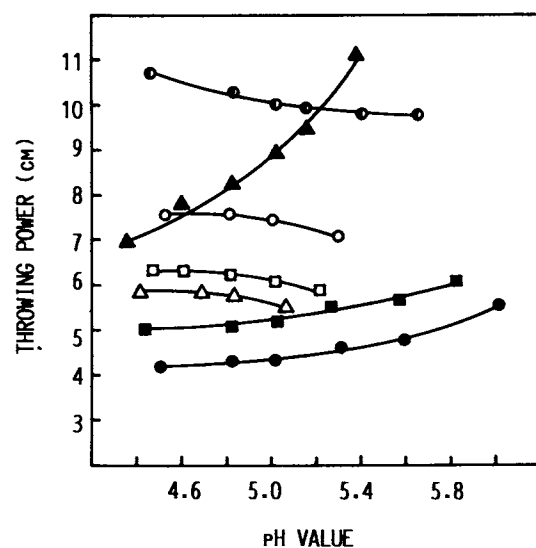


Figure 9 Effects of pH value on the throwing power of emulsions prepared from 6a-g: (○) 6a; (□) 6b; (△) 6c; (●) 6d; (■) 6e; (▲) 6f; (◐) 6g. Resin concentration = 5 wt %, BCS content = 1.5 wt %, deposition time = 1 min, applied voltage = 200 V.

Table II Rupture Voltage of the Emulsions of Resins 6a–g

Resin ^a	pH Value of Emulsion	Rupture Voltage
5a	5.04	300 V
5b	5.80	330 V
5c	5.11	340 V
5d	5.10	270 V
5e	5.07	290 V
5f	5.12	295 V
5g	5.06	290 V

^a The resin concentration is 5 wt % and the BCS content is 1.5 wt %.

of emulsions. This is because the emulsion conductivity increases at lower emulsion pH to increase the throwing power. However, the throwing power of resins 6d–f is contrary to the previous finding that emulsions having a higher conductivity give a higher throwing power.¹² It is likely that the pendant positively charged groups contained in resins 6d–f increase the water solubility of resins 5d–f. When resins 6d–f deposited on the cathode to become resins 5d–f, the low pH of emulsion (i.e., high acidity) makes it easy to redissolve the deposited film and leads to an emulsion with better conductivity but poor throwing power. The nature and the molecular weight of cationic resins also affects the throwing power of the emulsions, as shown in Figures 7–9. For resins 6a–c and 6g, the lower molecular weight of the resin gives higher throwing power (i.e., 6g > 6a > 6b > 6c), because the emulsion prepared from the resin with lower molecular weight contains more conductive ions when the resin concentration is kept the same. The resin with smaller molecular weight also gives a faster migration rate, so that high throwing power can be obtained. For the resins containing pendant positively charged groups, 6d–f, the throwing power increases with the increase of

the molecular weight of the resin. This is due to the fact that their water solubilities are so good, so that the resin with lower molecular weight is easy to redissolve during the deposition and results in lower throwing power.

Rupture Voltage

“Rupture voltage” can be defined as the maximum applied voltage that the emulsion of a resin can endure. Rupturing of an electrodeposition paint film is first observed as a sizzling sound, with a rapid secondary rise in current (breakdown of depositing coating), and an increase in electrocoat bath temperature. Inspection of the baked coating shows heavy rough films and cratering (pinholing) and/or blistering observed on precoated metals. But the exact cause of these defects is still unknown. Table II shows the rupture voltage of emulsions of resins 6a–g. It can be seen that the resin with higher molecular weight gives a higher rupture voltage. Cationic resin with pendant amino groups gives a lower rupture voltage. This 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 particles cannot be uniformly deposited onto the substrate, resulting in the rupture of the polymer emulsion.

Properties of the Crosslinked Films

The physical and chemical properties of the crosslinked electrodeposited films of the resins 5a–g are shown in Table III. For non-PG-TDI-urethane-containing resin 5g, the pencil hardness of its crosslinked deposited film is 5H. The pencil hardness of the crosslinked films prepared from PG-TDI-urethane-containing resins decreases to 3–4H.

Table III Physical and Chemical Properties of the Deposited Films

Property	5a	5b	5c	5d	5e	5f	5g
Adhesive strength	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Pencil hardness	4H	3H	3H	4H	3H	3H	5H
Alkali resistance ^a	OK	OK	OK	OK	OK	OK	OK
Acidic resistance ^b	OK	OK	OK	OK	OK	OK	OK

^a 0.1N NaOH 48 h.

^b 0.2N H₂SO₄ 48 h.

The higher molecular weight of the polyglycol contained in the resin gives a lower hardness crosslinked film, because the polyglycol contained in the resin lowers the crosslinking density of crosslinked film. The adhesive strength, alkali and acidic resistance of the crosslinked deposited films prepared from resins 5a-g is very good.

CONCLUSIONS

1. The gel content of urethane-modified resins increases significantly with an increase in curing temperature above 170°C and reaches a constant value at temperatures higher than 200°C.
2. The emulsion properties are strongly dependent on the pH value of the emulsions and the amount of solvent added.
3. The bath conductivity of emulsions decreases with an increase in the pH. At the same resin concentration in the emulsion, low-molecular-weight cationic resins give a higher conductivity.
4. Emulsions having a higher pH value give a higher deposition yield. The deposition yield also increases with increase in the molecular weight of the cationic resin.
5. The throwing power of the emulsion increases with increasing applied voltage and solvent content.

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