

# The Effect of Different Ammonium Structure of Quaternary Ammonium Resin on the Electrochemical Properties

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## SYNOPSIS

The quaternary ammonium resin is synthesized by the ring-opening reaction of an epoxy resin with a tertiary amine in the presence of a proton donor in the solution. This kind of resin can be dispersed in the water phase to form a conductible milky dispersion. In this study, different kinds of tertiary amines including the full-alkyl group and the ester group-containing or urethane group-containing tertiary amine are reacted with DGEBA-type epoxy resin to synthesize the quaternary ammonium resins. The resin characteristics and the electrochemical properties of its emulsion are investigated. In addition, properties of the emulsion prepared from tertiary amine salt resin are also measured for comparison. It is found that if the substituted groups of the ammonium structure of the quaternary ammonium resin are all alkyl groups, rupture voltage of the emulsion is very low. But when one of the substituted group contains an ester group or an urethane group, rupture voltage increases remarkably and the resin can be used for electrodeposition. Meanwhile, the electrodeposition theory of quaternary ammonium resin and its thermal cross-linking reaction and the electrochemical properties of coemulsion prepared by mixing the quaternary ammonium resin and the tertiary amine salt resin are also discussed. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The low molecular weight quaternary ammonium compound is prepared by reacting a compound containing tertiary amine with an alkyl halide. The reaction is often referred to as alkylation of amine. This compound always acts as a surfactant or polyelectrolyte,<sup>1</sup> but the studies of the preparation of quaternary ammonium resin and its electrochemical properties are seldom reported.

As the quaternary ammonium group is introduced, the insoluble resin can be dispersed in the water phase to form a stable milky solution because the introduced quaternary ammonium group is a water-soluble salt. At the same time, the dissoluble quaternary ammonium group makes the emulsion conductible. Then, the electrochemical properties of the emulsion can be studied.

In a previous study,<sup>2</sup> it was found that the quaternary ammonium resin was synthesized by the ring-opening addition reaction of epoxy resin with a full-alkyl group tertiary amine in the presence of acetic acid as the proton donor. Although this kind of resin has good solubility and stable emulsification, the rupture voltage of its emulsion is extremely low. Therefore, the electrochemical properties of this emulsion are not satisfied.

In this study, the tertiary amine-containing the ester group or the urethane group is reacted with DGEBA-type epoxy resin to synthesize the quaternary ammonium resins having the different kinds of terminal ammonium structure, which then will be dispersed in deionized water to obtain stable emulsions. The effect of the terminal ammonium structure of the quaternary ammonium resin on rupture voltage and the effects of resin concentration and pH value of the emulsion on the electrochemical properties are investigated. Meanwhile, all properties of the tertiary amine salt resin are measured for comparison and the thermal cross-linking reaction of the deposited film of the quaternary ammonium

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resin is also investigated. Finally, the emulsion of quaternary ammonium resin as an additive and the effects of its content in the coemulsion bath on electrochemical properties are also studied.

## EXPERIMENTAL

### Material

2EH-half-blocked TDI was synthesized by 2-ethylhexanol (2EH) (Hayashi EP grade) and commercial toluene diisocyanate (TDI). The DGEBA-type epoxy resin (Epon 1004, Shell Chemical Co.) has the average equivalent weight per epoxy group of 950. Amines used as ring-opening agents include diethylamine (DEA) (Wako EP grade), methyl 3-(dimethylamino)propionate (MDMAP) (Aldrich Chemical Co.), and two kinds of derived amines synthesized by dimethyl ethanolamine (DMEA) (Fluka EP grade) and phenyl isocyanate (PI) (Ferak EP grade) or 2EH-half-blocked TDI. The organic cosolvent is ethylene glycol mono-*n*-butyl ether (BCS) (Hayashi EP grade).

### Apparatus

A thermal analyzer (Rigaku TAS100), a pH meter, a conductivity meter, an electrodeposition apparatus, and a throwing power testing vessel<sup>3</sup> were employed.

### Synthesis

#### Quaternary Ammonium Resins (Ia–c)

Into a 1000 mL five-necked flask equipped with an electric stirrer, 189 g (0.1 mol) of Epon 1004 and 200 mL toluene were added and heated to 80–90°C for better mixing. After a mixture of 26.2 g (0.2 mol) MDMAP and 12.6 g (0.21 mol) acetic acid was added completely, the mixture was reacted at this temperature range over 4 h. After toluene was distilled off under reduced pressure, 227.8 g of the quaternary ammonium resin **Ia** was obtained.

The MDMAP was replaced with two kinds of derived tertiary amines synthesized by DMEA and PI (or 2EH-half-blocked TDI) and the mentioned experimental procedure was repeated to obtain other quaternary ammonium resins **Ib** and **Ic**.

#### Tertiary Amine Acid Salt Resin (II)

Epon 1004, 189 g (0.1 mol), and 200 mL toluene were added into a 1000 mL five-necked flask equipped with an electric stirrer and heated up to

80–90°C for thorough mixing. After 15.36 g (0.21 mol) DEA was added completely, the mixture was kept at this temperature range over 4 h for the ring-opening reaction. Then, 12.6 g (0.21 mol) acetic acid was added for neutralization. After toluene was distilled off under reduced pressure, 217 g tertiary amine acid salt resin **II** was obtained.

### Preparation of Emulsion

Into a 300 mL three-necked flask equipped with an electric stirrer, 20 g of cationic resin and 3 g of BCS were added and heated up to 70–80°C for a complete mixing. Then, 77 g deionized water was added dropwise and kept the mixture stirring violently. Finally, 100 g of stable emulsion possessing 20 wt % of resin concentration and 3 wt % of BCS content was obtained.

### Measurement of Rupture Voltage

The electrodeposition test was applied under standard electrodeposition conditions: increasing the bath dc voltage slowly and regularly until the decreasing current value increased again. This point voltage is the so-called rupture voltage of electrodeposition coating. The effect of the resin concentration and pH value of emulsion or the composition of coemulsion on rupture voltage were examined.

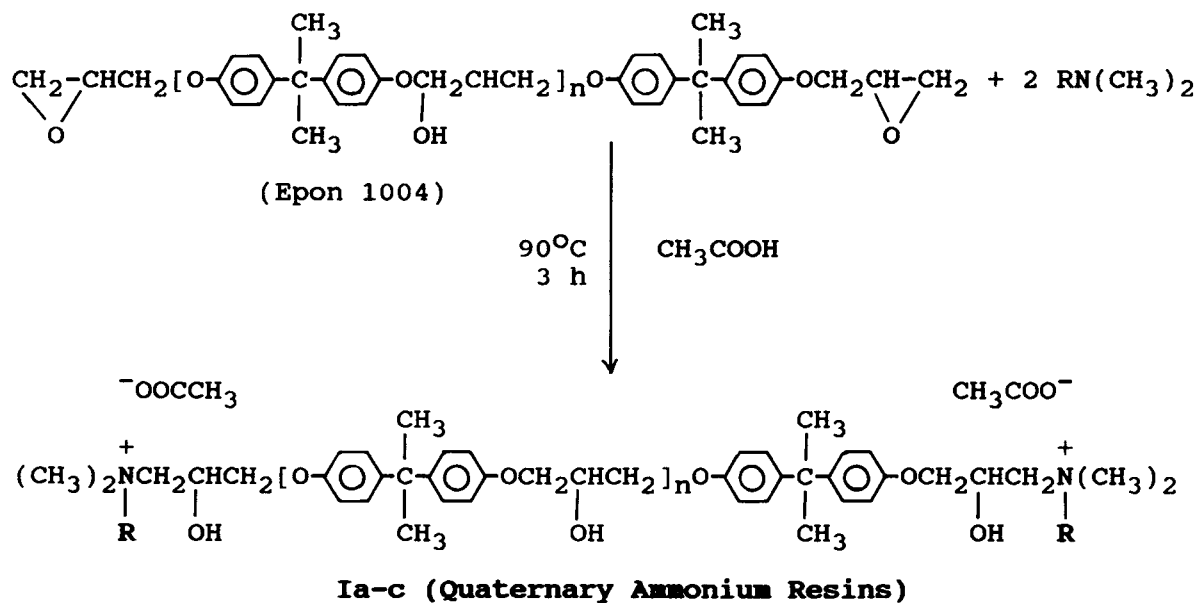
### Measurement of Throwing Power

The throwing power was determined by the height of the deposited resin in a throwing power testing vessel. The effect of the resin concentration of emulsion, pH value of emulsion, and the composition of coemulsion on throwing power were studied.

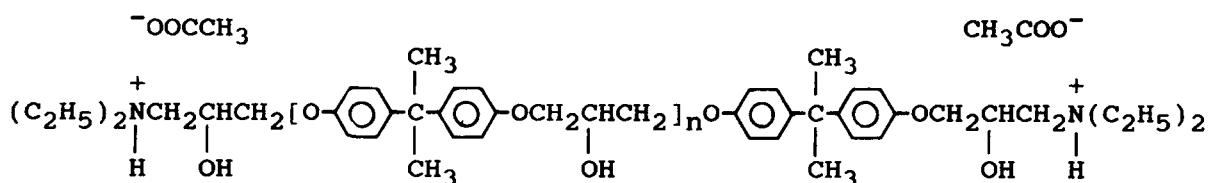
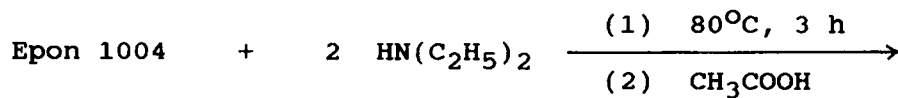
## RESULTS AND DISCUSSION

### Synthesis

The quaternary ammonium resin was prepared by the ring-opening reaction of DGEBA-type epoxy resin and tertiary amine salt. In this study, three kinds of non-full-alkyl group tertiary amines were reacted with Epon 1004 individually to synthesize the quaternary ammonium resins **Ia–c** containing different ammonium structure in the end groups of these resins. In addition, the tertiary amine acid salt resin **II** was prepared by DEA and Epon 1004 for comparing the electrodeposition properties with resins **Ia–c**, as shown in Scheme 1.



	Ia	Ib	Ic
R	$-\text{C}_2\text{H}_4\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	$-\text{C}_2\text{H}_4\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\text{C}_6\text{H}_5$	$-\text{C}_2\text{H}_4\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\text{C}_6\text{H}_4-\text{N}-\text{C}(=\text{O})-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{CH}_3$



## II (Tertiary Amine Acid Salt Resin)

Scheme 1

## Electrodeposition Properties of Quaternary Ammonium Resin

### (A) The Effect of Ammonium Structure of Resin on Rupture Voltage

In a previous paper,<sup>2</sup> it was found that the rupture voltage of an emulsion was concerned with the terminal ammonium structure in the quaternary ammonium resin used for electrodeposition coating. As the used tertiary amine is a full-alkyl group structure, the measured rupture voltage of emulsion was very low. But rupture voltage increases significantly when the used tertiary amine contains an ester group. Table I compares the rupture voltages of resins **Ia–c** prepared by the non-full-alkyl group tertiary amines with those prepared by the full-alkyl group tertiary amines in the previous study. Since the terminal ammonium structure of resins **Ia–c** introduced different nonalkyl groups, such as the urethane or ester group, it is found that their rupture voltages become larger. In general, under the status of high rupture voltage, the electrodeposition process

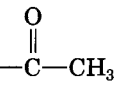
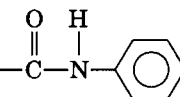
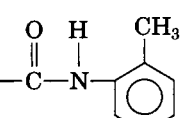
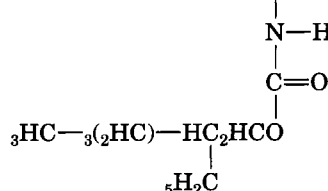
is more efficient because it can be applied under higher dc voltage. For ED coating, rupture voltage is as high as possible.

### (B) The Effect of Resin Concentration or pH Value of Emulsion on Deposited Yield

During the electrodeposition process, the ionized resin, dispersed and suspended in deionized water, was deposited on the surface of a metallic subject to form a polymer film. Thus, the higher the concentration of the ionized resin in the emulsion, the higher the deposited yield under the same applied voltage, as shown in Figure 1.

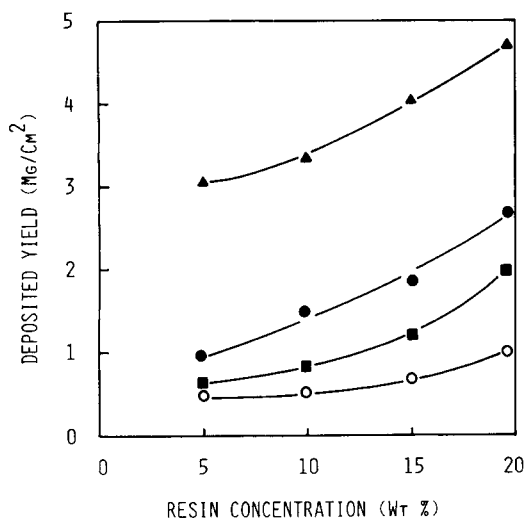
In addition, it is also shown that the sequence of deposited yield is resin **Ib** > **Ic** > **Ia** > **II**. All deposited yields of quaternary ammonium resins **Ia–c** are higher than that of the tertiary amine acid salt resin **II**. For resins **Ia–c**, the molecular weight of the used tertiary amine is not really concerned with the deposited yield. The deposited yield of resin **Ib** is the highest but its molecular weight is not.

**Table I** Rupture Voltages of Quaternary Ammonium Resins Containing Different Terminal Amine Structure at the Same Emulsion Conditions<sup>a</sup>

Resin	Tertiary Amine $N(R_1R_2R_3)$			MW	Rupture Voltage (V)
	$R_1$	$R_2$	$R_3$		
<b>Ia</b>	—CH <sub>3</sub>	—CH <sub>3</sub>	—C <sub>2</sub> H <sub>4</sub> O—  —CH <sub>3</sub>	131	275
<b>Ib</b>	—CH <sub>3</sub>	—CH <sub>3</sub>	—C <sub>2</sub> H <sub>4</sub> O—  —C <sub>6</sub> H <sub>5</sub>	208	260
<b>Ic</b>	—CH <sub>3</sub>	—CH <sub>3</sub>	—C <sub>2</sub> H <sub>4</sub> O—  —C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )	393	310
					
	—C <sub>2</sub> H <sub>5</sub>	—C <sub>2</sub> H <sub>5</sub>	—C <sub>2</sub> H <sub>5</sub>	101	5 <sup>b</sup>
	—C <sub>3</sub> H <sub>7</sub>	—C <sub>3</sub> H <sub>7</sub>	—C <sub>3</sub> H <sub>7</sub>	143	5 <sup>b</sup>
	—CH <sub>3</sub>	—C <sub>4</sub> H <sub>9</sub>	—C <sub>4</sub> H <sub>9</sub>	143	5 <sup>b</sup>
	—CH <sub>3</sub>	—CH <sub>3</sub>	—C <sub>8</sub> H <sub>17</sub>	157	5 <sup>b</sup>

<sup>a</sup> Resin concentration: 20 wt %; pH 4.8–5.0; BCS content: 3 wt %.

<sup>b</sup> Data obtained from Ref. 2.



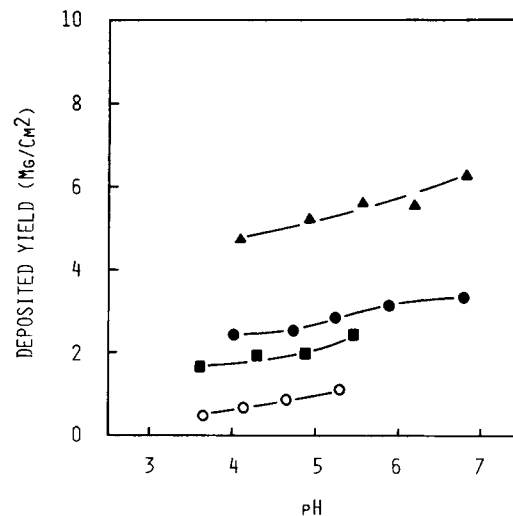
**Figure 1** Effects of resin concentration of emulsions on deposited yield. BCS content 3 wt %; pH 4.8–5.0; (■) resin Ia; (▲) resin Ib; (●) resin Ic; (○) resin II.

Figure 2 is the relation of the deposited yield with the pH value of emulsion. It is shown that the emulsion having a lower pH value caused by adding more acetic acid into the emulsion gives a lower deposited yield. This can be attributed to the fact that low pH value (i.e., high acidity) of the emulsion increases the “resolubility” of the deposited film. Resins Ia–c and resin II have the same result.

### (C) The Effect of Resin Concentration or pH Value of Emulsion on Throwing Power

The best advantage of ED coating is that the ionized resin micelle in the emulsion can electrophoresize, penetrate, and deposit to form a uniform film even on the surface of the recessed and shielded area where other coating methods cannot be applied. The ability of above phenomena can be measured by the throwing power.

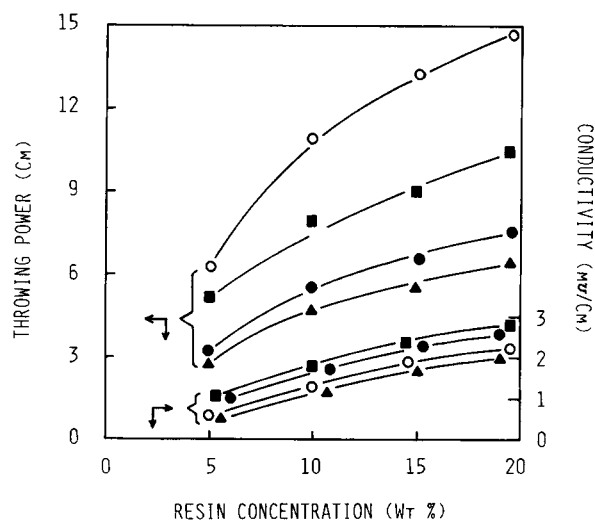
Furuno et al.<sup>4</sup> showed that the throwing power is proportional to the root square of the bath conductivity contributed by the ionized resin particle. Thus, the higher the resin concentration of the emulsion, the higher the emulsion conductivity. Figure 3 shows the effect of the resin concentration of emulsion on the emulsion conductivity and throwing power. It is shown that both conductivity and throwing power increase when the resin concentration of emulsion increases. Throwing power will increase as the emulsion conductivity increases. This result corresponds to the conclusion of Furuno et al. In Figure 3 it is also observed that the sequence of throwing power is resin II > Ia > Ic > Ib under the same



**Figure 2** Influences of pH value of emulsions for deposited yield. Resin concentration 20 wt %; BCS content 3 wt %; applied voltage 100 V; deposited time 3 min; (■) resin Ia; (▲) resin Ib; (●) resin Ic; (○) resin II.

conditions, which means that the tertiary amine acid salt resin II has better throwing power than that of quaternary ammonium resins Ia–c.

The pH value of emulsion will also relate to emulsion conductivity and throwing power. It is known that throwing power increases because of the increase of the conductivity, contributed by the increase of the ionized resin concentration in the emulsion. But, if the increase of the conductivity is

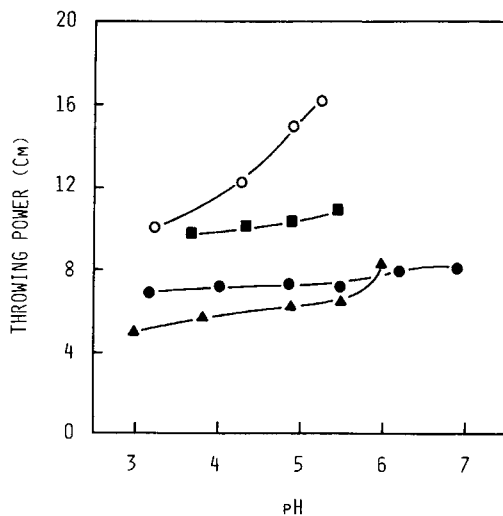


**Figure 3** Relationships of resin concentration of emulsions with throwing power and conductivity. pH 4.8–4.9; BCS content 3 wt %; applied voltage 100 V; deposited time 1 min; (■) resin Ia; (▲) resin Ib; (●) resin Ic; (○) resin II.

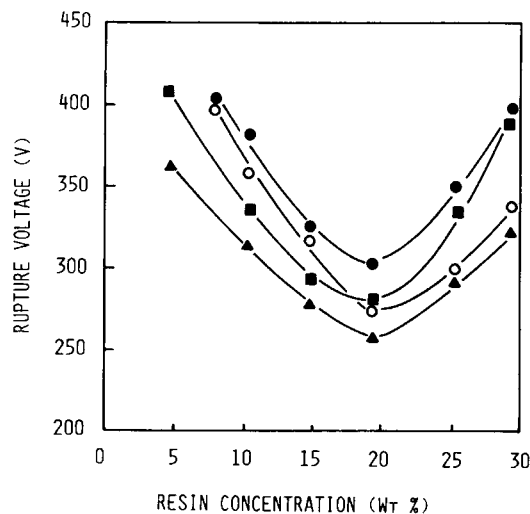
caused by adding supplemental acetic acid into the emulsion, throwing power will decrease contrarily. Figure 4 shows that all throwing power will decrease when the pH values of the emulsions are decreased by adding additional acetic acid into the emulsions. It is also observed that all decreases of resins Ia–c are more moderate than that of resin II. The reason is that the deposited film of resin II is to be reduced to the tertiary amine resin that can be reionized and resolvable easily at lower pH value; on the contrary, deposited films of quaternary ammonium resins Ia–c are still the quaternary ammonium form, which are more stable under lower pH.

#### (D) The Effect of Resin Concentration and pH Value of Emulsion on Rupture Voltage

Not only does the terminal ammonium structure of the cationic resin affect the rupture voltage, as shown in Table I, but so does the resin concentration or pH value of the emulsion. Rupture voltage decreases to a minimum first and then increases gradually as the resin concentration of the emulsion increases continuously, as shown in Figure 5. This may be ascribed to the emulsion conductivity and the deposited film thickness. The effect of emulsion conductivity on rupture voltage just reverses that of film thickness on rupture voltage. In general, the emulsion having a higher conductivity can offer stronger electric power when some dc voltage is applied; therefore, the deposited film will be ruptured easily



**Figure 4** Effects of pH value of emulsions on throwing power. Resin concentration 20 wt %; BCS content 3 wt %; applied voltage 100 V; deposited time 1 min; (■) resin Ia; (▲) resin Ib; (●) resin Ic; (○) resin II.

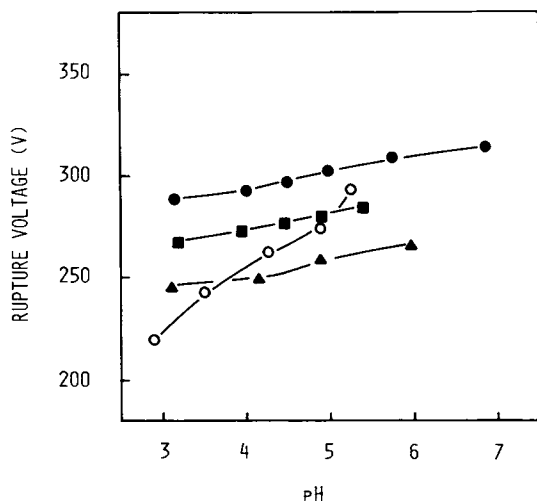


**Figure 5** Influences of resin concentration of emulsions for rupture voltage. BCS content 3 wt %; pH 4.8–5.0; (■) resin Ia; (▲) resin Ib; (●) resin Ic; (○) resin II.

at a lower applied voltage. On the contrary, the greater the film thickness, the higher the rupture voltage that will be obtained, because the deposited film, a semi-insulated polymer, can resist a higher voltage before being ruptured when its thickness is greater. Figures 1 and 3, show that both the film thickness (i.e., the deposited yield) and the emulsion conductivity increase as the resin concentration of emulsion increases.

But, in Figure 5, under the lower resin concentration (< 20 wt %), rupture voltage decreases contrarily when the resin concentration of emulsion increases. The reason may be that the positive effect of the deposition rate on rupture voltage cannot offset the negative effect of the increasing conductivity on the rupture voltage at this resin concentration range. With resin concentration over 20 wt %, rupture voltage increases when the resin concentration of emulsion increases, because at this time, the positive effect of the deposition rate on rupture voltage can surpass the negative effect of the conductivity on the rupture voltage.

It was already mentioned that the conductivity will increase but the deposited yield will decrease when the pH value of the emulsion decreases. Then, the rupture voltage will decrease as the pH value of the emulsion decreases, as shown in Figure 6. This figure also shows that the decreasing tendency of resin II is faster than those of resins Ia–c. This result is same as that shown in Figure 4. It means that the acidic resistance of the quaternary ammonium resin is superior to that of the tertiary amine acid salt resin.



**Figure 6** Relationships of pH value of emulsions with rupture voltage. Resin concentration 20 wt %; BCS content 3 wt %; (■) resin Ia; (▲) resin Ib; (●) resin Ic; (○) resin II.

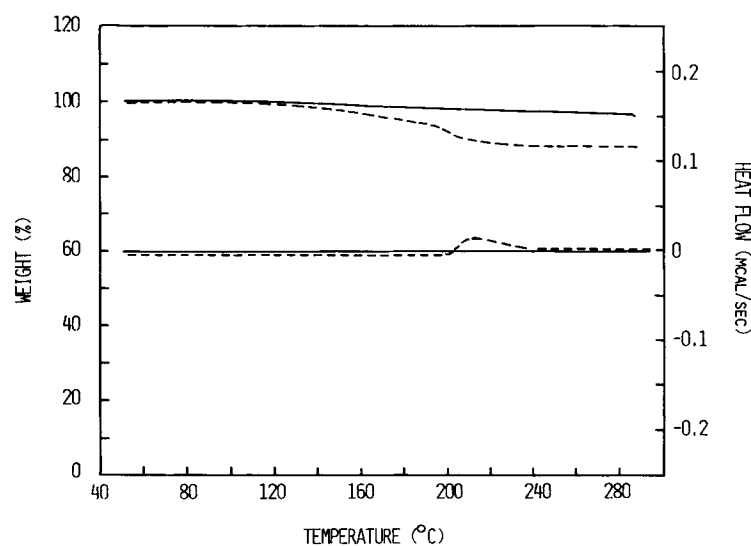
### The Thermochemical Reaction of Quaternary Ammonium Resin

It was proved that the electrodeposition mechanism of the quaternary ammonium resin is not same as that of the tertiary amine acid salt resin in the previous study.<sup>2</sup> The deposited film of the quaternary ammonium resin is still the quaternary ammonium form [—N(R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>)(OH)] but a bad solubility. As baked, this quaternary ammonium chain will break and reduce to the tertiary amine and the epoxy group and water will release at the same time. This reduced

tertiary amine can then catalyze the cross-linking reaction.

The deposited film of resin Ia was analyzed by DSC and TGA and compared with that of resin II. The result, as shown in Figure 7, is that the deposited film of resin II has no significant thermal change and weight loss as temperature increases, but that of resin Ia has an endothermic peak about 200°C and the weight loss, caused by the gasification of water and reduced amine, begins at 120°C and the final loss rate is about 8%, which is same as the content of DMEA and H<sub>2</sub>O in the deposited resin.

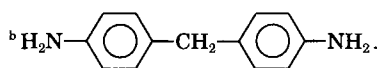
The mixture of resin Ia (or resin II) and the diamine was baked and then immersed in acetone to reflux for 24 h. Finally, the residual content was examined. In Table II, it is found that the residual content of resin Ia (i.e., quaternary ammonium resin) increases when the baked temperature increases at a fixed baked time (30 min). The residual content is 25 wt % at 150°C for 30 min, but the residual content of resin II (i.e., tertiary amine acid salt resin) is only about 1 wt % at the same conditions. In addition, the residual content of resin Ia also increases as the baked time is prolonged at the same baked temperature (150°C). The residual content of resin Ia is 40 wt % at 150°C for 60 min. But the residual content of resin II does not obviously change; all are below 2 wt %. It is concluded that quaternary ammonium resin easily reduces to epoxy resin and tertiary amine at higher temperature; then, the epoxy group will react with other functional groups, such as —OH and —NH<sub>2</sub>. On the other hand, tertiary amine resin and its acid salt



**Figure 7** Thermal analyses of (—) resin Ia and (---) resin II. Heating rate 5°C/min in a N<sub>2</sub> blanket.

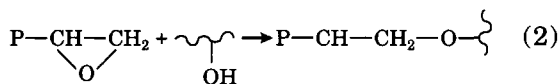
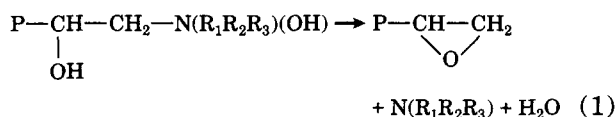
**Table II** The Gel Content<sup>a</sup> of the Product of Reacting of Resin Ia (or Resin II) with Diamine<sup>b</sup> as a Cross-linking Agent

Reaction		Gel Content (wt %)	
Time (min)	Temp (°C)	Resin Ia	Resin II
30	50	7.4	0.8
30	100	13.5	1.0
30	125	18.7	1.2
30	150	24.9	1.1
45	150	30.0	1.6
60	150	40.5	2.1

<sup>a</sup> To immerse in acetone to reflux for 24 h.

are hard to decompose at higher temperature; thus, the mentioned reaction will not happen.

From the above discussion, it is supposed that the thermal decomposition reactions of the quaternary ammonium resin are as follows:

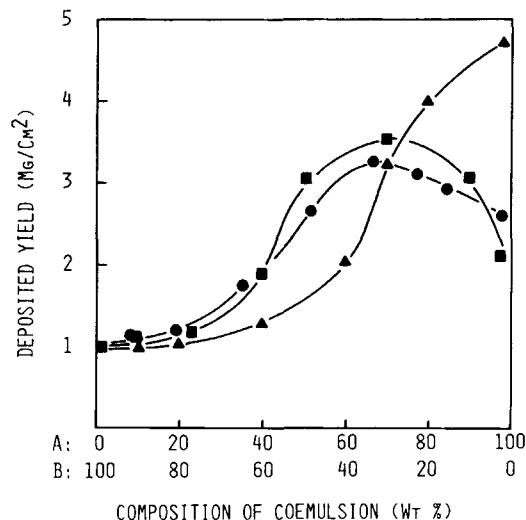


where *P* represents the long polymer chain.

### The Effect of Mixing the Quaternary Ammonium Resin and the Tertiary Amine Acid Salt Resin on the Electrodeposition Properties

Adding the quaternary ammonium resin into the tertiary amine acid salt resin to prepare a coemulsion can affect the original electrodeposition properties, especially in the deposited yield. The coemulsion was prepared by mixing the emulsion of resin Ia (Ib or Ic) and the emulsion of resin II with the same total resin concentration (20 wt %) but different weight ratio.

Figure 8 is the effect of the composition of coemulsion on the deposited yield. It is shown that the deposited yield increases when the content of resin Ia (or Ic) in the coemulsion increases. However, the maximum deposited yield is obtained at



**Figure 8** Effects of the composition of coemulsions on deposited yield. Total resin concentration 20 wt %; BCS content 3 wt %; pH 4.8–5.0; applied voltage 100 V; deposited time 3 min; (A) quaternary ammonium resin; (B) tertiary amine acid salt resin; (■) resin Ia; (▲) resin Ib; (●) resin Ic.

the content of resin Ia (or Ic) of 70% in the coemulsion. But the deposited yield increases in direct proportion to the content of resin Ib in the coemulsion and gives the maximum until the coemulsion is the pure emulsion of resin Ib. The reason for above result is not really understood and needs more detailed study.

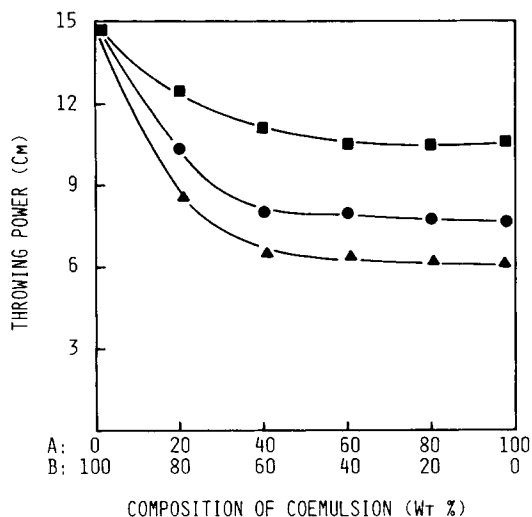
Figure 6 shows that the throwing power of resin II is higher than that of the others (resins Ia–c) at the same conditions. Therefore, increasing the content of the quaternary ammonium resin in the coemulsion will cause the throwing power of the coemulsion to decrease gradually, as shown in Figure 9.

Since all the rupture voltages of resins Ia–c and II have no effect, those of all coemulsions are not affected by changing the composition of the coemulsion. In general, adding the quaternary ammonium resin into the tertiary amine acid salt resin can increase the deposited yield but decreases the throwing power at the same time.

### CONCLUSIONS

1. The quaternary ammonium resin prepared with epoxy resin and tertiary amine containing an ester or urethane group can give a higher rupture voltage of its emulsion.





**Figure 9** Effects of the composition of coemulsions on throwing power. Total resin concentration 20 wt %; BCS content 3 wt %; pH 4.8–5.0; applied voltage 100 V; deposited time 1 min; (A) quaternary ammonium resin; (B) tertiary amine acid salt resin; (■) resin Ia; (▲) resin Ib; (●) resin Ic.

2. The high deposited yield, high rupture voltage, and high throwing power obtained must increase the resin concentration of emulsion and the pH value.

3. The deposited film of the quaternary ammonium resin is decomposed and reduced to the tertiary amine and the epoxy group during baking. Moreover, the reduced epoxy group can cross-link with the active hydrogen of the resin.
4. The quaternary ammonium resin, as the additional agent, added into the tertiary amine acid salt resin can increase the deposited yield but decrease the throwing power simultaneously.

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