

# Preparation of Quaternary Ammonium Resin by Epoxy Resin and Tertiary Amine and Its Electrodeposition Properties

CHIN-PING YANG\* and CHIH-YANG TING

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

## SYNOPSIS

A quaternary ammonium-containing cationic resin is prepared by the ring-opening reaction of epoxy resin and tertiary amine with the presence of a proton donor. Its emulsion can form a uniform polymer film on the cathodic metal by electrodeposition. In this study, the reaction conditions to prepare the quaternary ammonium resin from epoxy resin and tertiary amine, and effects of different proton donors on this reaction, were examined by gel permeation chromatography and infrared. Meanwhile, distinctions of electrodeposition properties between the quaternary ammonium resin and the tertiary amine acid salt resin were considered. Finally, the electrodeposition mechanism of quaternary ammonium resin was also determined. The results show that the quaternary ammonium resin prepared by triethylamine (TEA) and Epon 1004 has better solubility and emulsification than the tertiary amine acid salt resin prepared by diethylamine (DEA) and Epon 1004. Rupture voltage of this quaternary ammonium resin was very low because it was prepared by full-alkyl group tertiary amine. Therefore, this kind of quaternary ammonium resin was not suitable for use for the electrodeposition resin individually. But when this quaternary ammonium resin was added to the tertiary amine acid salt resin, the deposited yield was much increased.

© 1993 John Wiley & Sons, Inc.

## INTRODUCTION

In general, an epoxy-amine cationic resin is synthesized by reacting epoxy resin with amine, then neutralizing with acid. The resin obtained can be dispersed in deionized water to form a stable emulsion and electrodeposited on cathodic metal to form a protective polymer film when a voltage is applied in the emulsion bath. This kind of resin is mainly used for the coating of car bodies and other appliances. Thus far, the tertiary amine salt-containing cationic resin<sup>1-9</sup> prepared by epoxy resin and secondary amine is still the principal electrodeposition coating. Quaternary ammonium resins are seldom used for electrodeposition. Likewise, a detailed study of quaternary ammonium-containing resins to be used for this field has been seldom reported.<sup>10-12</sup>

In this study, the quaternary ammonium resin was prepared by reacting DGEBA epoxy resin (Epon 1004) with the acetic acid salt of triethylamine (TEA). At the same time, diethylamine (DEA) and the same epoxy resin were used to synthesize an amine-epoxy adduct and then neutralized to form the tertiary amine acid salt resin. The electrodeposition properties of these resins, the optimum reaction conditions of quaternary ammonium resin, and the theory of electrodeposition were investigated. In addition, effects of the composition of co-emulsion on electrodeposition properties were also studied.

## EXPERIMENT

### Materials

Phenyl glycidyl ether (PGE) was synthesized from phenol and epichlorohydrin (Wako extra pure grade) in  $\text{NaOH}_{(aq)}$ . The epoxy equivalent weight

\* To whom correspondence should be addressed.

(EEW) of the commercial DGEBA epoxy resin (Epon 1004, Shell Chemical Co.) is about 950. Amines reacted with the epoxy compound include DEA, TEA (Wako extra pure grade), *N*-methyl-dibutylamine (MDBA), *N,N*-dimethyloctylamine (DMOA), and methyl 3-(dimethylamino)propionate (MDMAP) (Aldrich Chemical Company, Inc.). In addition, acids included acetic acid and hydrochloric acid. Ethyl glycol monobutyl ether (Butyl Cellosolve, BCS, Wako EP grade) is the coalescing solvent.

### Apparatus

An FTIR spectrometer (JASCO, FTIR-7000), a Gel Permeation Chromatograph (GPC, Shimadzu LC-6A) and the electrodeposition apparatus<sup>8</sup> were employed.

### Synthesis

#### PGE-TEA Quaternary Ammonium Compound (1)

A mixture of 15 g (0.1 M) PGE, 11.1 g (0.11 M) TEA, and the calculated amount of CH<sub>3</sub>COOH (HCl or H<sub>2</sub>O) was added into a 100 mL flask equipped with a magnetic stirrer. The mixture was reacted at the desired temperature continuously. A series of samples were taken during the reaction to investigate the degree of reaction by IR and GPC.

#### Quaternary Ammonium Resin (2a-e)

Into a 1000 mL five-necked reactor equipped with an electric stirrer, 189 g Epon 1004 and 200 mL toluene were added. The mixture was heated to 80–90°C for a better mixing. After a mixture of 21.05 g (0.21 M) TEA and 12.6 g (0.21 M) acetic acid was completely added, the mixture were reacted at 80–90°C for 4 h. After toluene was distilled off under reduced pressure, 222 g of the quaternary ammonium resin was obtained.

TEA was replaced with TPA, MDBA, DMOA, or MDMAP and the above experiment repeated.

#### Tertiary Amine Acid Salt Resin (3)

Epon 1004 (189 g) and toluene (200 mL) were added to a 1000 mL five-necked reactor equipped with an electric stirrer and heated to 80–90°C for thorough mixing. Then DEA (15.36 g, 0.21 M) was added to the mixture dropwise. After complete addition of DEA, the mixture was reacted at 80–90°C for 4 h and 12.6 g (0.21 M) of acetic acid was treated sequentially and the mixture was vigorously stirred

for another 1 h. Finally toluene was distilled off under reduced pressure; 217 g of the tertiary amine acid salt resin was obtained.

### Preparation of Emulsion

The cationic resin (10 g) and BCS (5 g) were added to a three-necked glass reactor equipped with an electric stirrer. The mixture was heated to 70–80°C for complete mixing. Then, 85 g of deionized water was added dropwise and the mixture was stirred vigorously at the same time. Finally, a stable emulsion containing 10 wt % of the resin concentration and 5 wt % of BCS content was obtained.

### Measurement of Rupture Voltage

The electrodeposition test was applied under the standard electrodeposition conditions, increasing the bath voltage slowly and regularly until the decreasing electric current increased again. This voltage is the so-called rupture voltage of the emulsion.<sup>13</sup>

The effects of resin concentration and pH value of emulsion and the composition of coemulsion on rupture voltage were examined.

## RESULTS AND DISCUSSION

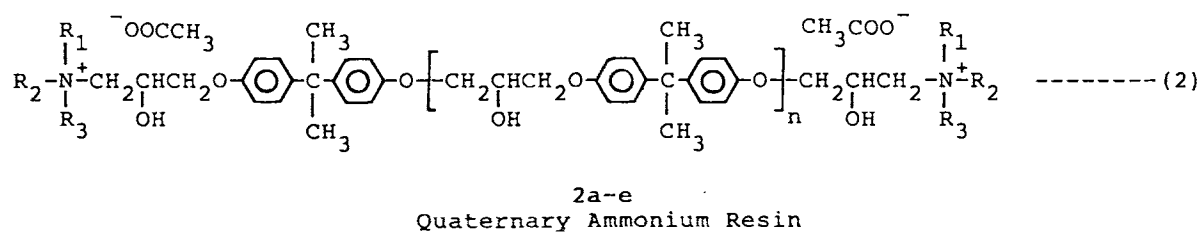
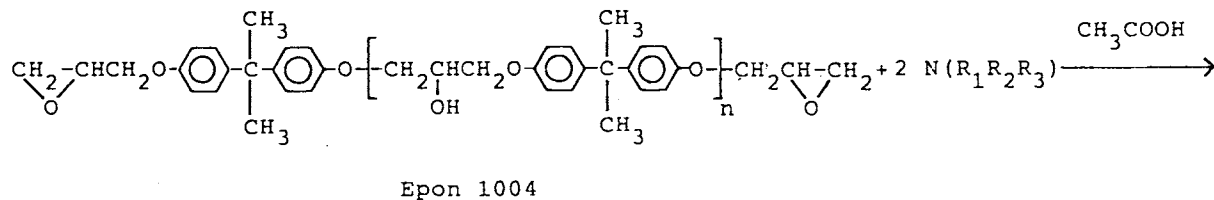
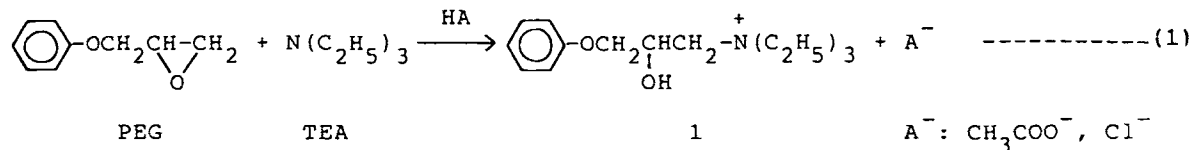
### Synthesis

The quaternary ammonium resin is prepared from epoxy resin and tertiary amine in the presence of a proton donor, as shown in Scheme 1, eq. (2). Because its end groups are quaternary ammonium groups, this kind of resin is also called a cationic resin. On the other hand, the tertiary amine acid salt resin, prepared by reacting epoxy resin with secondary amine and then neutralized by acetic acid, is also a cationic resin, as shown in Scheme 1, eqs. (3) and (4).

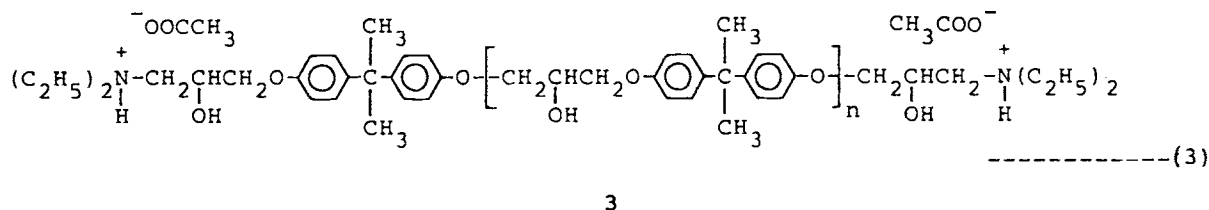
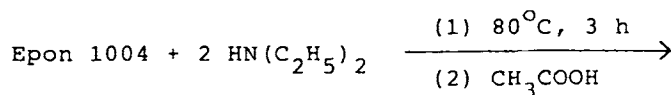
The preparation of tertiary amine acid salt resin is simple, but the preparation of quaternary ammonium resin is difficult with by-reaction reactions perhaps occurring simultaneously. Thus, the optimum reaction conditions will be studied.

#### Effects of Proton Donor on Preparation of Quaternary Ammonium Resin

The model compound, quaternary ammonium alcohol (1), was prepared by the ring-opening reaction of PGE and TEA in the presence of proton donor



	2a	2b	2c	2d	2e
R <sub>1</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>3</sub> H <sub>7</sub>	-CH <sub>3</sub>	-CH <sub>3</sub>	-CH <sub>3</sub>
R <sub>2</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>4</sub> H <sub>9</sub>	-CH <sub>3</sub>	-CH <sub>3</sub>
R <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>3</sub> H <sub>7</sub>	-C <sub>4</sub> H <sub>9</sub>	-C <sub>8</sub> H <sub>17</sub>	-C <sub>2</sub> H <sub>4</sub> O-C(=O)-CH <sub>3</sub>



Scheme 1 Tertiary Amine Acid Salt Resin

[Scheme 1, eq. (1)]. Because tertiary amine can promote anionic polymerization between epoxy groups, controlling the reaction conditions to make sure of complete reaction is important.

When phenyl glycidyl ether (PGE) is reacted with TEA at 90°C without proton donor, GPC data does

not change obviously during the reaction. But, when the reaction proceeds with a calculated amount of acetic acid as the proton donor for 4 h, the elution time for the GPC trace will diminish from 19.27 min to 17.20 min and the molecular weight (*M<sub>w</sub>*) will increase from 112 to 254. At this time, the polydis-

**Table I** GPC Data of PGE-TEA Reaction With Different Proton Donors

Proton Donor	GPC Data					
	Elution Time (min)		Relative $M_w^a$		Polydispersity	
	4 <sup>b</sup>	20 <sup>c</sup>	4	20	4	20
—	19.27	19.20	112	124	1.14	1.18
H <sub>2</sub> O	16.45	16.04	386	424	1.56	1.59
CH <sub>3</sub> COOH	17.20	17.09	254	265	1.07	1.20
HCl	17.67	16.98	237	277	1.19	1.21

PGE, phenyl glycidyl ether; TEA, triethylamine.

<sup>a</sup> Standard is PS.

<sup>b</sup> Reacting at 90°C for 4 h.

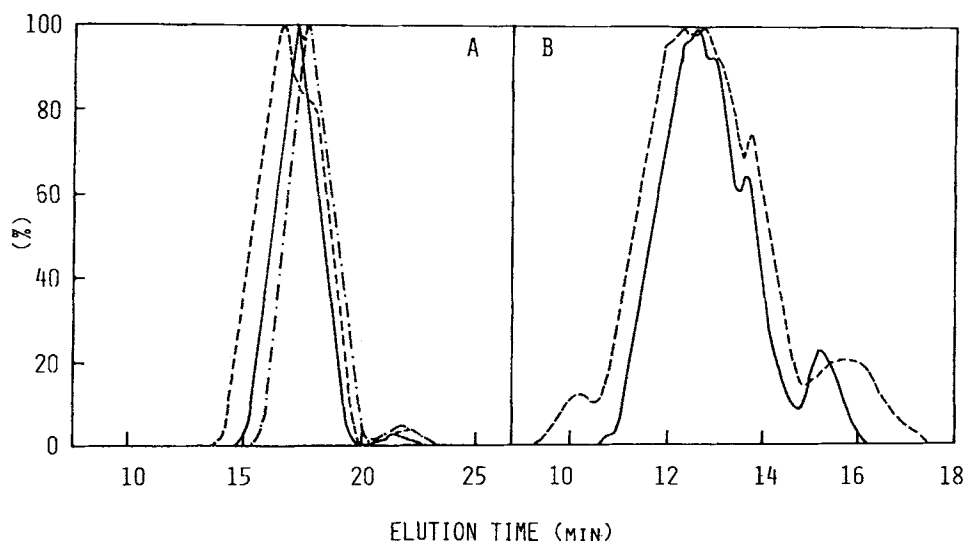
<sup>c</sup> Reacting at 90°C for 20 h.

persity of this product was 1.07, as shown in Table I. From the above data it is clear that PGE can react with TEA at the above conditions and that the product is quaternary ammonium alcohol having a narrow molecular weight distribution (MWD). Furthermore, the elution time does not significantly change after the reaction proceeds over 20 h, which means the reaction is almost completed at 90°C after 4 h.

If the proton donor was replaced by a strong acid such as HCl, the GPC data are similar to those using acetic acid as the proton donor. But when water is used as the proton donor, the elution time for GPC

trace will diminish to 16.45 min after 4 h and the polydispersity is 1.56; moreover, the  $M_w$  (386) is greater than the theoretical  $M_w$  (267) of this quaternary ammonium alcohol (Table I). The result is ascribed to the possibility that anionic polymerization of epoxy groups will proceed when water is used as the proton donor.

Figure 1 (A) shows that GPC curves of quaternary ammonium compounds using different organic acids as the proton donor are narrower than when using water as the proton donor. In addition, replacing PGE with Epon 1004 and reacting under the same conditions, the MWD of the product using H<sub>2</sub>O as



**Figure 1** GPC curves of (A) PGE-TEA reaction and (B) Epon 1004-TEA reaction in the presence of different proton donors at 90°C for 4 h. Proton donor: (—) CH<sub>3</sub>COOH; (---) HCl; (· · ·) H<sub>2</sub>O.

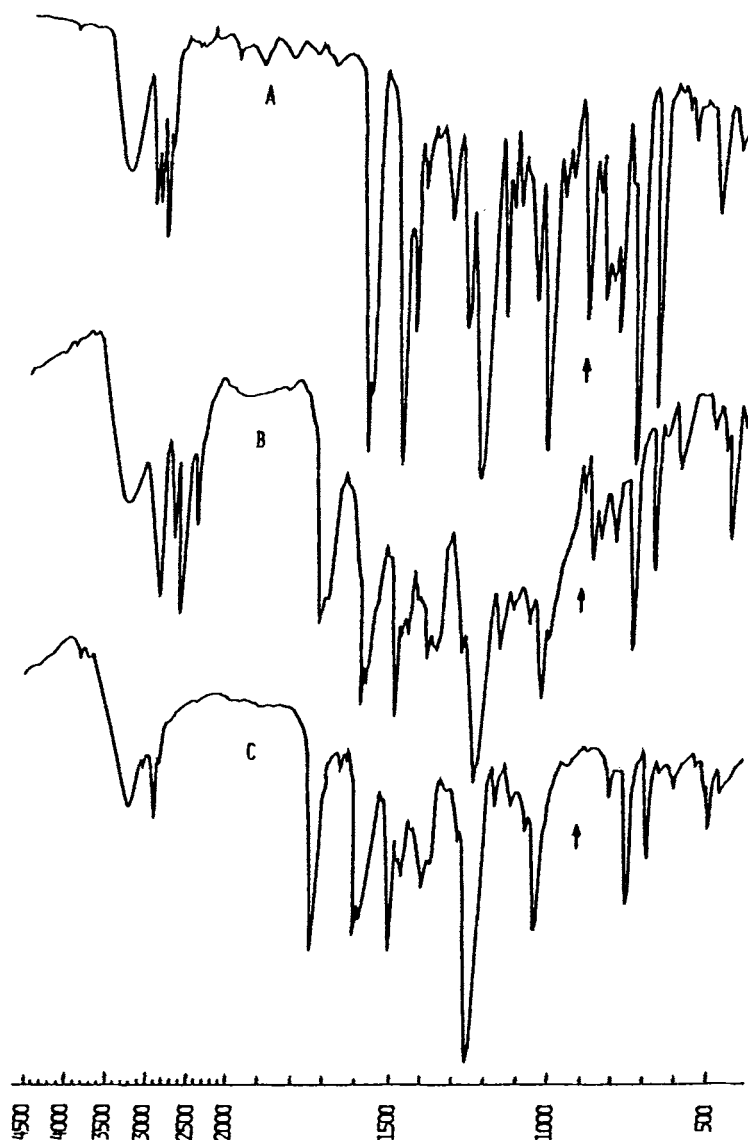
the proton donor is broader than when using acetic acid as the proton donor and tends to high molecular weight, that is, shorter elution time, as shown in Figure 1(B).

As a result, when the quaternary ammonium compound is prepared from epoxy resin and tertiary amine, the reaction will proceed with difficulty without the presence of proton donor. If using water as the proton donor, the reaction can proceed easily, but a side-reaction (anionic polymerization) appears to occur at the same time. Therefore, an organic acid such as  $\text{CH}_3\text{COOH}$  is a better proton donor for

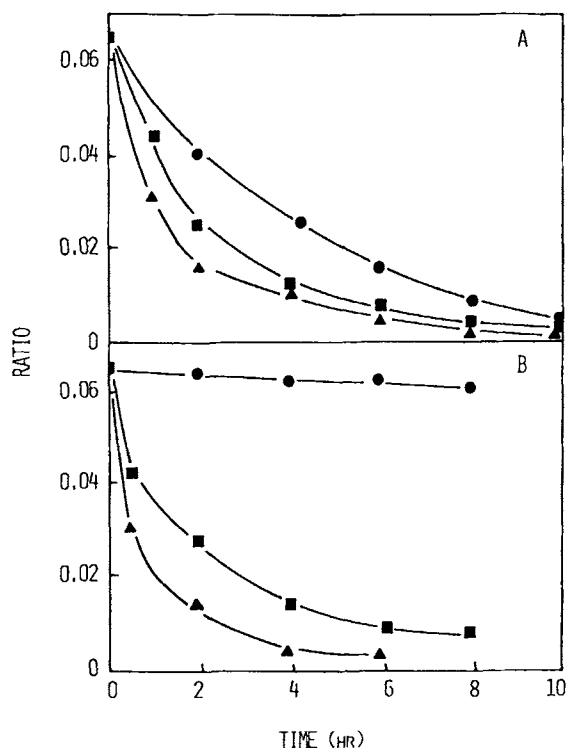
the preparation of quaternary ammonium compound.

#### The Effect of Temperature on the Reaction of Epoxy Resin with Tertiary Amine (or Secondary Amine)

The degree of reaction (or reaction rate) of the epoxy group with amine can be determined by an IR spectrum. The absorbance of epoxy group will disappear gradually during the reaction because the epoxy group is reacted with amine by the ring-opening re-



**Figure 2** IR spectra of (A) PGE; (B) the mixture of PGE, TEA, and  $\text{CH}_3\text{COOH}$ ; and (C) the PGE-TEA reaction in the presence of  $\text{CH}_3\text{COOH}$  at  $90^\circ\text{C}$  for 4 h.



**Figure 3** Effects of temperature and reaction time on the degree of reaction. (A) PGE-DEA reaction and (B) PGE-TEA reaction; temperature: (●) 70°C; (■) 80°C; (▲) 90°C.

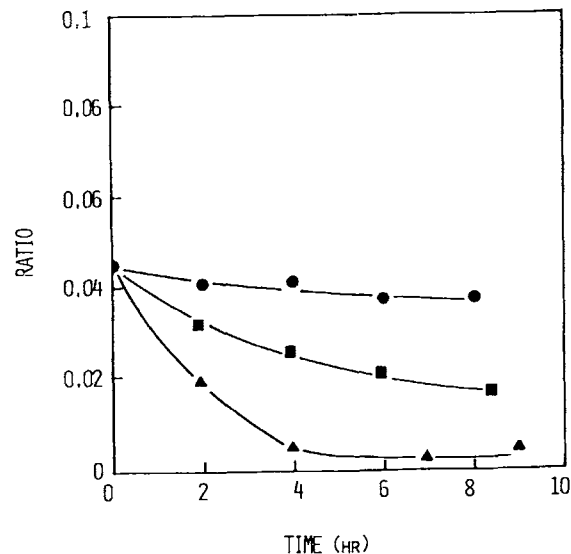
action (Fig. 2). On the other hand, we also can use the ratio of the absorbance of epoxy group stretching band ( $917\text{ cm}^{-1}$ ) with the absorbance of unreactive substituted benzene ring band ( $816\text{--}864\text{ cm}^{-1}$ ) to represent the degree of reaction.

ratio of absorbance

$$= \frac{\text{absorbance of epoxy group } (917\text{ cm}^{-1})}{\text{absorbance of substituted benzene ring } (816\text{--}864\text{ cm}^{-1})}$$

Figure 3(B) shows that the ratio does not change obviously at 70°C for the PGE-TEA reaction. But the ratio does decrease gradually when the reaction temperature rises above 80°C. On the other hand, for the PGE-DEA reaction, the ratio decreases gradually even at 70°C. Raising the reaction temperature, the ratio comes down rapidly [Fig. 3(A)]. This means preparing the quaternary ammonium compound needs a higher reaction temperature.

In Figure 4, replacing PGE with the commercial DGEBA epoxy resin (Epon 1004), the results are similar to those shown in Figure 3(B).



**Figure 4** Effects of temperature and reaction time on the degree of the Epon 1004-TEA reaction. Temperature: (●) 70°C; (■) 80°C; (▲) 90°C.

### Comparison of Quaternary Ammonium Resin (2a) with Tertiary Amine Acid Salt Resin (3)

#### Solubility and Emulsion Stability

Under appropriate conditions the epoxy-amine cationic resin can be dispersed in deionized water, so that the resin colloid can be suspended in the water phase to form a "stable" emulsion used for the electrodeposition coating. Therefore, good solubility and emulsion stability are very important for electrodeposition resin. In Table II, the solubilities of resin (2a) and resin (3) are tested. It is found that resin (2a) can dissolve in water at 80°C without any co-solvent because it is a stronger type salt.

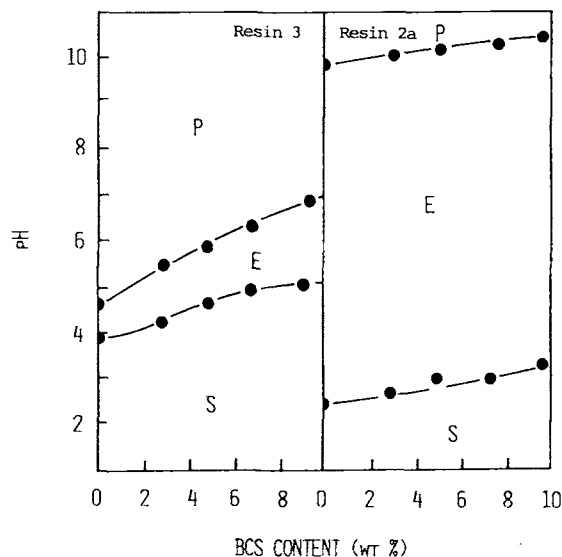
**Table II** Solubilities of Tertiary Amine Acid Salt Resin (3) and Quaternary Ammonium Resin (2a)<sup>a</sup>

Solvent	Resin (2a)	Resin (3)
H <sub>2</sub> O	±	-
BCS	+	+
HCS <sup>b</sup>	+	+
THF	±	±
Acetone	±	±
Toluene	±	±
MIBK <sup>c</sup>	-	±

<sup>a</sup> (+) Soluble at room temperature; (-) insoluble; (±) soluble at 80°C.

<sup>b</sup> Ethylene glycol mono-hexyl ether.

<sup>c</sup> Methyl isobutyl ketone.



**Figure 5** Effects of pH and BCS content on the emulsion behavior of the tertiary amine acid salt resin (3) and the quaternary ammonium resin (2a). Resin concentration 10 wt %; P, precipitation; E, stable emulsion; S, solution.

Figure 5 shows that the emulsion stability of resin (2a) is little affected by the pH value of the emulsion, the emulsion being stable in a wide pH range (pH = 3–9). However the emulsion of resin (3) precipitates at pH > 6 because its tertiary amine acid salt resin reduces to become the “insoluble” tertiary amine resin at higher pH and it converts to a semi-transparent solution at pH < 4. BCS, used as the coalescing solvent, can improve the solubility of the resin. As BCS content in the solution increases the solution becomes a stable emulsion at higher pH value.

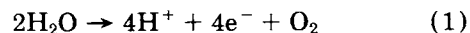
Therefore, the solubility and emulsion stability of the quaternary ammonium resin (2a) are better than those of the tertiary amine acid salt resin (3). In a H<sub>2</sub>O–BCS system, the required BCS content to make the solution of resin (2a) a stable emulsion area is small or even unnecessary and the pH range of stable emulsion is wider.

### Electrodeposition of Cationic Resin and Theory of Electrodeposition

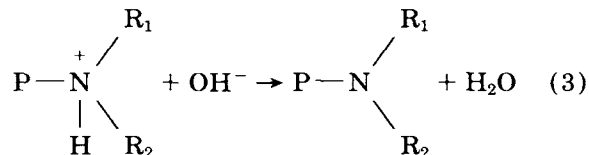
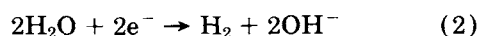
Since cationic resins contain an ionizable functional group, there will occur a series of electrochemical phenomena, such as electrophoresis, electroosmosis, electrolysis, and electrodeposition, when a voltage was applied in the emulsion bath. These phenomena will reduce the ionized resin colloid and deposit it

on the cathodic metal to form a uniform polymer film. The electrodeposition mechanism of tertiary amine acid salt resin has been proved to follow the following equations.<sup>14</sup>

Anode:



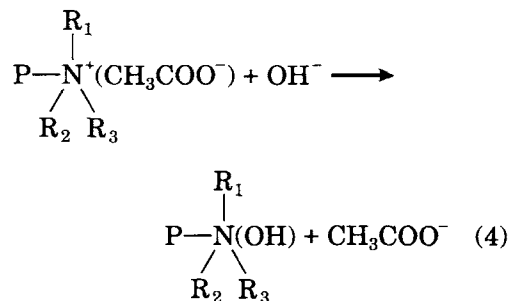
Cathode:



where P represents a long polymer chain.

For the quaternary ammonium resin, the anionic reaction is the same as eq. (1), but the cathodic reactions are supposed to occur as follows:

Cathode:



where P represents a long polymer chain.

Because of electrolysis of water, the concentration of hydroxyl ion is higher around the cathode. The hydroxyl ion will exchange with the acetate ion to form quaternary ammonium hydroxide, which has poor solubility and can electrodeposit easily, as shown in eq. (4).

In Figure 6, comparing the IR spectrum of quaternary ammonium resin (2a) with that of the deposited resin, it is found that the C=O absorbance peak (1750 cm<sup>-1</sup>) from carboxyl ion in the IR spectrum of the original quaternary ammonium resin (2a) has disappeared in that of the deposited resin. In addition, the intensity of the hydroxyl ion peak (3200 cm<sup>-1</sup>) intensifies. These data confirm the above electrodeposition mechanism.

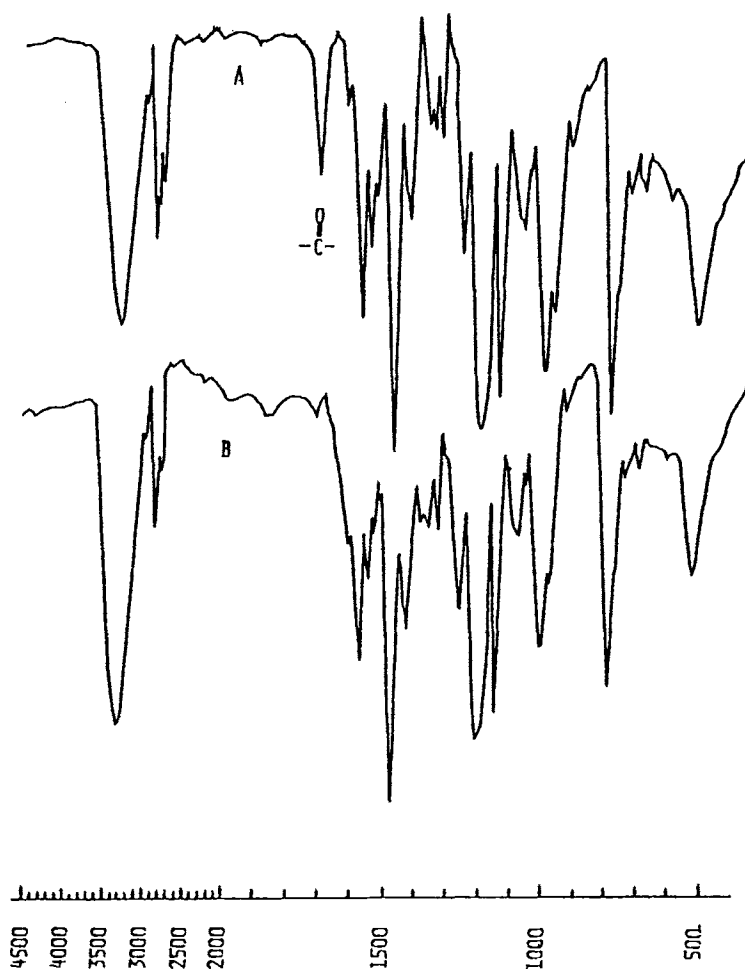


Figure 6 IR spectra of (A) quaternary ammonium resin (2a) (acetate form) and (B) its deposited film.

### Rupture Voltage

When rupture voltage is reached, not only is the current value increasing, but also a lot of gas ( $O_2$  and  $H_2$ ) will be generated because of the violent electrolysis. At this time, the appearance of the deposited film suddenly shows major defects (keloid, pit, etc.).

Figure 7 shows the effects of the resin concentration of emulsion on emulsion conductivity and rupture voltage. The emulsion conductivity is caused by ionized groups in the resin, thus the emulsion conductivity increases as the resin concentration of the emulsion increases. However, rupture voltage of the emulsion decreases contrarily at the same time. As a result, rupture voltage of the emulsion is the reverse of the emulsion conductivity for the same resin.

Under the same emulsion conditions, the conductivity of resin (2a) is slightly higher than that

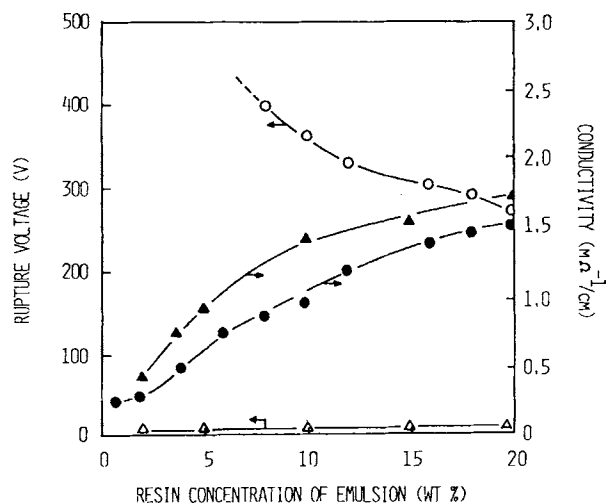


Figure 7 Effects of resin concentration of emulsion on rupture voltage and conductivity. pH 4.8–4.9; (○, ●) tertiary amine salt resin (3); (△, ▲) quaternary ammonium resin (2a).



**Table III Rupture Voltages of Resins (2a–e) at the Same Conditions<sup>a</sup>**

Resin	Tertiary Amine <sup>b</sup>			Rupture Voltage (V)
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	
(2a)	—C <sub>2</sub> H <sub>5</sub>	—C <sub>2</sub> H <sub>5</sub>	—C <sub>2</sub> H <sub>5</sub>	< 5
(2b)	—C <sub>3</sub> H <sub>7</sub>	—C <sub>3</sub> H <sub>7</sub>	—C <sub>3</sub> H <sub>7</sub>	< 5
(2c)	—CH <sub>3</sub>	—C <sub>4</sub> H <sub>9</sub>	—C <sub>4</sub> H <sub>9</sub>	< 5
(2d)	—CH <sub>3</sub>	—CH <sub>3</sub>	—C <sub>8</sub> H <sub>17</sub>	< 5
(2e)	—CH <sub>3</sub>	—CH <sub>3</sub>	—(CH <sub>2</sub> ) <sub>2</sub> O— $\overset{\text{O}}{\parallel}$ CCH <sub>3</sub>	280

<sup>a</sup> Resin concentration, 10 wt %; BCS content, 3 wt %; pH, 5.9–6.1.

<sup>b</sup> To prepare the quaternary ammonium resin.

of resin (3), but the rupture voltage of resin (2a) is very low (2–3 voltage only). The reason is ascribed to the fact that the quaternary ammonium resin (2a) prepared by TEA is a strong salt, which is easily dissociated in water.

When TEA is replaced by other all-alkyl group tertiary amines, such as TPA, MDBA, and DMOA, to prepare quaternary ammonium resins (2b–d), it is found that all rupture voltages are still very low. However when replaced by a substituted-alkyl group tertiary amine, methyl 3-(dimethyl amino) propionate, the rupture voltage of resin (2e) increases considerably. The results are shown in Table III. One concludes that the obtained rupture voltage for the quaternary ammonium resin is very low when the tertiary amine to prepare it is the all-alkyl group amine. But by introducing a nonalkyl group to the tertiary amine, rupture voltage will increase immediately. The real reason is not understood, and requires more detailed study.

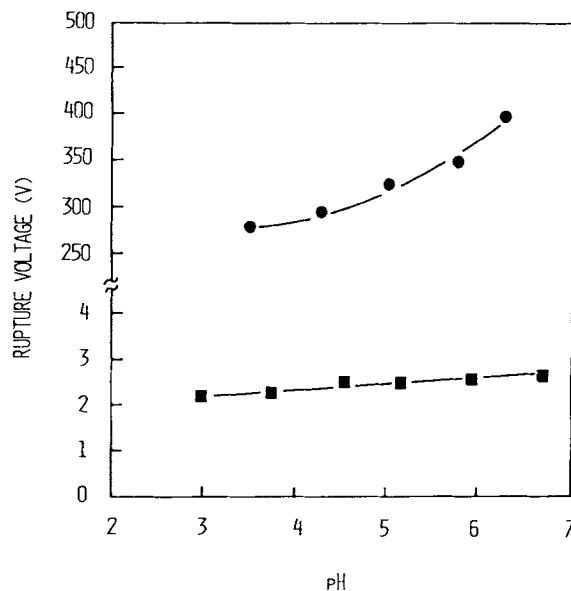
Now, the effect of hydrogen ion (H<sup>+</sup>) in the emulsion bath on the deposited yield of resin is discussed. The hydrogen ion can increase “redissolution” of the deposited film and the emulsion conductivity; thus rupture voltage decreases when the pH value of the emulsion is decreased by adding more acetic acid into the emulsion (Fig. 8). Since rupture voltage of resin (2a) is very low, the change of rupture voltage caused by the pH change is not obvious.

### Deposited Yield

Since rupture voltage of resin (3) is higher, its emulsion can undergo the electrodeposition process at higher applied voltage (100 V). The deposited yield of resin (3) increases when the resin concentration of emulsion increases (Fig. 9). Since rupture

voltage of resin (2a) is very low, the applied voltage to induce the standard electrodeposition process is limited to below 3 V. Thus, the deposited yield of resin (2a) is very low (below 0.1 mg/cm<sup>2</sup>) and its change with resin concentration is not obvious.

A series of coemulsions with different compositions using resin (2a) and resin (3), but with a fixed total resin concentration (10 wt %) was prepared. It is found that rupture voltage of coemulsion kept to the rupture voltage of pure resin (3), when the composition of resin (2a) (symbol A in Fig. 10) in the coemulsion is below 40% (wt). Under this composition range (A = 0–40%), the deposited yield



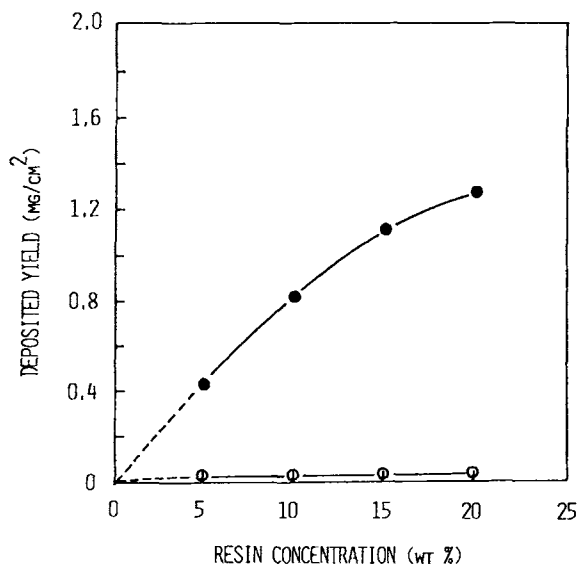
**Figure 8** Effects of pH value on rupture voltage. The resin concentration of emulsion 10 wt %; (■) quaternary ammonium resin (2a); (●) tertiary amine acid salt resin (3).

clearly increases when the composition of resin (2a) in the coemulsion increases. The deposited yield increases from 0.8 mg/cm<sup>2</sup> to 5.2 mg/cm<sup>2</sup>, almost 6.5 times, when the composition of resin (2a) increases from 0% to 20% in the coemulsion (Fig. 10).

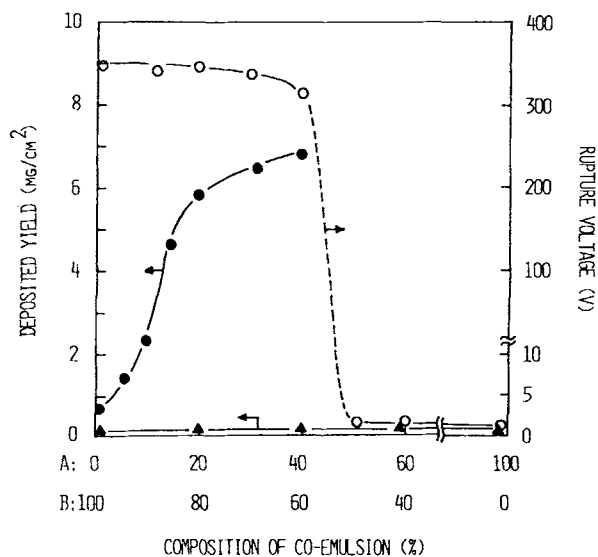
However, the rupture voltage of coemulsion will decrease rapidly to near the value of pure resin (2a) as the composition of resin (2a) increases above 50%. At this time, coemulsion can undergo the normal electrodeposition only below 3 V. If using this low voltage to electrodeposit at any composition, the deposited yield is very low (below 0.1 mg/cm<sup>2</sup>) because of too small an applied voltage to generate an effective electric power.

## CONCLUSIONS

1. When the quaternary ammonium resin is prepared by epoxy resin and tertiary amine without the presence of a proton donor, the reaction will proceed with difficulty. If water is the proton donor, the reaction can proceed easily, but a side-reaction (possibly anionic polymerization) happens simultaneously. Therefore, an organic acid like CH<sub>3</sub>COOH is a better proton donor for the preparation of quaternary ammonium resin. In addition, the reaction temperature must be higher than the preparation of tertiary amine acid salt resin.



**Figure 9** Effects of resin concentration of emulsion on deposited yield. pH 5.3–5.5; conductivity 1.4–1.6 m/cm; deposited time 3 min; (●) tertiary amine acid salt resin (3) and applied voltage 100 V; (○) quaternary ammonium resin (2a) and applied voltage 2 V.



**Figure 10** Effects of the composition of coemulsion on deposited yield and rupture voltage. pH 5.9–6.1; BCS content 5 wt %; resin concentration 10 wt %; conductivity 1.5–1.6 m/cm; applied voltage (●) 100 V and (▲) 2.5 V; (A) quaternary ammonium resin (2a); (B) tertiary amine acid salt resin (3).

2. During electrodeposition, the quaternary ammonium resin can be deposited because it will change to the quaternary ammonium hydroxide resin, which has poor solubility.
3. The solubility and the emulsion stability of the quaternary ammonium resins are better than those of the tertiary amine acid salt resin. But the rupture voltage of quaternary ammonium resin prepared from a fully alkyl group tertiary amine is very low.
4. Because of the low rupture voltage, the quaternary ammonium resin prepared by fully alkyl group tertiary amine is not useful for electrodeposition alone. But if a little amount of this quaternary ammonium resin is added to the tertiary amine acid salt resin, the deposited yield can be significantly increased.

We are grateful to the National Science Council of R.O.C. for the support of this work (Grant 81-0405-E-036-03).

## REFERENCES

1. J. F. Bosso, U.S. Pat. 4,294,741 (1981).
2. J. Gimpel, H. Hartmann, and H. U. Schenck, U.S. Pat. 4,310,398 (1982).
3. T. C. Moriarity, U.S. Pat. 4,452,930 (1984).

4. T. L. Anderson, T. K. Deb Roy, and D. Y. Chung, U.S. Pat. 4,575,523 (1986).
5. K. W. Anderson and R. A. Hickner, U.S. Pat. 4,698,141 (1987).
6. C. P. Yang and L. T. Lee, *J. Appl. Polym. Sci.*, **28**, 1861 (1990).
7. C. P. Yang and L. T. Lee, *J. Appl. Polym. Sci.*, **41**, 1995 (1990).
8. C. P. Yang and Y. H. Chen, *J. Appl. Polym. Sci.*, **42**, 1097 (1991).
9. C. P. Yang, L. T. Lee, and W. T. Yu, *J. Appl. Polym. Sci.*, **42**, 1465 (1991).
10. L. C. Sturni and J. F. Bosso, U.S. Pat. 3,936,405 (1976).
11. K. F. Schimmel, U.S. Pat. 4,069,210 (1978).
12. J. F. Bosso, R. M. Nugent, and J. E. Plasynski, U.S. Pat. 4,260,720 (1981).
13. R. E. Smith and D. W. Boyd, *J. Coat. Tech.*, **60**, No. 756 (1988).
14. M. Wismer, P. E. Pierce, J. F. Bosso, R. M. Cristerson, R. D. Jerabek, and R. R. Zwack, *J. Coat. Tech.*, **54**, No. 688 (1982).
15. J. F. Bosso and M. Wismer, U.S. Pat. 4,001,156 (1977).

*Received July 10, 1992*

*Accepted September 15, 1992*