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Double electrodeposition (II)-acrylic resin as topcoat and quaternary ammonium-epoxy resin adduct as primer, and methods for increasing the topcoat thickness

Chin-Yang Ting and Chin-Ping Yang*
Department of Chemical Engineering, Tatung Institute of Technology, Taipei, Taiwan, Republic of China

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The primer of double electrodeposition coating is formed by electrically depositing a thermosetting quaternary ammonium-epoxy resin adduct on the metallic material, and then the topcoat, a self-crosslinkable acrylic resin, is formed upon the wet primer, by electrodeposition again. It is observed that the quaternary ammonium-type adduct, used as the primer, can lead to thicker topcoat film, than the tertiary amine-type adduct. Meanwhile, a higher applied voltage, a longer deposition time or a higher resin concentration of emulsion for the topcoat electrodeposition can also increase the topcoat thickness. Moreover, when the primer contains the conductive compound, such as carbon black powder, a thicker topcoat can also be formed. © 1997 Elsevier Science Ltd.

(Keywords: electrodeposition coating; primer; topcoat)

INTRODUCTION

The double electrodeposition (ED) coating means a thermosetting resinous film, referred to as the primer, is electrically deposited on the metallic material and then another thermosetting resinous film, referred to as the topcoat, is deposited upon the wet primer also by using the electrodeposition process. Under a high temperature, these deposited films will crosslink respectively to form the cured double film. The advantage of this coating method is that the characteristics of each resin can be formed at the required level. In part I[1], the tertiary amine-epoxy resin adduct was used to form the primer, and acrylic resin to form the topcoat. It was found that the performances of anti-corrosion and weather-resistance can be improved by using the double electrodeposition coating. However, the topcoat thickness is limited because of the electric insulation of the polymeric primer.

It has been reported that not only the tertiary amine-epoxy resin adduct, but also the quaternary ammonium-epoxy resin adduct, can be used as the primer for corrosion resistance[2–7]. Using tertiary amine-epoxy resin adduct as the primer of the double electrodeposition coating is already discussed in part I[1]. In this study, it is intended to use a quaternary ammonium-epoxy resin adduct as the primer. The factors that affect the thickness of double electrodeposition will be investigated, and compared with using the tertiary amine-epoxy resin adduct as the primer. The factors include the primer thickness, the topcoat electrodeposition conditions, such as the resin concentration of emulsion, applied voltage and deposition time, and the conductive additive.

The epoxy-type resins used include the tertiary amine- or quaternary ammonium-epoxy resin adduct, which were prepared by reacting diglycidyl ether of bisphenol A (DGEBA) epoxy resin with secondary or tertiary amine and then neutralized with acid; meanwhile, partial pendent hydroxyl groups in the epoxy resin have already reacted with toluene diisocyanate. On the other hand, the hydroxyl group-containing acrylic resin was synthesized by radical copolymerization of styrene, *n*-butyl acrylate, 2-hydroxy ethyl methacrylate, *N*-(*n*-butoxy methyl) acrylamide and *N*,*N*-dimethyl amine ethyl methacrylate, and then also neutralized by acid.

EXPERIMENTAL

Materials

All agents were used as received. The DGEBA epoxy resin used in Epon 1004 (Shell) having an equivalent weight per epoxy group (EEW) of 900–1000. The crosslinking agent and blocking agent are toluene diisocyanate (TDI, 2,4/2,6 mix) and 2-ethyl hexanol (2EH) respectively. *N*-methyl ethanol amine (MEA) is used for the ring-opening reaction and the neutralizer is acetic acid.

The acrylic resin was prepared by the copolymerization of the following monomers including styrene (St), *n*-butyl acrylate (BA), 2-hydroxy ethyl methacrylate (HEMA), *N*-(*n*-butoxy methyl) acrylamide (NBMA) and *N*,*N*-dimethyl amine ethyl methacrylate (DMAEMA), and the neutralizer was lactic acid. Ethylene glycol mono-butyl ether (BCS) was used as the coalescing solvent. The initiator is 2,2′-azobisisobutyronitrile (AIBN). Carbon black was used as conductive additives.

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* To whom correspondence should be addressed

Syntheses

Quaternary ammonium-epoxy resin adduct (Resin Q). First, 112.40 g (0.64 mol) TDI was charged into a suitable vessel reactor with an electric stirrer. Then, 83.98 g (0.646 mol) 2EH was added slowly into the reactor below 18°C in inert nitrogen blanket. After the addition was completely charged, the mixture was kept at 40°C during 1 h. The product was transparent, sticky 2EH-half blocked TDI. Then, 63.84 g (0.21 mol) of this 2EH-half blocked TDI was added into another reactor and heated to 80°C, followed by slowly adding 18.69 g (0.21 mol) DMEA. After the addition was charged, many drops of dibutyltin dilaurate was added as the catalyst and the mixture was held at 80°C for an additional 1 h. When 12.6 g (0.21 mol) acetic acid was added for full neutralization, the tertiary amine acid salt (I) was obtained.

Into a 1000-ml vessel reactor equipped with a water remover and an electric stirrer, 200 g Epon 1004 and 400 ml toluene were added and heated to the reflux temperature (over 110°C) for removing azeotropically any water present. The reaction mixture was cooled to 80°C in a nitrogen blanket, followed by slowly adding 132.54 g (0.436 mol) 2EH-half blocked TDI. After the addition was completely charged, the mixture was held at this temperature for another 3 h. Then the product (I) was added to the mixture for the ring-opening reaction and the temperature kept at 80–90°C for 3 h. After the toluene was distilled off under reduced pressure, 271.13 g solid quaternary ammonium-epoxy resin adduct (Resin Q) was obtained.

Tertiary amine-epoxy resin adduct (Resin T). The synthesis procedure of the tertiary amine-epoxy resin adduct was the same as the above mentioned. Only the amine acid salt (I) for the ring-opening reaction was changed, by 15.76 g (0.21 mol) MEA. Finally, the tertiary amino groups in Resin T were fully neutralized by 12.6 g (0.21 mol) acetic acid to obtain the 'cationic' Resin T, referred to as Resin CT, for preparation of the electrodepositable emulsion.

Acrylic resin (Resin A). Into a reactor equipped with condenser, stirrer, thermometer and dropping funnel, there were charged 150 g BCS, and this was heated to 80°C. Then, there was added to the reactor a mixture of 48 g (0.46 mol) St, 100 g (0.78 mol) BA, 40 g (0.308 mol) HEMA, 80 g (0.512 mol) NBMA, 16 g (0.1 mol) DMAEMA and 3.4 g AIBN, over a period of 3 h. The reaction was held at 100–110°C for an additional 3 h, to obtain Resin A. Then, all tertiary amine groups in the resin were neutralized by lactic acid to also obtain the 'cationic' Resin A, referred to as Resin CA, for preparing the electrodepositable emulsion. The final non-volatile content of the mixture was 66.5 wt%.

Preparation of emulsion for electrodeposition

The electrodeposition emulsion of Resin Q (or Resin CT) was prepared by charging 30 g Resin Q (or Resin CT) into a suitable vessel with stirrer and heated to the soft point, followed by adding 15 g BCS to the vessel and mixing completely. Then, the mixture was cooled to room temperature, 255 g deionized water was added slowly, and the mixture was stirred completely to form the stable, electrodepositable Emulsion Q (or Emulsion CT), having a resin concentration of 10 wt% and a BCS content of 5 wt%.

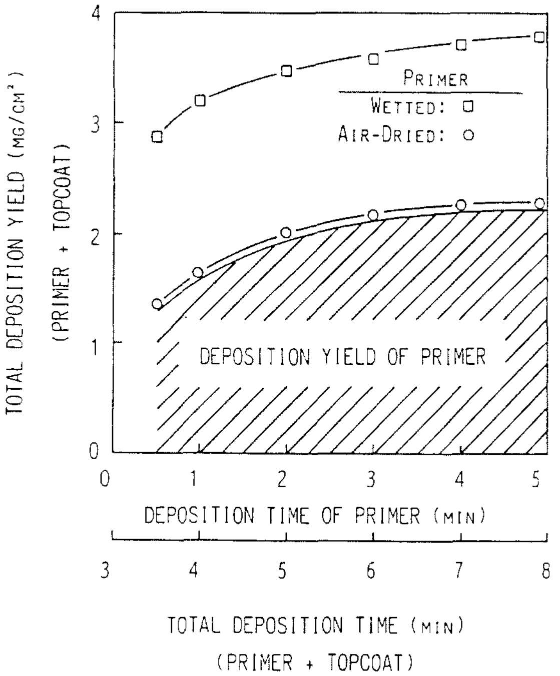


Figure 1 The relationships between deposition time and deposition yield of each film. The primer (shadow area) is deposited by Emulsion Q at different deposition times; the topcoat is deposited by Emulsion CA at constant deposition time (3 min). Applied voltage, 150 V; resin concentration of emulsion, 10 wt%

In addition, Emulsion CA was prepared by dispersing 45 g Resin CA with 255 g deionized water. The resin concentration and BCS content of emulsion are also 10 and 5 wt% respectively.

Double electrodeposition coating

A piece of aluminium plate divided into two parts having the same surface area (A cm^2) and weight (W_0 mg) was completely immersed into Emulsion Q (or Emulsion CT) and then connected with the cathode of a DC power supplier. Two stainless steel strips were used as an anode, and located each side of the aluminium plate in the bath. When a certain voltage was applied, ED coating began, and the resin was continuously deposited on the surface of the aluminium plate during the assigned time. After completion of the primer electrodeposition, the film-covered plate was removed from the bath and rinsed to obtain wet primer. One part of the wet primer-covered aluminium plate was then immersed into Emulsion CA for the topcoat electrodeposition. Finally, these plates were baked at 180°C for 30 min. These are defined as the weight of the part only containing the primer is W_1 mg and weight of another part containing primer and topcoat is W_2 mg. Thus, the deposition yield (mg cm^{-2}) of primer was $(W_1 - W_0)/A$ and the total deposition yield of primer plus topcoat was $(W_2 - W_0)/A$. The deposition yield of the topcoat was $(W_2 - W_1)/A$.

Measurement of current density. The change of electric current (mA) with time (1/100 s) during electrodeposition was recorded by video, and the surface area (cm^2) of the deposited film was measured. The current density is defined as electric current divided by surface area (mA cm^{-2}).

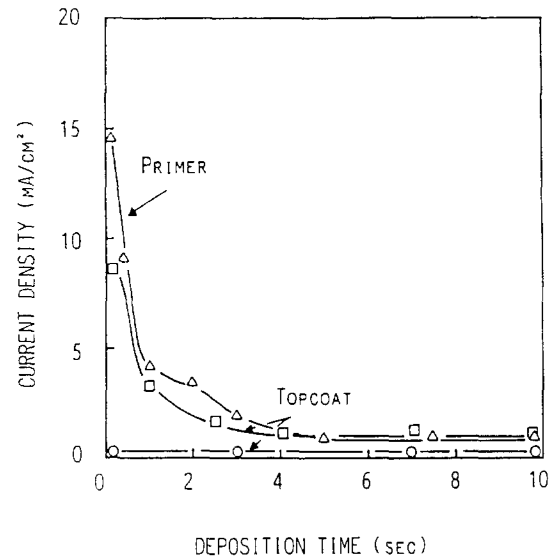


Figure 2 The change of current density with time during electrodeposition. Applied voltage, 150 V; deposition yield of primer, 0.5–0.6 mg cm^{-2}; resin concentration of emulsion, 10 wt%; topcoat on wet primer, □; topcoat on air-dried primer, ○

RESULTS AND DISCUSSION

Double electrodeposited film

First, the distinction of deposition yield was investigated, to make sure of the possibility of double electrodeposition coating. The experimental process is that the variable deposition yield of primer is electrically deposited by Emulsion Q, and then Emulsion CA is used to form the topcoat on the primer by electrodeposition again, whether the primer is wet or not. The relationship between deposition time and total deposition yield of primer plus topcoat is shown in *Figure 1*. The shadow area in *Figure 1* is the deposition yield of primer with different deposition time. For the wet primer, it is clearly shown that a considerable deposition yield of topcoat is obtained for comparing the total deposition yield (□) with the deposition yield of the primer (shadow). This result indicates the existence of a electrodeposited topcoat under this situation. On the contrary, for the dried primer, which was dried at room temperature over 30 min, there was no topcoat electrodeposition observed. Thus, the existence of water in the primer can improve the topcoat electrodeposition.

The change of current density with time during each electrodeposition is plotted in *Figure 2*. At the beginning of primer electrodeposition, observation of a strong current density (△) signifies an electrochemical reaction. Then the current density declines quickly, due to the growth of insulated resinous film. Finally, when the deposition rate of resinous film balances to the redissolution rate of deposited film, a stable but weak current density is observed. Since the insulation of the resinous primer, the current density (□) during topcoat electrodeposition is always smaller than that (△) during primer electrodeposition. However, there is no current density (○) observed during topcoat electrodeposition when the primer is dried.

It follows that if the primer is electrically deposited by Emulsion Q and kept wet, then another resinous film, referred to as the topcoat, can be electrically deposited on this primer by Emulsion CA to form the double electrodeposited film.

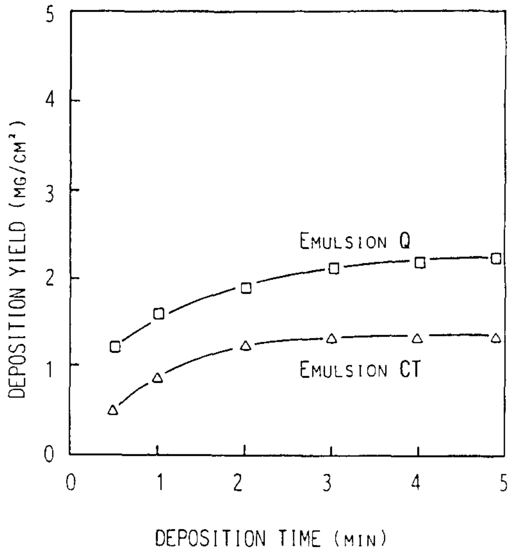


Figure 3 The relationships between deposition time and deposition yield of Emulsion Q (and Emulsion CT). Applied voltage, 150 V; resin concentration of emulsion, 10 wt%

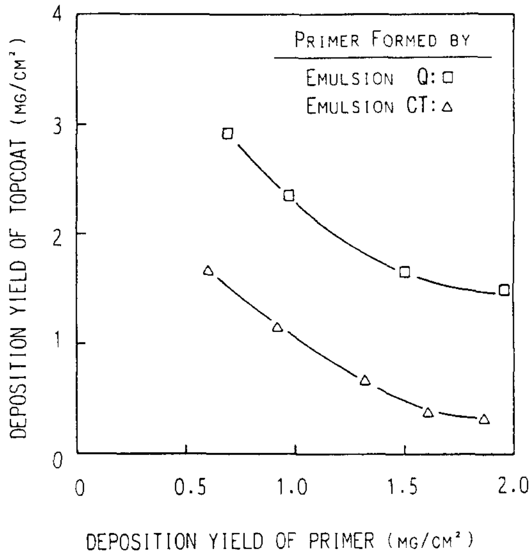
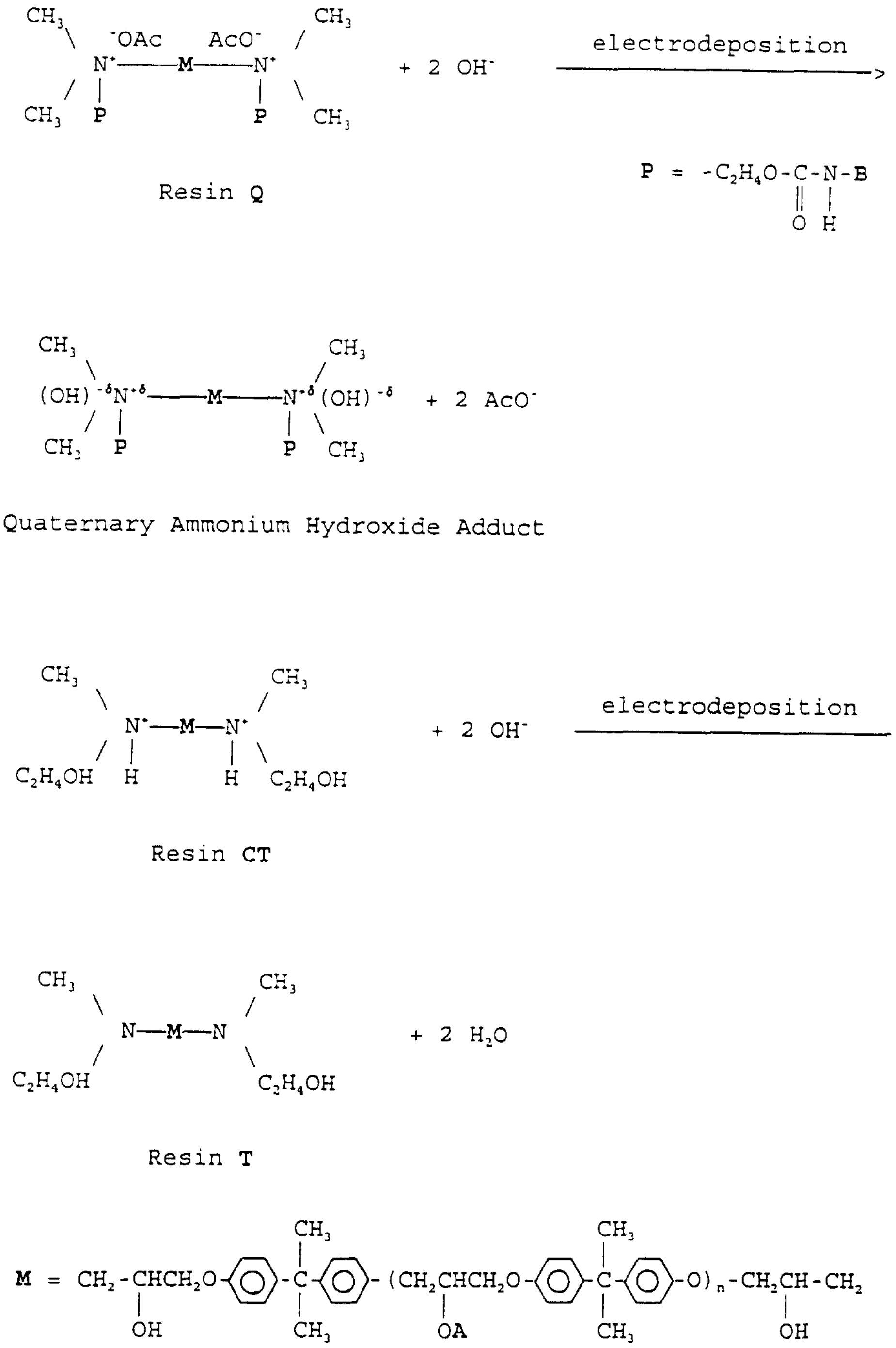


Figure 4 The dependence of deposition yield of wet primer on deposition yield of topcoat. The conditions of topcoating: 150 V; 3 min; resin concentration of Emulsion CA, 10 wt%

Factors to affect the deposition yield of topcoat

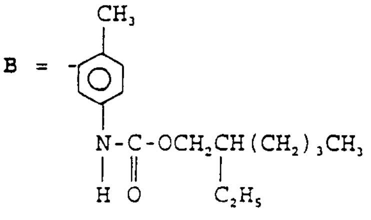
For the coatings, a required thickness has to be supplied for protecting the substrate. Thus, the method for increasing the thickness is necessary. For the double electrodeposited film, not only the wet extent of primer, but the following factors, such as properties of primer, conditions of topcoat electrodeposition, and the conductive additive in the primer, can directly affect the film thickness. In the following, each factor will be discussed individually.

The electric properties of primer. First, the distinction of Emulsion Q and Emulsion CT used for the primer electrodeposition to affect the deposition yield of topcoat is discussed. From *Figure 3*, it is seen that the deposition yield of Emulsion Q is always higher than that of Emulsion CT under the same operation conditions. In part I, it was found that the thicker primer makes electrodeposition of topcoat more difficult. Thus, we can estimate



A	number of A
-H	x
$-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{\mid}}{N}-B$	y

$y = (n/2)+1,\ x+y = n,\ n = 5.5$



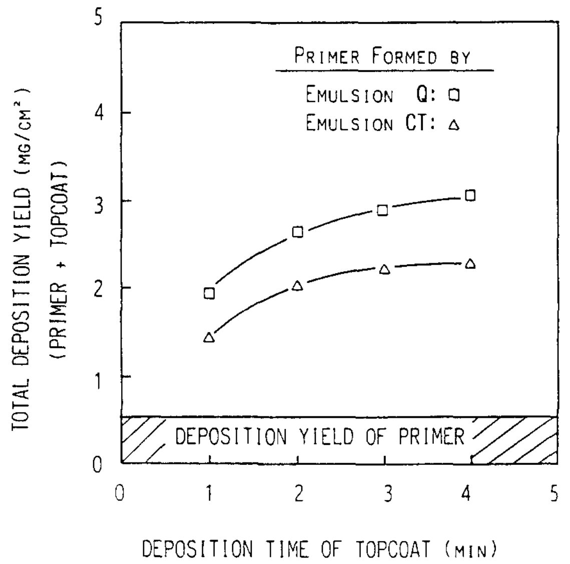


Figure 5 The effects of deposition time of topcoat on total deposition yield as the deposition yield of primer fixed. The conditions of topcoating: 150 V; resin concentration of Emulsion CA, 10 wt%

that the primer deposited by Emulsion Q is more difficult to progress the topcoat electrodeposition compared with Emulsion CT.

In fact, a higher deposition yield of topcoat was obtained when Emulsion Q was used for primer electrodeposition, as shown in *Figure 4*. The explanation for this result is that the deposited film of Emulsion Q is also an ion pair-containing quaternary ammonium hydroxide[8], but that the deposited film of Emulsion CT is reduced to a non-ionic tertiary amine-epoxy resin adduct (Resin T), as shown in *Scheme 1*. Since this quaternary ammonium hydroxide adduct also has some conductivity when the film is wet and uncured, the double electrodeposition easily occurs on top of it. Therefore, the different type of resinous primer can affect the topcoat electrodeposition. In addition, it is also shown that the deposition yield of topcoat generally decreases with increasing primer thickness.

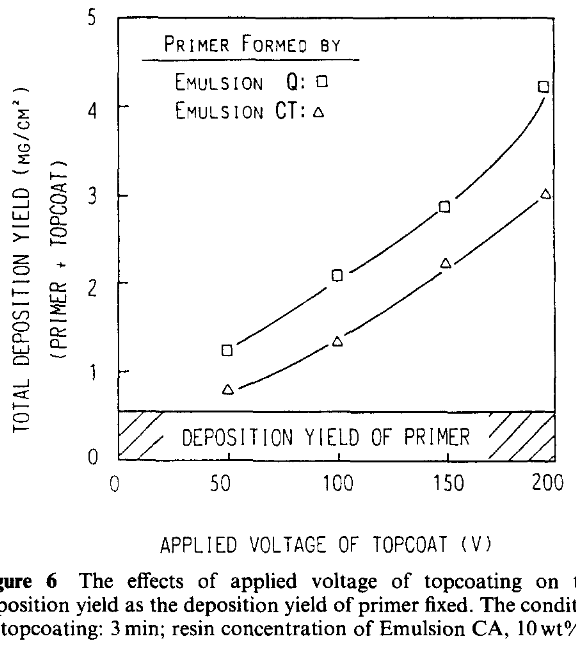


Figure 6 The effects of applied voltage of topcoating on total deposition yield as the deposition yield of primer fixed. The conditions of topcoating: 3 min; resin concentration of Emulsion CA, 10 wt%

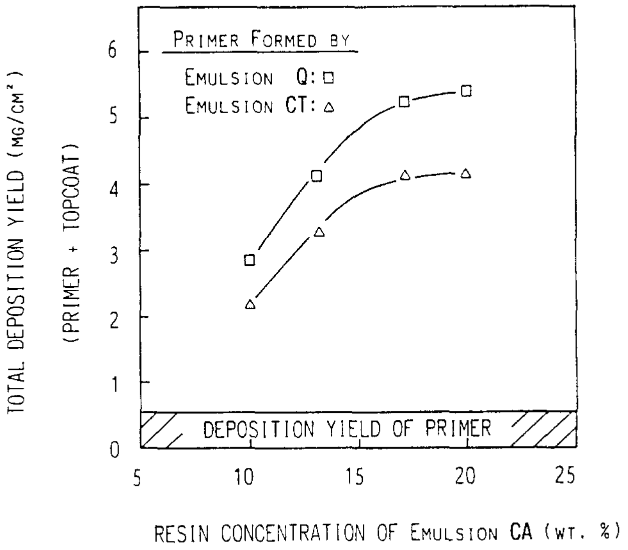


Figure 7 The dependence of resin concentration of Emulsion CA on total deposition yield as the deposition yield of primer fixed. The conditions of topcoating: 150 V; 3 min

The operation conditions of topcoat electrodeposition. The variable factors during electrodeposition include deposition time, applied voltage, the resin concentration of emulsion used etc. *Figure 5* shows the relationship between the total deposition yield and the deposition time of topcoating when the deposition yield of primer was fixed. The result is the same as that for general electrodeposition, that is the total deposition yield of primer plus topcoat increases with the increment of deposition time of topcoating, but tends to a limitation after a few minutes.

On the other hand, applying a higher voltage during electrodeposition can accelerate the electrochemical reaction. Thus, below the rupture voltage[9–11], increasing the applied voltage can make the deposition yield of topcoat increase effectively, as shown in *Figure 6*. This is another method for increasing the deposition yield of topcoat by electrodeposition.

Finally, the effect of resin concentration of emulsion on the deposition yield of topcoat is plotted in *Figure 7*. This shows that the deposition yield of topcoat increases with a higher resin concentration of emulsion used for the topcoat electrodeposition. But the increase becomes slow as the resin concentration of emulsion exceeds 20 wt%.

Consequently, because of the interference of primer, longer deposition times, higher applied voltage and higher resin concentrations of emulsion are required for forming a thicker topcoat for the double electrodeposition.

The addition of conductive additive. Carbon black powder is generally used as the major source of black pigment in deep colour paint. It is sometimes used for improving the electric conductivity of polymer film in some patents[12,13]. Therefore, we try to use carbon black as the additive, and disperse with Resin Q (or Resin CT) to increase the conductivity of the wet primer. The effect of variation in content of carbon black in Emulsion CT and Emulsion Q on the deposition yield of topcoat are shown in *Figures 8* and *9* respectively. It is found that a higher deposition yield of topcoat can be truly obtained on top of the carbon black-contained primer, and the

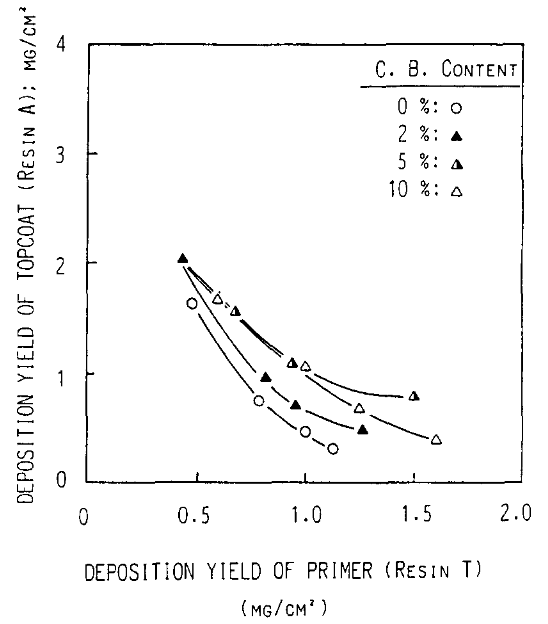


Figure 8 The effect of carbon black content in the primer (Resin T) on the deposition yield of topcoat

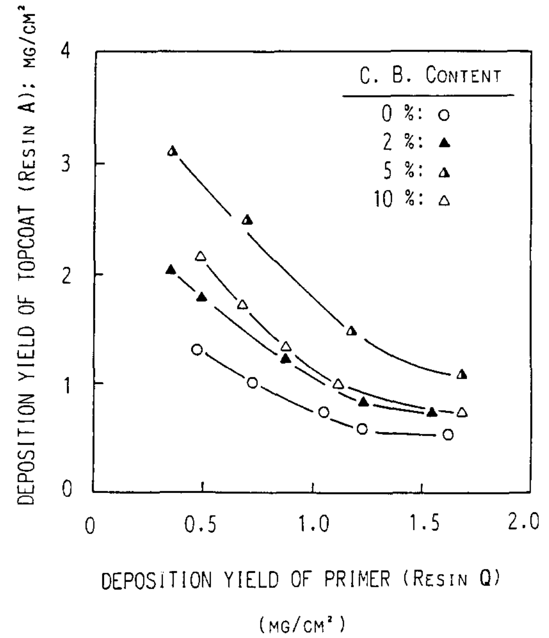


Figure 9 The effects of carbon black content in the primer (Resin Q) on the deposition yield of topcoat

deposition yield of topcoat increases as the content of carbon black increases. However, the deposition yield of topcoat decreases when the content of carbon black is over 10 wt%. This unusual behaviour can be explained by the mean diameter distribution (MDD) of particles in the emulsion by means of sub-microparticle sizer manufactured by Nicomp, USA. In *Table 1*, it is shown that the MDD will change from a single Gaussian distribution to a two-peak Nicomp distribution, as the content of carbon black in the emulsion increases. This means the carbon black does not grind as easily as the content in the emulsion increases. At 10 wt%, the flocculation of the carbon black powder makes the aqueous dispersion become unstable and easily precipitate, therefore, the electrodeposition properties are unusual at higher carbon black contents.

CONCLUSION

Since the quaternary ammonium-epoxy resin adduct contains ion pairs in the main chain, using this kind of resin as the primer can obtain a higher deposition yield of topcoat; that is, a thicker double electrodeposited film can be formed. During topcoat electrodeposition, prolonging the deposition time, increasing the applied voltage or using a higher resin concentration of emulsion can overcome the problem of electric insulation caused by the resinous primer, and improve the deposition yield of topcoat. In addition, the wet primer containing carbon black can truly increase the deposition yield of topcoat. However, the content of carbon black recommended is below 10 wt%.

ACKNOWLEDGEMENT

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Table 1 The solid particles analysis of emulsion

Emulsion	Carbon black content (wt%)	Analysis method[a]	Mean diameter (nm)	Volume (%)
	0	Gaussian	57.9	100.00
	2	Gaussian	63.9	100.00
Emulsion CT	5	Nicomp	1) 72.9	84.25
			2) 215.2	15.75
	10	Nicomp	1) 89.3	85.23
			2) 318.3	14.77
	0	Gaussian	108.0	100.00
	2	Gaussian	119.9	100.00
Emulsion Q	5	Nicomp	1) 94.3	68.74
			2) 195.0	31.26
	10	Nicomp	1) 108.6	81.14
			2) 309.2	18.86

[a] Analysed by Nicomp particle sizing systems; the analysis software is C370 (V. 12.0)

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