Studies of Electrochemical Colored Coating

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ABSTRACT: The aqueous emulsion bath of cationic electrodeposition-colored coating was studied by cyclic voltammetry. The effects of pH and the distance between the cathode and anode on deposition potential and deposition current density were also observed. The deposition of colored coating was recorded by chronoamperometry, and the deposit was studied by UV/VIS absorption spectroscopy. The ratio of resin to pigment in the deposit was estimated from chronoamperometry. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2719–2727, 1998

Key words: deposition potential; resin to pigment ratio; cyclic voltammetry; chronoamperometry; UV/VIS absorption spectroscopy

INTRODUCTION

Electrocoat is a coating technology widely used in automobile body primer and appliances.[1–4] This technology has also been applied in the manufacturing of color filter for color liquid crystal display.[5–7] The anodic electrocoat was developed first, while the cathodic electrocoat was developed and commercialized later in the late 1960s and early 1970s. Anodic electrocoating involved the deposition of oxidized negatively charged pigment particles onto transparent indium tin oxide (ITO) glass anode. The polymer species for anodic electrocoat was acid functional and amine solubilized.[8,9] Another technique of anodic electrocoat was by a micellar disruption method.[10–12] Cathodic electrochemical coating was the deposition of reduced positively charged pigment particles onto the ITO glass cathode. The polymer species for cathodic electrocoat was amine functional and acid solubilized.[13–15]

For the manufacturing of color filter,[16,17] a color pigment was either printed, dispersion coated, or electrodeposited onto a substrate by: (1) exposing a photosensitive film through a mask having patterns of different degrees of light transmittances; (2) developing and removing the first color hue region; (3) electrodepositing the first colored coating by applying an electrical voltage to the pixels to be coated; and (4) repeating the described steps (2 and 3) of developing, removing, and electrodepositing to form different colored layers.

Color filter used for color liquid crystal display device requires high transmission of light in the spectral regions of its associated color and low transmission of light in the other spectral region; therefore, fine dispersion of pigment in aqueous medium, even deposition of pigment onto the substrate, as well as composition analyzing of the deposit, are important techniques in the manufacture of quality color filter. In the present experiment, the aqueous emulsion of cationic electrodeposition-colored coating was studied by cyclic voltammogram to find a suitable deposition potential. Composition of electrodeposition-colored coating was studied by chronoamperometry

and UV absorption. The effects of pH and the distance between the cathode and anode on the deposition were also studied.

EXPERIMENTAL

The cationic electrodeposition aqueous phase emulsion used in the present experiment consisted of three major ingredients: the cationic resin of an amine-modified copolymer of methyl methacrylate, 2-hydroxy ethylacrylate, dimethyaminoethyl methacrylate, and benzyl acrylate (called cationic acrylic resin)—a block diisocyanate curing agent from Bayer LS2062 having a preliminary crosslinking temperature ⟨100°C—⟩ and a pigment paste containing a pigment (copper phthalocyanate for blue from BASF C.I. No. 15 : 6; bromine-substituted phthalocyanate for green from BASF C.I. No. 36; and dianthraquinon for red from Ciba C.I. No. 177, mixed with a minor amount of isoindoline from BASF C.I. No. 139 or dioxazine from Hoechst C.I. No. 23) dispersed in a cationic pigment-dispersing resin neutralized with lactic acid. The pH of the emulsion was ~ 5.2, unless otherwise noted. The weight ratio of cationic resin, curing agent, and pigment to deionized water was ~ 3 : 0.7 : 0.7–1 : 100.

Three emulsions—namely the cationic electrodeposition emulsion (or complete emulsion bath), an emulsion containing cationic acrylic resin without pigment (or resin emulsion bath), and an emulsion containing cationic pigment-dispersion resin only without cationic acrylic resin (or pigment emulsion bath)—were studied at 19°C by cyclic voltammetry with an electrochemical interface from Schlumberger Model SI 1286. The working electrode was an ITO glass electrode, and the reference electrode connected together with counter electrode was a platinum electrode. The voltammograms were taken by scanning from 0 V *vs.* a reference electrode toward −12.0 V, with a scan rate of 100 mV s^{-1}.

The colored coating of the present experiment was electrodeposited on an ITO glass cathode for a certain period of time at 19°C (pH 5.2), otherwise noted under −16.0 V, −9.0 V, or −5.0 V separately. The distance between cathode and anode was kept at 15 cm unless otherwise noted. The current density of each cathode reaction was recorded by chronoamperometry from EG&G potentiostat Model 273A. The total amount of charge density for each deposition was calculated by integrating the current with time for each chronoamperomogram. The colored coating was preheated at 90°C for 10 min after 45–60 min postcure at 250°C. The cured-colored coating was then examined by UV/VIS spectrophotometer from the Perkin–Elmer Model Lambda 5.

RESULTS AND DISCUSSION

Electrochemical Studies of Colored Coating Emulsion Bath

The aqueous emulsion bath for the electrochemical deposition of colored coating was in a metastable state with the following possible schematic equilibria:

$$HA \rightleftharpoons H^+ + A^- \tag{1}$$

$$\text{Acrylic resin-N :} + HA \rightleftharpoons$$
$$\text{acrylic resin-N : } H^+ + A^- \tag{2}$$

$$R-N=C=O + HA \rightleftharpoons R-\overset{\overset{\displaystyle H}{|}}{\underset{\cdot\cdot}{N}}-\overset{\overset{\displaystyle A}{|}}{C}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \tag{3}$$

$$\text{Pigment-dispersion resin-N :} + HA \rightleftharpoons$$
$$\text{pigment-dispersion resin-N : } H^+ + A^- \tag{4}$$

In the process of electrodeposition, according to the chemical structure of the ingredient of the emulsion, the possible chemical reactions at the ITO glass cathode schematically were:

$$\text{Acrylic resin-N : } H^+ + e^- \rightarrow$$
$$\text{acrylic resin-N : } \tfrac{1}{2} H_2 \tag{5}$$

$$\text{Pigment-dispersion resin-N : } H^+ + e^- \rightarrow$$
$$\text{pigment-dispersion resin-N : } + \tfrac{1}{2} H_2 \tag{6}$$

$$2HA + 2e^- \rightarrow 2A^- + H_2 \rightleftharpoons$$
$$A^- + H_2O \leftrightarrow HA + OH^- \tag{7}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{8}$$

The reaction at the platinum anode was: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$. Therefore, during electrolysis, the local pH near the anode was supposed to be decreasing and the local pH near the cathode was increas-

Figure 1 Cyclic voltammogram of the emulsion containing acrylic resin without pigment. The distance of the cathode and anode is: (a)—, 3 cm; (b) – ·· –, 7 cm; (c) . . . . , 15 cm.

ing. The acid and base should be well balanced, and the pH of the emulsion would be kept constant if there was no other side reaction. In the present experiment (up to 300 s of electrolysis), the pH of the emulsion was still kept constant. However, the pH of the emulsion bath was proportional to the inverse of the temperature, as expected from the Nerst equation.

Each electrochemical reaction was supposed to give one peak on the voltammogram. Although only the amine functional group of the cationic polymer resin might receive an electron, each cationic polymer resin might have many such amine sites. Thus, it was capable of receiving more than one electron and gave rise to more than one peak on the voltammogram. Furthermore, the sizes of the cationic resin molecules were random, and the mobility of the resin molecule of difference size was different. Another reason was that the resin molecules might aggregate together forming a larger cationic particle that could also be reduced when it moved to the surface of the electrode. Therefore, the reduction reaction of cationic resin might give more than one peak on the voltammogram, and some of them might overlap because the reduction potentials were very close to one another.

The three reduction peaks of −5.0 V, −6.0 V, and −8.0 V for acrylic resin emulsion bath (Fig. 1) were, in fact, peaks for the deposition of acrylic resin. All of these three reduction peaks were shifted more positively, and their current density increased as the distance between ITO working electrode and the platinum reference electrode was shortened from 15 cm to 3 cm. The reduction peak of diisocyanate (hardener) was not observed; the reaction was probably very rare, and it was also covered within the reduction peaks for cationic acrylic resin. On the reverse anodic scan, there was no obvious peak, except the peak for the oxidation of water (i.e., $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$), near −1.0 V. Reduction of the pigment emulsion bath showed a linear increase of current with voltage and did not show any particular characteristic peak (Fig. 2). The current density of the reduction also increased as the distance between the ITO working electrode and the platinum reference electrode was shortened from 15 cm to 3 cm. The mixed peaks around −7.0 V for the complete emulsion baths containing either red-, blue-, or green-colored pigment were due to the reduction of cationic pigment-dispersion resin and cationic acrylic resin (Figs. 3–5). The main reduction potential shifted from −7.0 V to −5.5 V to −4.5 V, and the current density increased when the distance between the ITO working electrode and the platinum reference electrode was moved from 15 cm to 7 cm to 3 cm. It did show that the infrared drop was larger when the distance between the cathode and anode was longer. From Ohm's law, the resistance overvoltage should be proportional to resistance (distance between working electrode and reference electrode in this case), but as the distance of the two electrodes decreased from 15

Figure 2   Cyclic voltammogram of the emulsion containing pigment-dispersion resin only. (a) —, blue pigment; (b)– · · –, green pigment; (c) . . . . , red pigment.

cm to 3 cm, the overvoltage changed from -7.0 V to -4.5 V, which was not directly proportional. Indicating that, although the size of cationic resin molecule or particle was rather large, besides the mobility of the resin molecule (or particle), the deposition potential was also dependent on the activational energy of the electrode process.

The cyclic voltammograms of the complete green emulsion bath (Fig. 6), the resin emulsion bath, and the pigment emulsion bath at 19°C showed that all of the redox-mixed peaks shifted more negatively, and the current density in-

creased as the pH of the bath decreased from 5.2 to 3.0. The possible explanation for such a phenomenon is that, as the pH decreased, the proton concentration increased and the equilibria of eq. (1) to eq. (4) were shifted to the right; thus, more polymer resins in the emulsion were protonated and/or more than one amine site in one polymer resin was protonated. Therefore, the current density of the same potential increased. When more than one protonated amine site was reduced in one polymer resin, the reduction potential would become more negative as the protonated amine

Figure 3   Cyclic voltammogram of the complete red emulsion bath. Distance of the cathode and anode is: (a) —, 3 cm; (b) – · · –, 7 cm; (c) . . . . , 15 cm.

Figure 4 Cyclic voltammogram of the complete green emulsion bath. Distance of the cathode and anode is: (a) —, 3 cm; (b) . . . . , 7 cm; (c) – – –, 15 cm.

was subsequently reduced, resulting in the shift of reduction mixed peak to the more negative potential.

Composition of Colored Coating

From the redox potential of the emulsion bath observed by cyclic voltammetry, we chose to study the colored deposit by depositing at a potential that was more positive than the mixed peak, -5.0 V; a deposition potential that was more negative than the mixed peak, -9.0 V; and another depo-

sition potential was much more negative than the mixed peak, -16.0 V.

The sample of colored coating was prepared by applying a constant negative voltage (-5.0 V, -9.0 V, or -16.0 V) on an ITO glass cathode in the complete emulsion bath for 20 s at room temperature (pH 5.2). When the negative voltage was applied, the cationic molecules (and particles) of acrylic resin and the pigment–dispersion resin in the bath would move toward cathode, receive electron, and result in the deposition of the acrylic resin and pigment particle. In the emulsion containing

Figure 5 Cyclic voltammogram of the complete blue emulsion bath. Distance of the cathode and anode is: (a) —, 3 cm; (b) – – –, 7 cm; (c) . . . . , 15 cm.

Figure 6   Dependence of reduction potential on pH: (a) —, pH 4.94; (b) . . . . , pH 4.54; (c) – · · –, pH 4.15.

cationic green pigment-dispersion resin only (no acrylic resin), most of the pigment particle did not well adhere to the ITO glass. Therefore, as the negative voltage was applied, the surface did not shield the pigment particle, and the current density did not decrease with time. In the complete cationic electrodeposition emulsion bath, the acrylic resin and the pigment molecules or particles competed with each other for deposition, and the pigment particle would well adhere to the ITO glass because of its codeposition with acrylic resin.

After deposition, the colored coating was then preheated at 90°C for 10 min; subsequently, it was cured at 250°C for 45–60 min. After curing, the colored coating was examined by UV/VIS absorption spectroscopy. The UV/VIS absorption spectrum of colored coating showed that the maximum absorption was at 650 nm for the green-colored coating (Fig. 7), 300–600 nm for the red-colored coating (Fig. 8), and 500–800 nm for the blue-colored coating, with the other absorption maximum at 350 nm (Fig. 9). The absorption of acrylic resin coatings was smaller than 0.3 (Fig. 10). The intensity of UV/VIS light absorption was getting higher for all three colored coatings when it was deposited at a more negative potential (Figs. 7–9) because the deposition current was larger at a more negative potential (Figs. 3–5). The increase of deposition current at a more negative potential was not completely fitted. The Tafel equation indicated that the rate of electrochemical deposition was a mixed control of diffusion rate and the electron transfer rate at the cathode surface.

It was found that the total deposition charge density calculated from chronoamperometry increased with deposition time [Fig. 11(a)], and the intensity of UV/VIS absorption at 650 nm for the green-colored coating was higher as the total deposition charge density increased [Fig. 11(b)]. It was very possible that, for longer periods of deposition, the nonconducting deposit had a minor shielding effect and the deposition current decreased a little as the deposition period was longer; therefore, for a 120-s or longer period of deposition, the total charge density was smaller than expected from the linear plot [Fig. 11(a)]. Therefore, for longer periods of deposition, besides activational overvoltage and infrared drop, ohmic overvoltage caused by film formation should be considered. The linear relationship between the

Figure 7   UV absorption of green color coating. Deposition potential is: (a) −16.0 V, (b) −9.0 V, (c) −5.0 V.

Figure 8   UV absorption of red color coating. Deposition potential is: (a) −16.0 V, (b) −9.0 V, (c) −5.0 V.

Figure 10   UV absorption of the acrylic resin deposit without pigment. Deposition potential is: (a) −16.0 V; (b) −9.0 V; (c) −5.0 V.

intensity of UV/VIS absorption and the total deposition charge density showed that deposition composition was kept constant during the period of deposition (i.e., the ratio of pigment to acrylic resin was constant).

Although the total deposition charge density of the deposition of green-colored coating at −9.0 V calculated from the chronoamperomogram increased as the pH of the emulsion decreased, the intensity of UV/VIS absorption at 650 nm decreased as the pH of the emulsion decreased (Fig. 12). At pH 3.5 and lower, there was almost no pigment deposition at al. It was very possible because, at a lower pH, the deposited pigment was quickly redissolved, thus resulting in the decrease of net pigment deposition as the pH decreased. A detailed mechanism of deposition needs further study.

The current densities of a complete emulsion bath of green-colored coating, a resin emulsion

bath, and a pigment emulsion bath were recorded separately with chronoamperometry at 19°C (pH 5.0) by stepping to −9.0 V for 20 s. The average deposition current density was then calculated from the chronoamperomogram. Results of the present experiment showed that the amount of average deposition current density of the green complete emulsion bath (Ic = 3.58 mA) was approximately equal to the sum of the average deposition current density of the acrylic resin emulsion bath (Ir = 1.66 mA) plus the average deposition current density of the pigment emulsion bath (Ip = 1.84 mA) (i.e., Ic = Ir + Ip). The ratio of the average deposition current density of acrylic resin to pigment could be used as a reference for the replenishment and control of the bath in practical operation.

CONCLUSIONS

Deposition potential and deposition current density of cationic electrodeposition emulsion were affected by many factors, such as mobility of pigment/resin particles (particle size), pH (i.e., charge of pigment/resin particles), temperature, electron transfer rate of pigment/resin particles, and the distance between the cathode and anode. The following conclusions were drawn from the results of the present experiment. (1) In general, the deposition potential of cationic electrodeposition emulsion of a complete colored bath was a mixed peak that was shifted more positively, and the current density of the peak increased as the distance between the ITO working electrode and the platinum reference electrode was shortened. (2) The reduction mixed peak was

Figure 9   UV absorption of blue color coating. Deposition potential is: (a) −16.0 V; (b) −9.0 V; (c) −5.0 V.

Figure 11 (a) Deposition charge density at various periods of time. (b) Relationship of the intensity of UV absorption with deposition charge density.

shifted more negatively, and the current density increased as the pH of the bath decreased. (3) The intensity of UV/VIS absorption of the colored coating was higher if the deposition potential was more negative. (4) Total deposition charge density for a longer period of deposition was smaller than expected, from the linear plot of charge density *vs.* the deposition period. (5) The ratio of resin to pigment in the deposit was kept constant in the period of up to 20 s to 300 s of deposition. (6) Total deposition charge density for green emulsion increased as the

pH decreased, but the intensity of UV/VIS absorption at 650 nm decreased as the pH of the emulsion decreased. (7) The ratio of acrylic resin to pigment in the deposit could be estimated from the study of chronoamperometry.

Figure 12 (a) Dependence of deposition charge density on pH. (b) Dependence of intensity of UV absorption on pH.

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