Electrochemical Formation of Organic Thin Films and Composite Plating Using Redox-active Surfactants with an Azobenzene Group

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Electrochemical formation of organic thin films and composite plating using surfactants with an azobenzene group are explained. These surfactants lose their dispersing ability by reduction, which enables formation of organic thin films and high particle content Ni/ceramic particle composite plating. Mechanisms of these formations are discussed based on adsorption behavior of these surfactants. Properties and applications of the organic thin films and the composite coatings are also discussed.

Key Words: Organic Thin Film, Composite Plating, Surfactant, Azobenzene

1 Introduction

Previously, we prepared redox-active cationic and non-ionic surfactants with a ferrocenyl group. Cyclic voltammograms of these surfactants show the reversible one-electron oxidation step corresponding formation of a ferrocenium group in these surfactants, which leads to increase of hydrophilicity of the surfactants. The micelles formed by these surfactants can be broken up into monomers when the surfactants are oxidized chemically or electrochemically. Accidentally we found that the solubilize released from the micelles by electrochemical oxidation of the surfactant deposited on the electrode (Fig. 1, mechanism A). This phenomenon was applied for electrochemical formation of organic thin films using these surfactants. Later, we have presented the preparation of phthalocyanine thin films by this method using nonionic surfactants with a ferrocenyl group. These studies showed that these phthalocyanine particles are not actually incorporated in the micelles formed by the surfactants, but are dispersed by adsorption of the surfactants onto the particle surface. The phthalocyanine particles are released when the surfactants adsorbed on the particles are desorbed by the oxidation and finally the particles deposit on the electrode (Fig. 1, mechanism B). This method (micelle disruption method) has some advantages. However, this method using the surfactants with a ferrocenyl group has following limitations:

(i) We could not prepare a film on a base metal using this surfactant owing to its potential of electrolysis for the film formation (+0.5 V vs. SCE).

(ii) We could not prepare a film of inorganic particles.

In order to overcome (i), we should use surfactants that lose its dispersing ability by reduction. Recently, we found surfactants with an azobenzene group which lose their dispersing ability by reduction, and thereby enables formation of an organic thin film on a base metal by the electrochemical or chemical reduction of the surfactants. Furthermore, we could apply these surfactants to the high particle content Ni/ceramic particle composite plating. In this article, we present the details of behavior of these surfactants, applications of these surfactants to the preparations of organic thin films and the high particle content composite plating.

2 Properties of Surfactants with an Azobenzene Group

Non-ionic (AZPEG, Fig. 2) and cationic (AZTAB, Fig. 2) surfactants with an azobenzene group were prepared from 4-[(4-hexylphenylazo) phenol and alkylaniline in following two steps as described in our previous papers.  

2.1 Interfacial properties of the surfactants

The hydrophilic-lipophilic balance (HLB) of AZPEG can be controlled by choosing a proper alkyl-chain of the alkylaniline and length of polyethylene glycol. For the increment of every two carbon atoms in the alkyl-chain, the surface activity of the AZTAB was found to increase by 10 times in pH 1. The plots of these surface tensions (γ) of the aqueous solution of AZTAB and AZPEG versus the concentration show the critical micelle con-
centration (cmc). On the other hand, the same plots of the aqueous solution of the reduced species of these surfactants do not show the micellization phenomenon (Fig. 2).

2.2 Electrochemical behavior of the surfactants

The cyclic voltammogram of AZPEG in a 0.1 M HCl (1 M = 1 mol dm−3) aqueous solution shows a irreversible reduction peak at -0.2 V vs. SCE. A 1.0 mM AZPEG and 0.1 M HCl solution solubilized 93 μM aniline blue. In contrast, this solution of reduced species of AZPEG solubilized only less than 2 μM aniline blue. This difference suggests that the micelles of AZPEG are broken up into the monomeric form by reduction owing to the enhancement in their hydrophilic character. The redox-active center in AZPEG is −N=N− bond of the azobenzene group. In an acidic condition, these nitrogen atoms of the azobenzene group undergo protonations to form the hydrazobenzene derivatives. In lower pH conditions, the irreversible reduction peak of AZPEG reveals the further protonation of the nitrogen atom of the −HN−H− unit of the hydrazobenzene derivative followed by the cleavage of this −HN=N=− bond as shown in Fig. 3. Finally, the −NH2 group of all the aniline derivatives undergoes protonation to give ammonium ions. Thus, the hydrophilicity of all the aniline derivatives increases and thereby the dispersing ability of AZPEG disappears.

3. Application of AZPEG to the Formation of Organic Thin Films

3.1 Organic film formation

Aqueous dispersions containing 1-2 mM AZPEG, 0.1 M HCl and 10-30 mM pigment were prepared by ultrasonic agitation. Using a low power agitator which is used for washing purposes, longer time agitation was necessary for film formation.

Electroless plating on base metals were done by immersing these base metal plates in above dispersion. In the following discussion, as a typical pigment, β-type copper phthalocyanine (CuPc) is used. A blue film with reflectance from the metal surface was formed on nickel plate by immersing in the dispersion containing 2.0 mM AZPEG, 0.1 M HCl and 28 mM CuPc for a few min without electrolysis. Similar CuPc blue films were also obtained on copper, lead, tin, aluminum and their alloy plates by the similar method. Such an electroless plating may be explained by the chemical reduction of AZPEG with these base metals, since the standard potentials of these base metals are more negative than the reduction potential of AZPEG (−0.2 V). On the other hand, any blue film was not formed on the noble metals, ITO and stainless steel plates.

In the field of metal plating, the term "Contact Plating" has been used for deposition of a metal without the use of an external source of electricity by immersing of substrate into a solution in contact with another metal (e.g., aluminum or zinc). We can apply this technique to the
formation of pigment film on noble metal and ITO plates. A transparent blue film of CuPc was formed on the ITO plate by immersing both the ITO and aluminum plates in above dispersion, where these two plates were short-circuited. A blue film was also formed on silver, palladium, gold, platinum and stainless steel plates by the same method.\(^{10}\)

Formation of the organic film depends on pH of the dispersion. At acidic condition (pH 1), the film was formed. This may be explained by the following mechanism: AZPEG is reduced to hydrazobenzene, followed by acid-catalyzed formation of the aniline derivatives, and loses its function as a surfactant due to enhancement of the tall group’s hydrophilicity as described above.\(^{10}\) Effect of sodium n-dodecyl sulfate (SDS) on pH dependence of the film formation was studied.\(^{10}\) Upper limit of pH for the film formation was increased from 1 to 3 for iron substrate and to 4 for zinc substrate. These phenomena were ascribed to acceleration of N-N bond breaking by the addition of SDS, which leads to the loss of the dispersing ability of AZPEG.

The film thickness of the CuPc film increases with immersion time. The thickness of the film increased to more than 10 μm during overnight immersion of the substrate. This may be explained by the fact that the surfactant can penetrate into the film, owing to the existence of small space in the film, and eventually reaches the substrate surface.

The dependence of the rate of the film growth can be explained by the adsorption isotherm of AZPEG on the particles.\(^{10}\) Figure 4 shows the adsorption isotherm of AZPEG on CuPc particles. The amount of adsorbed surfactant (Γ) sharply increased with an increase in \(C_{eq}\) until \(C_{eq}\) was 15-30 μM, which is slightly larger than the cme of AZPEG (10 μM), and gently increased above that range. This result indicates that AZPEG is abruptly desorbed from the pigment particle below the cme.

There is an AZPEG concentration at which the amount of the film is a maximum (optimum AZPEG concentration, \(C_{opt}\)).\(^{10}\) The amount of free surfactant is low at the optimum condition. Excessive free AZPEG may disturb the desorption of AZPEG adsorbed on the particles and lead to a decrease in the amount of the particle deposition. \(C_{eq}\) is proportional to the surface area of the particles and very close to the AZPEG concentration of monolayer adsorption (\(C_{mic}\)).

The mechanism of the film formation can be summarized as follows: AZPEG is reduced to hydrazobenzene derivative followed by acid-catalyzed formation of the aniline derivatives, and loses its function as a surfactant owing to enhancement of hydrophilicity of the tail group. The concentration of the surfactant in the vicinity of a substrate decreases to less than the cme. The surfactant adsorbed on the particles are desorbed, which leads to the deposition of the particles on the substrate.

3.2 Scope of film forming materials

We could prepare films of a wide variety of organic compounds. These compounds are satisfying following conditions:

(i) Compounds should be hydrophobic and not soluble in water.

(ii) Organic particles should be dispersible using surfactants. Size of the particles must be submicron. Precipitation of the particles larger than 1 μm predominates over Brownian motion. Films of more than twenty pigments were prepared using this method.\(^{16}\) We can not prepare film of inorganic particles except for silica particles treated with silane coupling agent,\(^{18}\) which is ascribable to the lack of adsorption ability of these particles to the electrode.

3.3 Properties of organic films

A typical scanning electron micrograph of the Dianthraquinoyl Red film prepared by the contact plating method is shown in Fig. 5, which indicates that this film has a uniform thickness and is composed of particles. Size and shape of these particles are the same with the particles for the preparation of the dispersion. Most of these films are transparent on the ITO. Visible light does not scatter owing to the fact that size of these particles in the films is less than the half of wavelength of the incident light. The agreement of absorption spectra between the CuPc film and the aqueous dispersion of CuPc particles indicates that the crystalline form of pigment particles is maintained throughout the film preparation processes, which means that we can control the

![Fig. 4 Adsorption isotherm of AZPEG at pH 1 on β-CuPc particles at 25°C.](image)

![Fig. 5 Scanning electron micrograph of a cross-section of the Dianthraquinoyl Red film on an ITO plate.](image)
crystalline structure of the film. Content of AZPEG and CuPc in the film are 3-4 and 96-7 wt %, respectively, which means that the film is mainly composed of pigment particles.

3.4 Mechanical strength of organic films

Mechanical strength of the film is not strong owing to absence of the binder among particles and the substrate. In order to reinforce the film, following three methods have been proposed: (i) Coating of polymer film over the particle film. (ii) Thermal treatment of composite plating of polymer/particle.\(^{20}\) (iii) Composite plating of Ni/particle film. The deposited Ni occupies the space among particles and the substrate.\(^{19}\)

3.5 Application of organic films

We can prepare the color filters which meet to the LCD using the dispersion containing two or three pigments. The three primary color filters prepared by this method transmit more than 80 % of visible light at peak wavelength.\(^{5,19}\)

The advantages using AZPEG are following:

(i) This method may enable formation of thin films of a wide variety of organic compounds which are solubilizable or dispersible in a surfactant solution.

(ii) The film forming compounds are not electrolyzed.

(iii) We need not organic solvent.

(iv) Control of film thickness is easy.

(v) Preparation of a large area film is possible.

(vi) We can prepare films only by immersion of base metal substrate into dispersion.

(vii) Control of crystalline structure of the film is easy.

(viii) Preparation of AZPEG is easier than that of the surfactants with a ferrocenyl group.

4 Application of AZTAB to High Particle Content Composite Plating

Last a few decades, research for metal matrix composite plating containing ceramic particles has been growing due to its high hardness, anti-wear and anti-corrosion properties than those of metal without particles. These properties depend on the content of particles in the coating. Investigations reveal that the larger content of particles usually shows better properties of the coating.

Generally, surfactants are added in a plating bath as a dispersing agent, which enhances the particle co-deposition with the metal being plated. However, this effect of the surfactant is limited because of the surfactant layer adsorbed on the particles. When such particles with the adsorbed surfactant in their surface come in contact with the cathode, they can hardly cling there long time enough to be embedded by the growing metallic layer. As a result, the re-dispersion of the particles into the plating solution takes place. If the adsorbed surfactant can be removed from the particles before they come in contact with the cathode, the particles near the cathode surface can not be dispersed and the phenomenon of particle re-dispersion can be avoided. In such cases, the particles with bare surface in the vicinity of the cathode get deposited on the electrode surface. This type of concept is similar to the above organic film formation using redox-active surfactants. Fortunately, the reduction potential of AZTAB (-0.15 V vs. SCE) is more positive than that of Ni\(^{2+}\) so that AZTAB may be reduced during electroplating of Ni. Therefore, AZTAB was applied to enhance the content of ceramic particles in composite plating.

4.1 Ni/Ceramic particle composite plating

Following plating bath was used. To a Watts nickel bath, AZTAB and ceramic particles were added and this bath was ultrasonically agitated to uniform adsorption of the surfactants on the ceramic particles. Electroplating was carried out galvanostatically. There are several parameters, which affect particle co-deposition. As explained in the case of organic film formation, the -NH-NH- bond of the hydrazobenzene derivatives formed by the reduction of AZTAB gets broken at pH 1. Besides the pH, AZTAB concentration, particle loading, current density, and temperature are the variable parameters that directly affect the particle co-deposition. Therefore, these parameters must also be optimized for each kind of particles as well as the same kind of particles with different particle sizes\(^{11}\) to get their maximum incorporation in the composite coatings. As shown in Fig. 6, AZTAB successfully enabled the particle content of various types of ceramics particles to a significantly higher level.\(^{5,11,20-23}\) When electro-inactive surfactant is used, the content of these particles is less then 20 vol.%. The surface morphology of the Ni/diamond composite coatings prepared using AZTAB under an optimum condition is shown in Fig. 7. A uniform distribution of the co-deposited particles can be clearly seen in these SEM images.

Plots of the content of diamond particles in the composite plating versus current density and AZTAB concentration shows the different optimum current and AZTAB concentration corresponding to the maximum particle content with nickel for various particle sizes.\(^{11}\) The maximum particle content of 58 vol.% was achieved for smallest diamond particles (0.2 μm). Similarly, the maximum content of 45 vol.% was achieved for surface-modified hydrophobic SiO\(_2\) particles.\(^{20}\) The particle content in the case of the SiO\(_2\) particles without surface modification was less than 1 vol.%. This difference is ascribable to the difference of the hydrophilicity between these particles.

The basic mechanism for particle co-deposition under the influence of AZTAB is illustrated in Fig. 8. This mechanism can be explained as follows: Particles are dispersed in the plating solution due to the adsorption of AZTAB on their surface. These particles are brought to the cathode by the bath agitation. At the cathode surface, the free AZTAB not adsorbed on the particles are reduced electrochemically. As a result, the concentration of the free AZTAB in the vicinity of the cathode is decreased and thereby the adsorption equilibrium of AZTAB in that region is collapsed. In order to satisfy the adsorption equilibrium, AZTAB adsorbed on the particle surface in that region is desorbed. AZTAB upon reduction loses its dispersion ability. Therefore, the particles after desorption of the AZTAB from their surface cannot be re-dispersed. Consequently, these particles get deposited and buried under the growing layer of the
metal at the cathode surface.

Based on above discussion, we can get high particle content in composite plating using AZTAB which satisfying following conditions: (i) Particles are hydrophobic and not dispersible in water. (ii) Size of Particle is small.

4. 2 Properties of the composite coatings

Many properties of composite coatings like high hardness, high resistance to wear, abrasion and oxidation, and enhanced creep resistance have been reported. It is believed that the ideal condition for a strong composite coating would be the one with very small inter-particle spacing. This can be achieved by co-depositing high amount of particles with uniform distribution throughout the coating, i.e., high volume % of the particles in the coating. Therefore, generally high particle content is desirable for the better performance of the coated materials. As an example, the anti-wear performance of the Ni/SiC composite coating prepared using AZTAB has been demonstrated in Fig. 9. This figure is clearly exhibiting the influence of the particle content on the wear-resistance of the coating. The degree of the wear resistance of the coatings increases with increasing the SiC content up to about 52 vol %. Further increasing the
SiC content, magnitude of the wear resistance decreased. It shows that the Ni/SiC composite coating should have an optimum SiC content in order to act as a good anti-wear material. As an another example, the surface having ultra high water repellency property was prepared using AZTAB. The contact angle between a water droplet and the surface of a nickel coating was 67°, but it reached 156° when the hydrophobic SiO$_2$ content in the coatings was 43 to 45 vol.%.

5 Conclusion

We could prepare films of a wide variety of organic particles and high particle content composite coatings with nickel using the electro-active surfactant containing an azobenzene group. The principle of this method is the electrochemical control of dispersing ability of the surfactants. However, such a method using these surfactants has still following limitations:

(i) The surfactants lose their dispersing ability by reduction at acidic condition, so that we can not apply these surfactants to an electroless composite plating. Usually, the electroless plating is carried out at higher pH conditions.

(ii) The surfactants do not regenerate by oxidation of the reduced species of the surfactants.

We are still searching for new redox-active surfactants that overcome above limitations.

References