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Electrochemical Coating of Phthalocyanines on an Al Substrate Using Aqueous Surfactant Solutions

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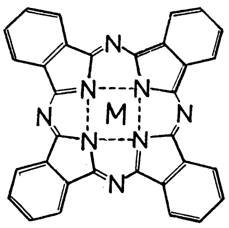
Thin films of copper phthalocyanine and metal-free phthalocyanine were electrochemically prepared on an Al substrate from their aqueous surfactant solutions. Surface coverage of these pigments was investigated as a function of the amount of electricity. Characterization of the films were performed with SEM, IR, and visible absorption spectroscopies.

A novel film-formation technique has been developed and named as the micellar disruption method (MD method).1-3) This method is based on controlled release of a solubilizate onto an electrode from micelles that are formed with surfactant molecules bonded to a ferrocenyl moiety and are broken up into isolated molecules when the surfactant is rendered to anodic oxidation.4) The solubilizate released from the micelle deposits on the electrode in film. Continued research of this method has led to preparations of a metal-free2) and a copper phthalocyanine5) film on an indium tin oxide electrode. However, this method is not applicable to substrates which dissolve by anodic polarization such as Al, Cu, etc. Aluminum is one of most useful substrate in practical applications. For instance, it is exclusively used as the electrode for organic photoconductors in electrophotography, because of its blocking contact.6) Therefore, our objective has been directed to preparing organic thin coatings on an Al substrate. We report here preliminary results on a novel MD method for preparing thin phthalocyanine layers on an Al substrate by its cathodic polarization. In this particular case, the layers deposited even using a surfactant in which no redox moiety such as the ferrocenyl group was included.

In the present investigation, the surfactant used was polyoxyethylene dodecyl ether (Wako Pure Chemicals)(**1**). This surfactant has an advantage of dispersing pigments such as phthalocyanines.7) Copper (**2**) and metal-free (**3**) phthalocyanines were used as the film-forming materials. These were chosen because their cast and/or evaporated films have been utilized as organic photoconductors in the field of electrophotography.8)

$CH_3(CH_2)_{11}O(CH_2CH_2O)_{23}H$

1


M:Cu 2

M:H_2 3

Controlled-current electrolysis and cyclic voltammetry were carried out with a two-electrode and a three-electrode cell, respectively. An Al electrode (Tokai Kinzoku) and a saturated calomel electrode, SCE, were used respectively as a working and a reference electrode. The Al electrode was cleaned by sonication in acetone before use.

The deposition of 2 or 3 on the Al electrode was electrochemically performed using an electrolyte solution prepared as follows; LiBr (0.1 M, 1 M = 1 mol/dm^3) and 1 (2 mM) were dissolved in water and 2 (or 3) was added to the concentration of 7 mM with stirring. The suspension was sonicated for 1 h (125 W). Stirring was continued at 25 °C for more than 4 days. The excess or insoluble part of 2 (or 3) was removed after standing the solution at least for 12 h. The supernatant solution was used for spectral and electrochemical experiments. Visible absorption spectroscopy revealed that 2.5 mM of 2 (or 1.4 mM of 3) is dispersed. Films were galvanostatically deposited on the Al electrode using the electrolyte solution described above, where the Al electrode acted as the cathode. The current density of 0.2 mA/cm^2 flowed across the cell at 25 °C, until the electricity passed reached the desired amount, Q. Deposited films were rinsed in ethanol by sonication. The electrode surfaces (area = 10 cm^2) were uniformly coated and beared an intense blue color. FT-IR measurements revealed that 1 was incorporated in as-grown films, as evidenced by the absorption at 3000-2800 cm^{-1} assignable to aliphatic C-H bonds of 1. In the spectrum of the films after the sonication, however, the band was not observed any longer. The spectrum of this post-treated films was the same in positions of peaks as that of 2 (or 3) in a KBr pellet. In addition, visible absorption spectrum of a solution prepared by dissolving the films with 1-chloronaphthalene was entirely the same as that described in the literature.[9)] These results indicate that the films were consisting of 2 (or 3). For a control experiment, an Al electrode was immersed in the electrolyte solution without electrolysis for 1 h, but nothing deposited on that.

Cyclic voltammograms were taken in the electrolyte solutions with and without 2 (or 3) at the Al electrode. Both voltammograms had the same shape with reduction current rising at -1.5 V vs. SCE. This cathodic reaction likely consists of the dissolution of the passive film and hydrogen evolution.[10,11)]

Figure 1 shows SEM images of film surfaces obtained by the cathodic polarization of the Al electrode (Q = 0.83 C/cm^2) in aqueous solutions of (A) 2.5 mM 2, 2 mM 1, and 0.1 M LiBr, and (B) 1.4 mM 3, 2 mM 1, and 0.1 M LiBr. Included in this figure for comparison are SEM images of the electrode (C) before and (D) after the cathodic polarization in an aqueous solution that contained 2 mM 1 and 0.1 M LiBr (Q = 0.83 C/cm^2) but no 2 or 3. A continuous lace-like network structure was formed on the Al electrode by the cathodic treatment (Fig. 2D). This is presumably a result of corrosion of the electrode, i.e., the dissolution of the passive film.[10,11] The decomposition of water to form hydroxyl ions and hydrogen gas was also observed during the electrolysis. The SEM images of Fig. 1A and Fig. 1B clearly demonstrate that the micropores observed in Fig. 1D are filled with **2** and **3**, respectively, indicating that the deposition of the phthalocyanines was associated with the formation of the microporous network of the Al surface.

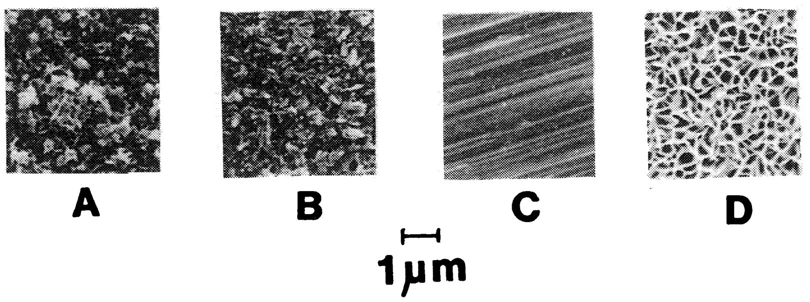


Fig. 1. SEM images of deposited film surfaces of **2** (A) and **3** (B) on Al substrates at Q = 0.83 C/cm^2. (C) and (D) are SEM images of the substrate before and after the cathodic polarization (Q = 0.83 C/cm^2), respectively.

The reflection spectroscopy on the deposited film indicated that the electrolytic process is accompanied by no crystal structural changes, e.g., β to α-form transformation. Films were deposited with varying Q but maintaining the solution composition. Figure 2 shows plots of the surface coverage, Γ, for **2** (o) and **3** (•) vs. Q. The value of Γ was determined spectrophotometrically after dissolving films into 1-chloronaphthalene.[12] The effect of Q on Γ was less pronounced above Q ≈ 0.4 C/cm^2 for **2** or above Q ≈ 0.2 C/cm^2 for **3**, bringing the coverage to a saturation. The Γ value at the saturation permits one to evaluate the maximum thickness of the deposition from the reported density value.[13,14] The calculated thickness of films deposited at Q = 0.83 C/cm^2 thus corresponds to ca. 1000 Å. Such an estimation may not be reliable enough because of the porous structure of the substrate surface as in Fig. 1.

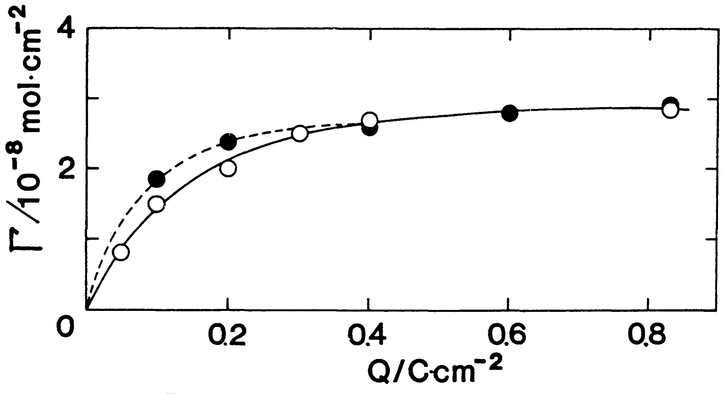


Fig. 2. Plots of Γ vs. Q for the films of **2** (o) and **3** (•).

The present authors showed that thin films of phthalocyanines are electrochemically preparable on the Al substrate. Considering that the technique involved consists of an easy and economical procedure, this method will promisingly be applied to the preparation of various organic thin coatings on oxide covered substrates such as Al.

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