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Electrophoretic Deposition of Composite Phthalocyanine Films with Inorganic Particles Using Organic Solutions Containing Trifluoroacetic Acid

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Abstract

Composite blue films of inorganic particles (SiO_2, Al_2O_3 and TiO_2) with phthalocyanine (MPc, M = Cu and Pb) were prepared by electrophoresis of protonated MPc using dichloromethane solutions containing trifluoroacetic acid, particles and MPc. The charging of the particles by the adsorption of protonated MPc species from the solution was ascribed to the electrophoresis of these particles. In this way, composite film of MPc with the inorganic particles was formed. SEM images of the composite film reveal a uniform distribution of the particles throughout the composite film, and most of the particles were bonded by fibrous MPc crystallites.

Key-words: *Phthalocyanine, Electrophoresis, Composite, Trifluoroacetic acid, Inorganic particle*

1. Introduction

Since their first synthesis early last century, research on phthalocyanines (MPc, **Fig. 1**) has increased due to their chemical stability and strong color. Therefore, they are used as dyes, pigments[1,2], and in many devices as pure or composite thin films[2,3]. However, they have poor solubility in aqueous as well as organic solvents. Therefore, the technique for the preparation of their thin films from MPc monomers is limited to vacuum sublimation. Recently, we reported the wet processes for thin film formation of phthalocyanine particles by micelle disruption method using redox-active surfactants[4-6], and by the electrophoretic deposition method[7]. In the literatures[8,9], it has been reported that some phthalocyanines could be dissolved in some organic solvents containing various kinds of acids and these dissolutions are due to the stepwise protonation of periferic aza nitrogen atoms of the phthalocyanines. In previous studies by us[10,11] and Su *et al.*[12], the electrophoretic deposition of the MPc film from monomers of protonated MPc using trifluoroacetic acid (TFAA)/organic solvent solutions was reported. Later, Takada *et al.* reported that CuPc films prepared using this method exhibit a p-type semiconducting behavior[13]. In this paper, we report the electrophoretic preparation of composite MPc (M = Cu and Pb) films with inorganic particles (SiO_2, Al_2O_3 and TiO_2) from their dispersed particles using organic solutions containing TFAA. The mechanism of this film formation is discussed based on the adsorption equilibrium among inorganic particles and protonated MPc.

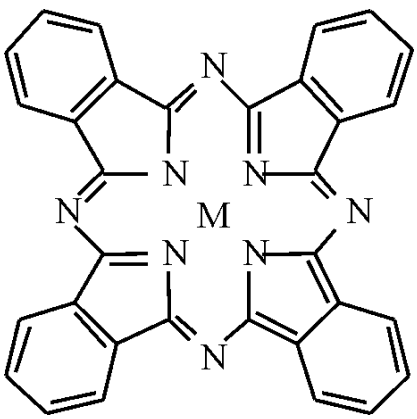

Fig. 1 Molecular structure of phthalocyanines (MPc, M = Cu or Pb).

2. Experiments

All chemicals used in the present investigation were reagent grade and were used without further purification. As inorganic particles, SiO_2 (0.48 μm, Nippon Shokubai Co. Ltd), α-type Al_2O_3 (1 μm, Wako Pure Chem. Ind. Ltd.) and TiO_2 (0.1 - 0.3 μm, Wako Pure Chem. Ind. Ltd.) were used. A known amount of MPc and inorganic particles were dispersed in the dichloromethane (DCM) containing TFAA (Kanto Chemicals, Jpn.) by stirring the mixture for about 30 min. The electrophoretic cell consisted of a copper plate (20 mm × 40 mm) as an anode and an ITO plate (15 mm × 40 mm) as a cathode. These electrodes were fixed vertically at a distance of 10 mm in parallel position and this cell was immersed in the above solution. Potential of 40 V (10^4 Vm^{-1}) was applied using D.C. power regulator (*B418A-125*, Metronix Jpn.) for 1 or 5 min. The films were dried naturally in air. The amount of MPc in the composite film was determined by dissolving the film in DCM containing 1 M TFAA and analyzed colorimetrically using UV/VIS spectrophotometer (*V-560*,