Formation of Organic Pigment Films by Photochemical Reduction of Surfactants Containing an Azobenzene Group

Hiroaki Yamanouchi and Tetsuo Saji*
Department of Chemical Engineering, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152

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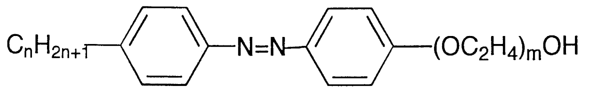
A copper phthalocyanine **1** thin film and photoimage were formed on a polyester film by irradiation of an aqueous dispersion containing a surfactant with an azobenzene group **2a**, dispersed **1**, hydroquinone **3** and 0.1 M HCl. A spectroscopic study showed that the photochemical reduction of **2a** with **3** leads to the deposition of **1**.

The formation of organic pigment thin films is important due to their thermal and heat stabilities. Previously, we demonstrated that micelles formed by redox active surfactants can be dissociated into monomers using an electrochemical redox reaction.[1,2] These phenomina were applied to formation of organic pigment thin films by the electrochemical oxidation of surfactants containing a ferrocenyl group.[3-5] Later, photochemical formations of pigment thin films using this surfactant were reported by three groups.[6-8] These methods require a conductive substrate, because electrochemical oxidation of the surfactant occurs at the substrate. Furthermore, we reported the photochemical formation of a pigment thin film on a non-condutive substrate using the photochemical isomerization of a surfactant containing a spyropyrane moiety.[9] However, this surfactant requires many synthesis steps, and the total yield was low. Recently, we reported the electroless plating of a pigment thin film by the reduction of the following surfactant containing an azobenzene group **2b**:[10]



2a (n = 4, m = 22.0)
2b (n = 6, m = 21.4)

On the other hand, previous investigations of azobenzene photochemistry have dealt almost with the photoisomerization. Only a few papers have dealt with the photochemical reduction of azobenzene.[11,12] In this paper, we report the photochemical formations of pigment thin films and photo images on a non-conductive substrate by the photochemical reduction of surfactant **2a**.

The preparation of surfactant **2a** was prepared by a method similar to **2b**.[10] As the film-forming material, β-type copper phthalocyanine (particle size 0.1-0.2 μm, Dainichiseika Color & Chemicals, **1**) was used. A dispersion containing 1 mM (1 M = 1 mol dm^{-3}) **2a**, 0.1 M HCl and **1** was prepared by sonicating the mixture for 10 min twice (Tomy Seiko Ultrasonic Disruptor Model UR-200P). The dispersion was then irradiated from the side of polyethyelene terephthalate (or slide glass) plate by UV light (500 W Xenon lamp).

A transparent blue film was prepared on the polyethyelene terephthalate plate by UV light irradiation of a dispersion containing 1 mM **2a**, 20 mM **1**, 100 mM hydroquinone **3**, and 0.1 M HCl for 30 min. A light image was also formed when a photomask was used (Figure 1). The resolution was on the order of 10 μm by micrcroscopic observation. On the other hand, this blue film was not formed without **3**. The absorption spectrum of this film is very similar to that prepared by other methods.[4,13] The scanning electron micrograph of a cross section of the film shows that thickness of the film is approximately 1 μm for 30 min of UV irradiation and is composed of 0.1-0.2 μm particles (Figure 2), which are the same as those for the dispersion.[4] These agreements indicate that the crystalline form of **1** is maintained through the film preparation processes.

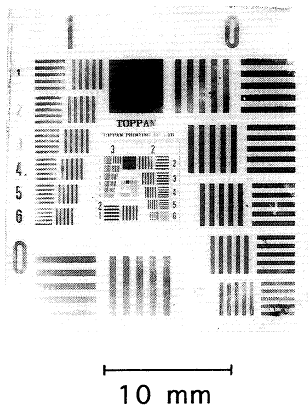


Figure 1. Photograph of **1** film and photoimage prepared by UV irradiation of an aqueous dispersion containing 1 mM **2a**, 20 mM **1**, 100 mM **3**, and 0.1 M HCl for 90 min.

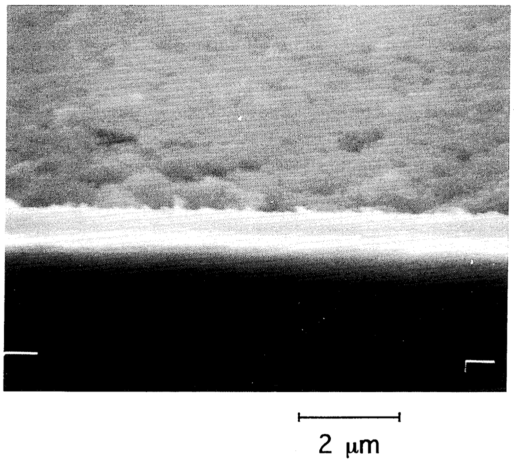


Figure 2. Scanning electron micrograph of cross section of **1** film prepared by the same method with Figure 1.

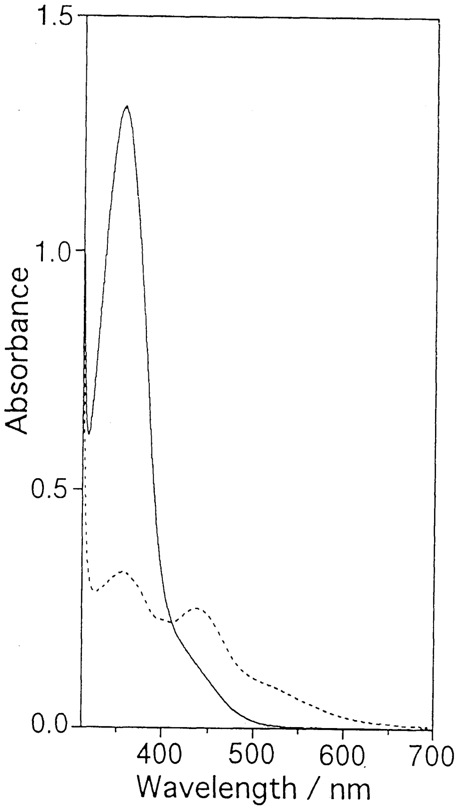


Figure 3. Absorption spectra of aqueous solutions prepared by dilution 50 times with water. Before (——) and after (-----) UV irradiation for 18 h.

Figure 3 shows the absorption spectrum of **2a**、**3** and 0.1 M HCl aqueous solutions. UV light irradiation for 18 h changed the color of this solution from light yellow to wine red, and the absorption peak at 352 nm decreased to 25 %. This peak recovered to 32 % after standing for 5 h at 40 ℃. This solution could not disperse **1**. In the case of the solution without **3**, this peak recovered 80 % after standing for 5 h at 40 oC. The decrease in the peak is ascribable to the photochemical reduction of the excited triplet azobenzene moiety with **3**.[11,12] Hashimoto et al. reported the photochemical reduction of azobenzene in isopropyl alcohol in the presence of **3**.[11] In acidic solution, azobenzenes are reduced to hydrazobenzenes and following acid-catalyzed rearangement leads to amines.[14]

Such film formation may be explained by the mechanism to that for electroless plating using **2b**.[10] **2a** is excited by UV light irradiation and is reduced to hydrazobenzene which follows the catalytic reaction to amine derivatives, and loses its function as a surfactant. Finally, its leads desorption of the surfactant from the pigment and deposition of the pigment onto a substrate.

Present experiments demonstrated that photochemical formations of a pigment thin film and photoimage on a non-conductive substrate are possible by reduction of surfactants containing an azobenzene group.

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