

## Electrodeposition of Hydrophobic Nickel Composite Containing Surface-Modified SiO<sub>2</sub> Particles under the Influence of a Surfactant with an Azobenzene Moiety

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Electrodeposit of nickel with high content of the surface-modified silica particles by a silane-coupling agent was prepared from the Watts nickel bath containing the silica particles dispersed with the aid of a surfactant containing an azobenzene moiety. This composite coating plated under optimized conditions exhibited the ultra high water repellency property with the contact angle of 156°.

Being less sensitive to water, hydrophobic composites are applied in many fields where the devices and the materials can be hardly used in an aqueous medium. For example, electrodes with hydrophobic composite coating have high oxygen-hydrogen overpotential and therefore these electrodes can be used in a wide range of potential window to the electrosynthesis of organic compound from an aqueous solution.<sup>1</sup> Similarly, hydrophobic composite coatings possess high degree of corrosion resistance since these coatings are hardly attacked by the aqueous solution of acid, base and salts. Such hydrophobic coatings can be prepared by incorporating the inert and hydrophobic particles into a metallic matrix from the metal plating bath<sup>1</sup> and by the treatment of a metal/silica composite with a silane-coupling agent.<sup>2</sup> The properties of such composite coating depend on the amount of reinforcement and generally, high content of the reinforcements are desirable for many applications. However, the amount of the particle reinforced by the composite plating technique is often limited to few vol %. In our previous experiments, we demonstrated that redox-active surfactants with an azobenzene group losses its surface activity upon electrochemical reduction and this phenomenon was applied to the electrochemical formation of organic thin films.<sup>3,4</sup> Further, we demonstrated that this phenomenon can be applied as a device to promote the particle co-deposition of various ceramic particles with nickel. The particle content in this case was considerably higher than that from a nickel bath with the similar type of surfactant without an azobenzene group.<sup>5,6</sup> SiO<sub>2</sub> is a well-known ceramic, which is used to synthesize a metal matrix composite in order to apply as a protecting coating form corrosion.<sup>7</sup> Recently, we have shown that SiO<sub>2</sub> particles hardly co-deposit with nickel from an aqueous nickel bath owing to its strong hydration energy but it readily deposits to some extent from a non-aqueous nickel-plating bath.<sup>8</sup> Tari *et al.*<sup>9</sup> had also found that there was almost no interaction between SiO<sub>2</sub> particles and nickel ions in an aqueous solution. Therefore, they could not co-deposit these particles with nickel from an aqueous nickel-plating bath. In order to overcome this difficulty to co-deposit with nickel, they treated these particles with a silane-coupling agent. In the present investigation too, we could hardly deposit the SiO<sub>2</sub> particles into the nickel deposits from Watts bath even using various surfactants. Therefore, in order to promote the co-deposi-

tion of the particles, the hydrophilic surface of these particles were modified into hydrophobic by the treatment with a functional short-chain siloxane, viz. oligodimethyl siloxane- $\alpha,\omega$ -diol (OHDMS), which was synthesized according to the method proposed by Kobayashi.<sup>10</sup> 100 g of the SiO<sub>2</sub> particles ( $\phi = 0.8\ \mu\text{m}$ , Soekawa Chemical Co. Ltd.) was treated with 10 g of the OHDMS in toluene using the method of Terzieva *et al.*<sup>11</sup>

For the composite plating, 10 g dm<sup>-3</sup> of these hydrophobic SiO<sub>2</sub> particles was added to the Watts nickel bath (pH 1) containing 300 g dm<sup>-3</sup> NiSO<sub>4</sub>·6H<sub>2</sub>O, 60 g dm<sup>-3</sup> NiCl<sub>2</sub>·6H<sub>2</sub>O, 40 g dm<sup>-3</sup> H<sub>3</sub>BO<sub>3</sub> and various amount of azobenzene surfactant (AZTAB, Figure 1). This mixture was stirred with a magnetic stirrer until all the floated particles were being suspended in the electrolyte. Even in the presence of AZTAB, it took about an hour or more to suspend all the added particles in the bath showing the strong hydrophobic surface property of the particles. This suspension was ultrasonically agitated for 10 min before it was used for the composite plating. A polished and cleaned copper plate was used as the substrate. This substrate was immersed into the nickel bath in a vertical position parallel to a nickel anode plate at a distance of 15 mm and electrodeposition was carried out under the current density of 3 A dm<sup>-2</sup> for 30 min at the temperature of 50 °C. After the deposition, the deposits were cleaned ultrasonically in water for 10 min. The contact angle between a water drop and the coating surface was measured using a contact angle meter (FACE CA-D). The particle content in the coatings was analyzed gravimetrically as described in our previous paper.<sup>6</sup>

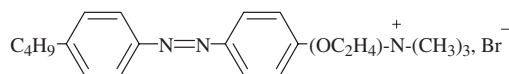
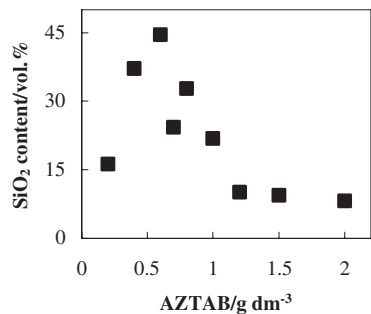


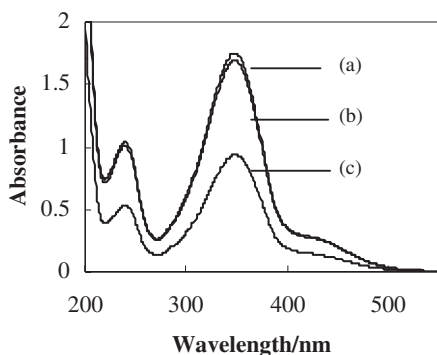
Figure 1. Molecular structure of AZTAB.

The Influence of AZTAB on the co-deposition of surface-modified hydrophobic SiO<sub>2</sub> particles with nickel is shown in Figure 2. The maximum particle co-deposition of 45 vol % was achieved when the concentration of AZTAB in the bath was 0.6 g dm<sup>-3</sup>. A similar type of co-deposition behavior for other kinds of particles with nickel was observed under the influence of AZTAB.<sup>5,6</sup> Such a large amount of particle co-deposition using other types of surfactant is hardly possible. For example, despite the equivalent surface activity of the *n*-tetradecyl trimethylammonium bromide (TDTAB) to that of the AZTAB,<sup>12</sup> the amount of particle co-deposited from a bath containing this surfactant (TDTAB) was hardly about 10 vol %. This difference between the above two surfactants for promoting particle co-deposition might be due to their different redox activity. As explained earlier,<sup>5,6</sup> AZTAB is electrochemically reduced during the deposition of nickel. This surfactant after reduction loses its surface activity, which leads to deposit the particles on the cathode.

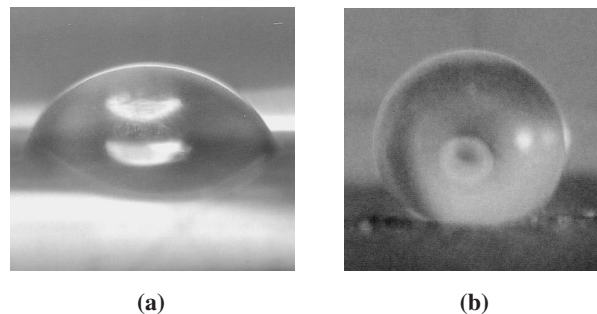


**Figure 2.** Influence of AZTAB on the co-deposition of surface-modified SiO<sub>2</sub> with nickel.

These particles are then embedded into the growing nickel crystals. Unlike AZTAB, TDTAB is not reduced and does not deposit the particles. Moreover, its adsorbed layer at the cathode surface acts as a barrier for nickel deposition and particle co-deposition. However, the particle co-deposition in the case of the SiO<sub>2</sub> particles without surface modification was less than 1 vol % even in the presence of AZTAB in the nickel bath. This might be due to the strong hydrophilic nature of the SiO<sub>2</sub> particle. Owing to its strong hydrophilic nature, there might be a strong interaction between the particle surface and the surrounding water molecules and hence, the structured water layers might wrap the particle. Probably this might be the main reason for no interaction between the AZTAB and the hydrophilic SiO<sub>2</sub> particles in the present investigation (Figure 3). The absorption spectra of the AZTAB before and after adsorption on the hydrophilic SiO<sub>2</sub> particles overlapped each other with only a very small separation at around 349 nm. We believe that this small separation of the spectra is not due to the adsorption of AZTAB on the particles, but it may be due to the instrumental error as well as due to the adsorption of AZTAB at the surface of the glass container. Previously,<sup>3-6</sup> we have shown that the influence of AZTAB on the particle co-deposition with a metal being plated is based on a phenomenon of adsorption of AZTAB on the particles in the bulk region and its desorption from the particles near the cathode in the interface region. However, in the case of the hydrophilic particles, even the adsorption of the AZTAB hardly deposit the particles because the hydrophilic particles are strongly wrapped by the structured water molecules, which probably sep-



**Figure 3.** Absorption spectra of (a) an aqueous solution of 1 mM AZTAB in 0.1 M HCl (b) that of (a) after adsorption on 50 g dm<sup>-3</sup> hydrophilic SiO<sub>2</sub>, and (c) that of (a) after adsorption on 50 g dm<sup>-3</sup> hydrophobic SiO<sub>2</sub>. Adsorption experiment was performed by stirring the above mixture for 5 days at 25 °C.



**Figure 4.** Photographs of a water drop on a (a) pure Ni-plate showing contact angle of 67°, and that on a (b) Ni/SiO<sub>2</sub> hydrophobic composite coating showing 156° of contact angle.

arates the particles from the cathode surface at a distance greater than the thickness of the electrical double layer. Therefore, these particles hardly deposit at the cathode unless the rupture of the aqueous film between the particle and the interface occur. This might be the reason for the different co-deposition behavior of the SiO<sub>2</sub> particles with and without surface modification. SEM analysis for the cross-section of the coating revealed that the distribution of the incorporated particles was not only on the surface but they were well distributed throughout the coating.

The contact angle between a water droplet and the surface of a pure nickel coating was 67°, but it reached the maximum of 156° when the hydrophobic SiO<sub>2</sub> content in the coatings was 43 to 45 vol % (Figure 4). Such high content of SiO<sub>2</sub> particles in the nickel electrodeposits and the super high water repellency property of the Ni/SiO<sub>2</sub> coating is reported here in the first time. The anti-corrosion and the anti-wear properties of this coating are under the investigation.

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