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Hard and Glossy-Colored Films Composed of Micropatterned Organic Dots and Electrodeposited Honeycomb-Shaped Nickel Walls

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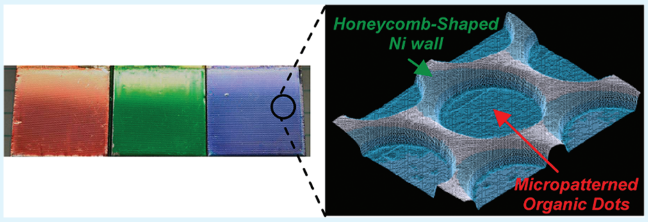
Supporting Information

ABSTRACT: This paper proposes a novel approach for the preparation of colored films with a metallic luster and high hardness. The colored organic films were patterned as microdots by photolithography, and then honeycomb-shaped Ni walls were electrodeposited between the micropatterning. The organic/inorganic composite films showed the hardest grade in a pencil hardness test and high durability in wear resistance tests because the honeycomb-shaped Ni walls protected the colored organic dots.



KEYWORDS: *glossy-colored film, hardness, photolithography, patterning, electrodeposition*

The coloring of surfaces is widely employed in industrial products, such as electronic appliances and automobiles. Because product sales are changed by the color, manufacturers fabricate products with a broad range of colors. In addition to controlling the color of the product, a metallic luster on surface of a film is also an important property because glossy-colored films are quite popular as a luxurious decoration. A representative method for preparing colored surfaces with a metallic luster is to coat a glossy metal surface with a colored organic film (typically, a polymer film containing pigment particles), in which the surface shows both a color and a metallic luster when the colored organic films on top of a glossy metal is thin.[1] However, the organic films are easily damaged by scratching due to their intrinsically low hardness. From a mechanical strength perspective, the use of inorganic compounds, such as metals and metal oxides, is preferable. However, it is difficult to prepare colored films composed of inorganic materials, and the coloring methods that employ inorganic materials are limited. Anodic oxidation of aluminum is a well-known method for preparing colored inorganic films and is widely used in industrial products.[2,3] In addition to anodic oxidation, chemical-conversion coatings[4,5] and vacuum coatings[6] are also known coloring methods using inorganic compounds. Nevertheless, these colored inorganic films have a common disadvantage: the precise control of the color is difficult because the principle of these coloring methods is based on the interference of visible light, which is induced by controlling the interference layers of the films on a nanometer-scale.

Electrodeposited metal films, such as Ni and Cr films, have excellent mechanical strength. Thus, using Ni and Cr films for coloring purposes is quite desirable but has not yet been achieved. Thus far, only black Ni and Cr films have been prepared by controlling the content of oxides and hydroxides in the films.[7,8] We previously reported the electrodeposition of Ni/organic pigments composite films in which the organic pigments of various colors were codeposited into an electrodeposited Ni matrix using a micelles disruption process.[9,10] Because the films were composite films of organic and inorganic compounds, they exhibited high hardness due to the Ni matrix, and the color of the film could be changed by modifying the type of organic pigment. However, from the perspective of decorative surface finishing, the composite-colored films had a drawback in that they did not exhibit a metallic luster, and instead had a dull appearance. The surface of composite coatings tends to be rough because of the presence of codeposited particles,[11−13] which results in the scattering of incident light and a decrease in its specular reflection.[14]

In this study, we report a new approach for preparing hard and glossy-colored films composed of both organic and inorganic materials. In these films, colored organic materials were patterned into dots, and then the dots were enclosed by honeycomb-shaped Ni walls, which were expected to protect the colored organic dots from physical damage. In addition, the film has a metallic luster because the glossy Ni substrates are present under the organic dots. Figure 1 illustrates the preparation process for obtaining colored films. Color photoresists as organic films were spin-coated on top of glossy Ni substrates and then micropatterned by photolithography. The pattern was composed of micrometer-sized dots, whose diameter and spacing were 120 and 30 μm, respectively. Because the colored dots were thin (0.8−1.2 μm), the appearance of the films exhibited a metallic luster that occurred in the presence of a glossy Ni substrate. Subsequently, the electrodeposition of Ni was performed. Because the colored dots are nonconductive layers, Ni was electrodeposited only on the exposed substrate areas, and as a result, the colored organic dots

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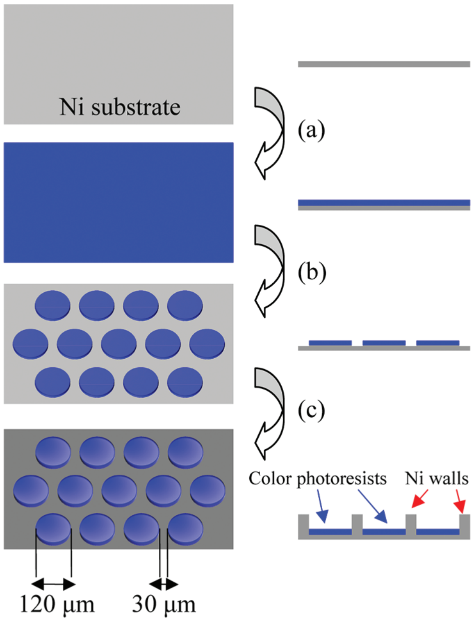

Figure 1. Illustration of preparation processes for obtaining colored films. (a) Spin-coating of color photoresists, (b) micropatterning by photolithography, and (c) electrodeposition of Ni walls.

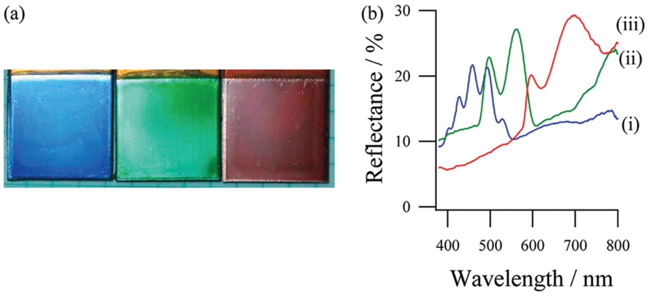

Figure 2. (a) Photograph of the blue, green, and red colored films. (b) Reflectance spectra of the (i) blue-, (ii) green-, and (iii) red-colored films.

were surrounded by honeycomb-shaped Ni walls. By controlling the electrodeposition time, we were able to grow higher Ni walls than the colored dots.

Figure 2a shows the appearance of the resulting films prepared using the three primary colors (i.e., red, green, and blue). As can be seen in this photograph, the films exhibit both a brilliant color and a metallic luster, and the glossy color of the film is controllable by the type of photoresist employed. We note that the colored dots in the films are not visible from a distance. The dot density of the colored films (approximately 170 dot per inch (dpi)) is higher than that of the liquid crystal display (LCD) (72−96 dpi). Because the dots appear essentially invisible on the LCD, it is reasonable that the colored films looked as if they were all one color with no pattern, which is a desirable property for decorative coatings. The reflectance spectra of the colored films are shown in Figure 2b. As in all the films, the reflectance bands are attributed to their own colors. In the reflectance spectra, split peaks were observed, which is a feature of the colored photoresists used (see Figure S1b shown in the Supporting Information). The reflectance of the films was higher than 5% for all wavelengths, resulting in glossy appearances. The increase in the sloping baseline of the reflectance is mainly due to both the glossy Ni substrates present under the colored dots and the honeycomb-shaped Ni walls.

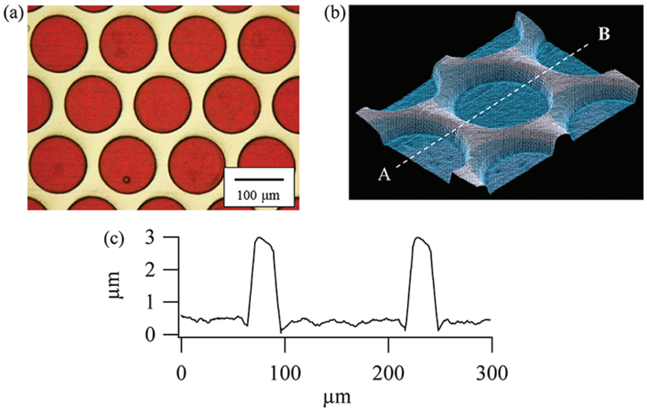

Figure 3. (a) Optical micrograph of the red-colored film. (b) 3D image of the topology of the colored film. (c) Height profile of A-B line shown in the 3D image.

An optical micrograph and a 3D image of the topology of the colored film are shown in Figure 3. The optical micrograph reveals that the Ni was electrodeposited only on the exposed areas in between the colored dots (Figure 3a). Note that the size of the dots and the Ni walls are considerably larger than wavelength of visible light (400−800 nm) so that the incident light is not significantly scattered by the 3D-structured films. The 3D image clearly demonstrates that the honeycomb-shaped Ni walls are higher than the colored dots (Figure 3b). The height profile of the AB-line in the 3D image is shown in Figure 3c and reveals that the honeycomb-shaped Ni walls are approximately 2.2 μm higher than the surface of the colored dot layers and that the Ni walls are grown vertically. In addition to Ni substrates, this coloring method can be applied to other conducting substrates such as a Cr substrate (see Figure S2 in the Supporting Information).

Table 1. Height of Ni Walls with Respect to Pencil Hardness

electrodeposition time (min)	height of Ni walls (μm)	pencil hardness
0	0	HB
4	1.7	HB
6	3.0	9H

The colored films were expected to have a higher hardness than the conventionally colored organic films because the colored organic dots are protected by the Ni walls. To examine the hardness of the colored films, we carried out a pencil hardness test in accordance with Japanese Industrial Standards K5600−5−4. The pencil hardness is a general indicator of the strength of the coating films and ranges from 6B (softest) to 9H (hardest). The pencil hardness test was performed for colored films with and without the honeycomb-shaped Ni walls. The results are summarized in Table 1, while the optical micrographs of the colored films after the pencil hardness tests are provided in the Supporting Information. The pencil hardness of the colored film without Ni walls (i.e., the height of Ni walls is 0 μm) was HB. As for the two films with Ni walls, the film with 3.0 μm Ni walls showed much greater hardness than the film with 1.7 μm Ni walls. Although 1.7 μm Ni wall was higher than a height of the dots (0.8 μm), the pencil hardness of the colored film with 1.7 μm Ni walls was the same as that of the colored films without Ni walls, indicating that a height of 1.7 μm is not enough to protect the colored dots from physical damage in the pencil hardness test. The colored film with 3.0 μm honeycomb-shaped Ni walls showed a pencil hardness greater than 9H, which indicated excellent hardness in coating films. This degree of hardness has not been previously achieved in conventionally colored organic films. For colored films with Ni walls that were higher than 3.0 μm, a pencil hardness greater than 9H was also confirmed (data not shown), but in these films, the silver-colored Ni walls dominated the appearance of the color on the surface. Therefore, we concluded that the optimum height for the Ni walls was approximately 3 μm.

On the basis of these results, the colored films in this study notably have the advantages of both organic and inorganic films. In conventional organic films, various colors and a metallic luster can be easily obtained, but they possess low hardness. In contrast, inorganic films possess high hardness but the precise control of the colors is difficult. Because the colored films in this study consist of colored organic dots surrounded by an inorganic material (i.e., honeycomb-shaped Ni walls), they have the advantage of both organic and inorganic films.

Because wear resistance is an indispensable property for practical applications of colored films, we examined the wear resistance of two samples: dot-pattern-colored films with and without the honeycomb-shaped Ni walls. For the film without the Ni walls, the colored dots were removed after the wear resistance test; while for the colored film with the honeycomb-shaped Ni walls, its color was maintained after the test (see Figure S4 in the Supporting Information), which indicates that the colored dots did not suffer physical damage during the wear resistance test. This was due to the high hardness of the Ni walls and the strong adhesion between the Ni walls and the substrates.

In summary, we prepared colored films with a high degree of hardness and metallic luster. The films consisted of colored organic dots and electrodeposited honeycomb-shaped Ni walls. Because the colored organic dots were surrounded by Ni walls, the dots were protected from physical damage. The colored films showed excellent film hardness. In this study, photolithography was utilized to prepare the microdots of organic films, and a simpler method (e.g., inkjet printing and screen printing) could also be useful for the preparation of colored microdots. This method would be applied in the surface finishing of various industrial products.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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