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Letter

Influence of Photo-illumination on Greenish Metallic Luster of Safflower Red Pigment Film

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Abstract: A visible photo-illumination on the carthamin red pigment solid film was carried out in the study. It was found that the greenish metallic luster of the film was weakened by the photo-illumination and the absorption of the film was also weakened at the same time. Because the deterioration of the carthamin chromophores was induced by the photo-illumination, the absorption in the green light band was probably an important factor of the metallic luster generation.

Key words: Carthamin solid film, Greenish metallic luster, Photo-fading, Carbonyl group

Pigments obtained from safflower (*Carthamus tinctorius L.*) has been used as herbal medicine, food, colorant and cosmetics. There are some difficulties (such as thermal decomposition and photo-fading) in the extraction of carthamin (red pigment) from petals. It is difficult to separate the water-soluble yellow pigment and the water-insoluble red pigment. Therefore, the red pigment is quite rare, and it is hard to obtain the pure commercial products. Kuroda reported in her paper that the red pigment solid with a high purity gave a greenish metallic luster. [1] Although the optical properties and the photo-fading characteristics of the red pigment were evaluated with a mixture sample such as the dyed textiles or liquid phases of low concentration, there is almost no discussion on its solid phase at higher purity. [2,3] In our previous study, a highly pure red pigment having a metallic luster was successfully obtained by a modification of the traditional extraction method. Our specular reflection measurements, showed that the angle dependence on the wavelength at the reflection maximum (λ_{max} : 550 nm) was not found for the red pigment film. Therefore, it was concluded that the greenish metallic luster of the pigment film was due to scattering by the bonding electrons not to interference color at multilayer structures. [4] In this study, photo-illumination for the solid film of the safflower red pigment was carried out to discuss the relationship between the absorption of the chromophores and the reflection.

The safflower red pigment was extracted by a traditional method with some modifications. [4] The pigment film was immobilized onto the quartz crystal plate by casting from the concentrated aqueous solution of the extracted pigment. These films were dried under dark and ambient atmosphere at room temperature. The photo-illumination for the pigment film was carried out with a metal-halide lamp (incident power: 30 mW) under humidified condition. Specular reflectance and transmittance spectra were obtained by a CCD array spectrometer connected with fiber optics. Changes in the chemical structures of the red pigment by the photo-illumination were evaluated with a Fourier transform infrared spectrometer (FT-IR) and a Raman micro-spectrometer.

Figure 1 shows the photograph of the safflower red pigment film (thickness : 0.4 μm) on the quartz crystal plate after photo-illumination through a multi-color filter for 30 min. After the photo-illumination, the greenish metallic luster turned red color. The biggest changing was found in the none filter part, and the secondary big changing was found in the green filtered part. On the other hand, the metallic luster was left as before under the red filtered part. Figure 2 shows the specular reflectance spectra of the pigment film after photo-illumination through color filters. The reflectance values at the wavelength of 550 nm decreased in the order of none filter, green filter, orange filter, red filter and unexposed part. Figure 3 shows the absorption spectra of these filters and the red pigment film. This figure indicates that the red filter can cut the light over the whole

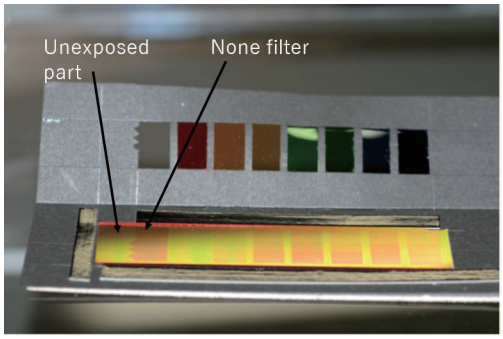

Fig. 1 Photograph of the safflower red pigment film (thickness : 0.4 μm) on the quartz crystal plate demonstrating the effect of photo-illumination through multi-color filter for 30 minutes.

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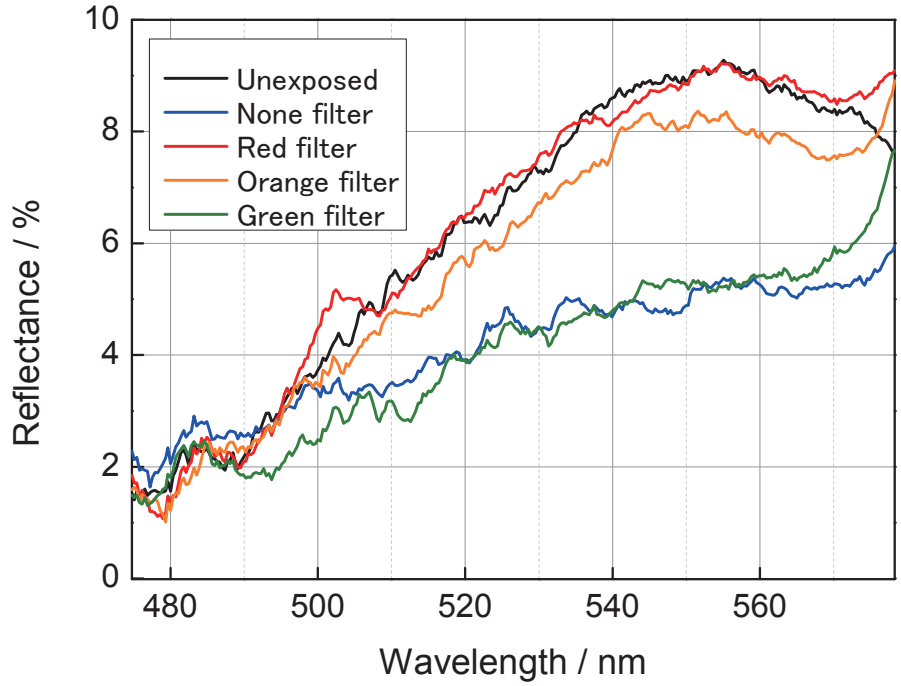

Fig. 2 Specular reflectance spectra of the pigment film (thickness : 0.4 μm) after the photo-illumination via color filters.

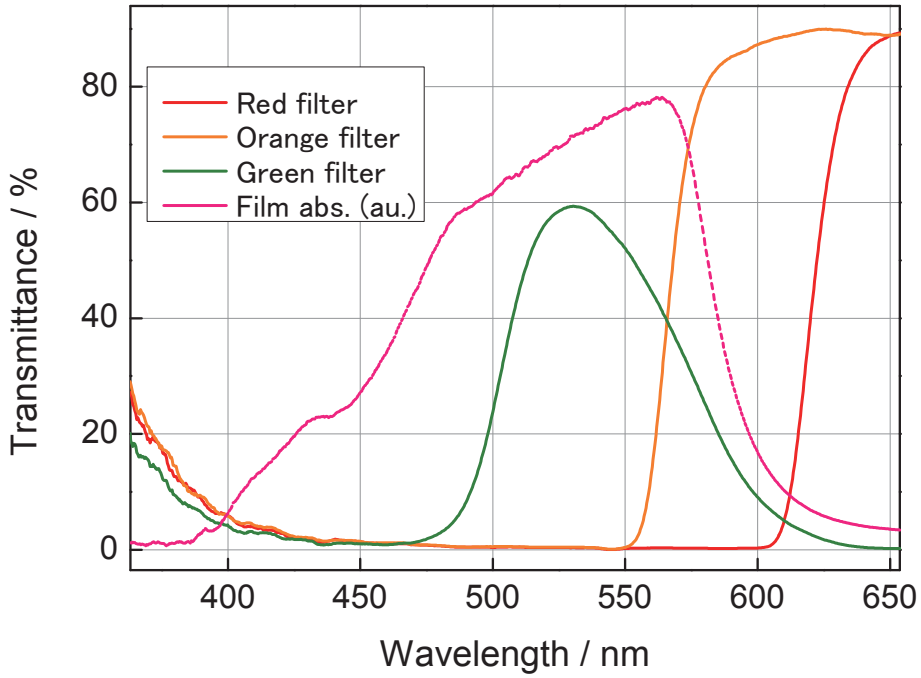

Fig. 3 Absorption spectra of color filters and the red pigment film (thickness : 0.4 μm).

absorption band of the red pigment, and the orange filter can transmit the light in the longer wavelength region of the red pigment. Therefore, it is confirmed that the absence of the metallic luster was induced by the photo-illumination with the visible light on the absorption band of the red pigment. On the other hand, the change in the absorption spectrum of the red pigment film caused by the exposure for 30 min. was very slight. These observations suggest that the deterioration of the pigment associated with the reduce metallic luster probably took place only in uppermost surface layer of the film.

Then, the film thickness of the pigment was reduced to about 80 nm and the photo-illumination time was extended to 139 min. Figure 4 shows the photograph of the pigment film after the long photo-illumination. With the black background (for reflection evaluation), the greenish metallic luster was observed in the unexposed part, and the color change from green to reddish orange was observed in the exposed part. With the white background (for transmission evaluation), the color of the pigment film turned orange in the exposed part. In this way, considerable color changes were achieved by the film thinning and the extended photo-illumination time. Figure 5 shows the specular reflectance spectra of the pigment film (80 nm) before and after the photo-illumination (139 min.). In

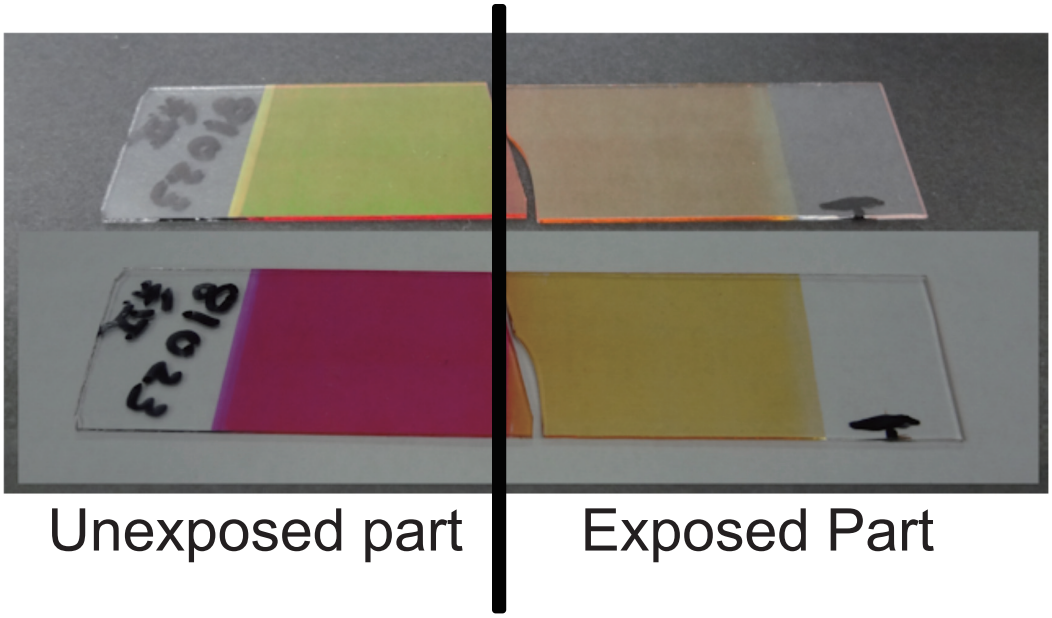

Fig. 4 Photograph of the pigment film (thickness : 80 nm) after the long (139 min.) photo-illumination.

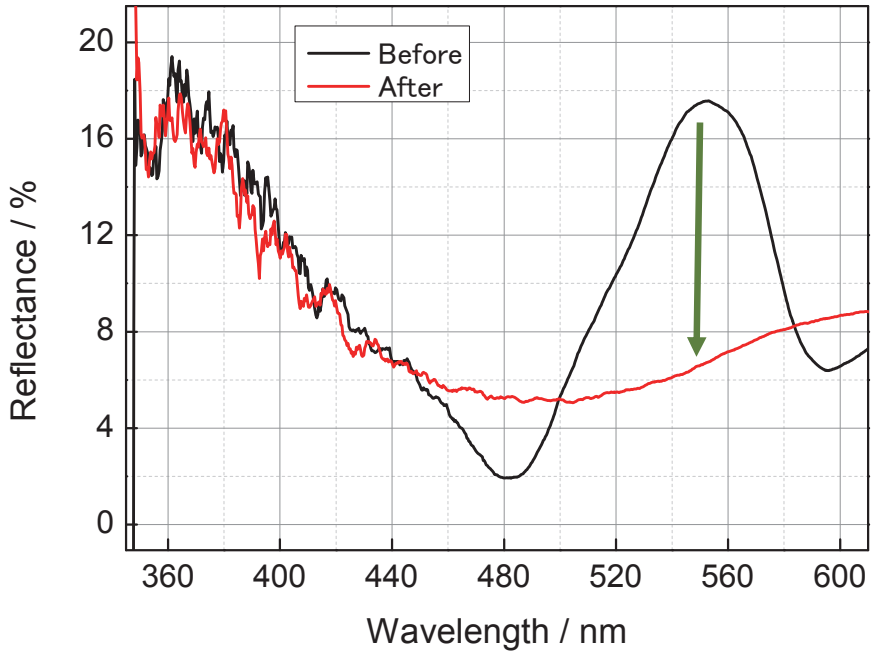

Fig. 5 Specular reflectance spectra of the pigment film (thickness : 80 nm) before and after the photo-illumination.

comparison with the rate of decrease in the reflectance at the 550 nm (-40%) for the thick film (0.4 μm) illuminated for 30 min. (Fig.2), the reflectance value at the wavelength of 550 nm remarkably decreased (-70%) by the photo-illumination. The spectrum shape after the photo-illumination had a curved part convex downward covering the green light band. Figure 6 shows the transmittance spectra of the pigment film before and after the photo-illumination. The absorption of the red pigment around the wavelength of 550 nm was remarkably weakened by the photo-illumination, and the absorption maximum shifted to 480 nm was found on the figure. The orange state (λ_{max} : 480 nm) is different from a yellow pigment having the absorption maximum around 410 nm. As a general understanding, the red color of carthamin was obtained by expansion of the π-conjugation due to coupling with the yellow molecules. It was suggested that this orange state is not simple recovery of yellow pigment, but to a different type of decomposition products of red pigment.

In order to study the change in the chemical structures of the red pigment, the measurement of the rotation and vibration spectra were carried out with a FT-IR and Raman spectrometer. As the obtained spectrum from the FT-IR measurement, some signals at 1515, 1585, 1624 cm^{-1} due to conjugated aromatic C=O (carbonyl group) stretching remarkably decreased after the photo-illumination. The carbonyl group is a part of the chromophore of the carthamin (red pigment). [5,6,7,8] Figure 7 shows the Raman spectra of the pigment film before and after the photo-illumination. The clear

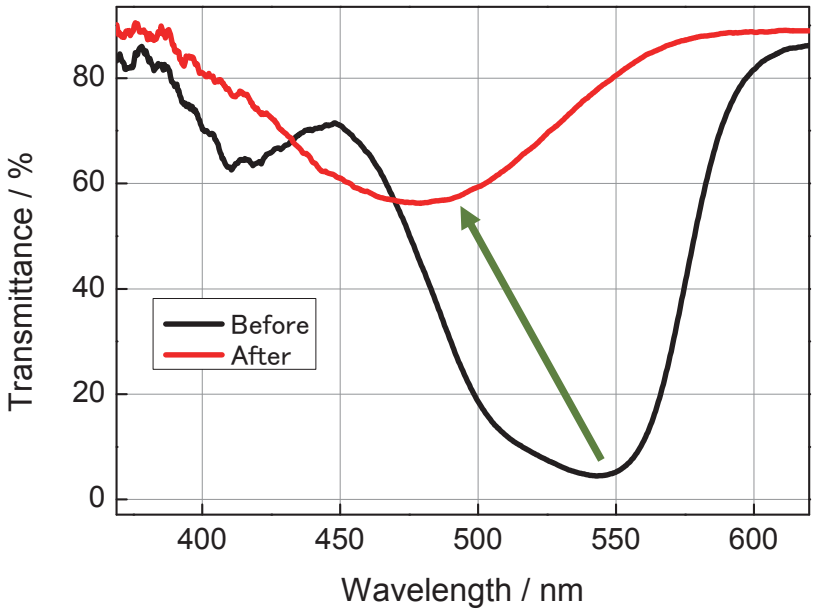

Fig. 6 Transmittance spectra of the pigment film (thickness : 80 nm) before and after the photo-illumination.

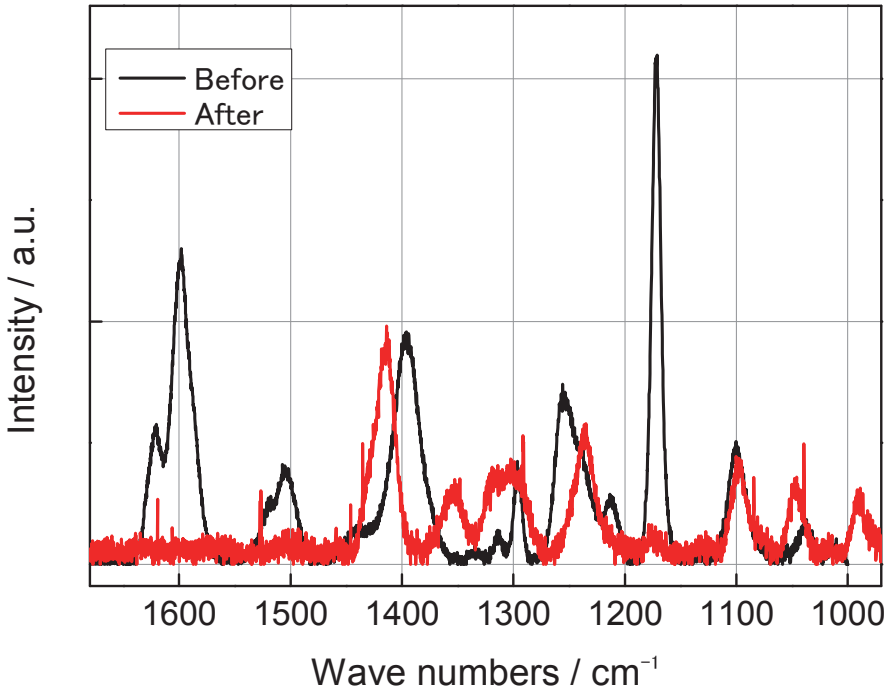

Fig. 7 Raman spectra of the pigment film (thickness : 80 nm) before and after the photo-illumination.

changes were found between the two spectra, especially, the absence of the strong signals 1176 cm^{-1} (substituted aromatic) and 1600 / 1620 cm^{-1} (C=C ring stretch doublet) was found between before and after the photo-illumination. [9,10] With these results, it was confirmed that the deterioration of the carbonyl group and /or the shortening of the π-conjugation were induced in the chemical structures of the red pigment by the photo-illumination. These discussions probably contribute to make sure that the greenish metallic luster of the red pigment film was directly associated with the light absorption of the chromophores.

The visible photo-illumination to the safflower red pigment solid film was carried out to discuss the optical characteristics in the study. The greenish metallic luster of the pigment film was influenced and weakened by visible photo-illumination. It was confirmed by the measurement of the rotation and vibration spectra that the deterioration of the carbonyl group and / or the shortening of the π-conjugation were induced in the chemical structures of the red pigment by the photo-illumination. We are just started the approach for the relationship between the metallic luster of the pigment film and the bonding electrons in the pigment. By the discussion with the basic models such as Drude and Lorentz theories, the generation mechanism of the metallic luster will be elucidated in more detail in near future. [11]

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