Scientific Research into the Green Metallic Luster of Safflower Red Pigment extracted by Traditional Method

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ABSTRACT

A visible photo-illumination to the carthamin red pigment solid film was carried out in the study. It was found that the greenish metallic luster of the film was weaken by the photo-illumination, and the absorption of the film was also weaken 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.

1. INTRODUCTION

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 the petal, 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 at the lower concentrations, there is almost no discussion on its solid phase at the higher purities. [2,3] 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.

2. EXPERIMANTAL

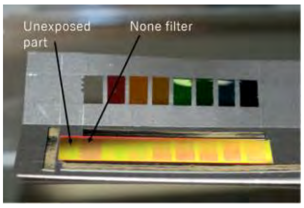
The safflower red pigment was extracted by a traditional method with some modifications.[4] The pigment film was immobilized onto the quartz crystal plate by casting from the concentrated aqueous solution of the extracted pigment. These films were dried under dark and ambient atmosphere at room temperature. 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.

3. RESULTS AND DISCUSSION

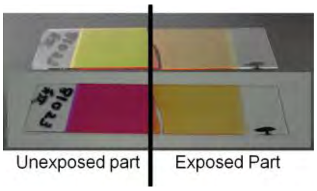
Figure 1 shows the photograph of the safflower red pigment film (thickness : 0.4 μm) on the quartz crystal plate as the result in photo-illumination though multi-color filter for 30 min. After the photo-illumination, the greenish metallic luster turned red color. The biggest changing was found at none filter part, and the secondary big changing was found under the green filter part. On the other hand, the metallic luster was left as before under the red filter part. The specular reflectance spectra of the pigment film was measured after the photo- illumination via color filters. The reflectance values at the wavelength of 550 nm were lowered in the order of none filter, green filter, orange filter, red filter and unexposed part. The absorption spectra of these filters and the red pigment film were measured. These results indicated that the red filter can cut the light at the all absorption band of the red pigment, and the orange filter can though the light at the longer wavelength regions of the red pigment. Therefore, it was confirmed that the absence of the metallic luster was induced by the photo-illumination with the visible light at the absorption band of the red pigment. On contrary, the change in the absorption spectrum of the red pigment film could not be found in the least by the short time exposure for 30 min. According to the result, the deterioration of the pigment associated with the absence of the metallic luster probably took place only the uppermost surface layer of the film by the photo-illumination.

Then, the film thickness of the pigment was reduced to about 80 nm, the photo-illumination time was extended to 139 min. Figure 2 shows the photograph of the pigment film after the long photo-illumination. In the case of the black color substrate (for reflection evaluation), the greenish metallic luster was observed in the unexposed part, and the color change from red to reddish orange was induced by the photo-illumination. By the observation with the white substrate (for transmission evaluation), the color of the pigment film turned the orange color by the photo-illumination. As the result, considerable color changes were achieved by the film thinning and the extended photo-illumination time. Figure 3 shows the specular reflectance spectra of the pigment film (80 nm) before and after the photo-illumination (139 min.). In 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



(a)



(b)

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. (a) Fig. 2 Photograph of the pigment film (thickness : 80 nm) after the long (139 min.) photo-illumination.(b)

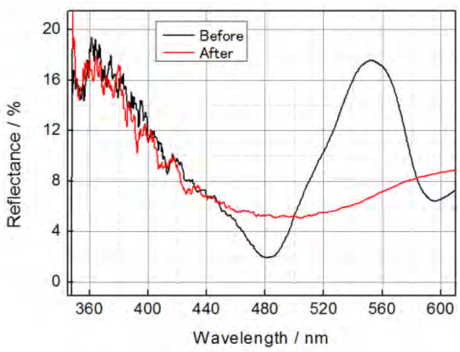


Fig. 3 Specular reflectance spectra of the pigment film (thickness : 80 nm) before and after the photo-illumination.

photo-illumination had a curved part convex downward covering the green light band. The transmittance spectra of the pigment film were evaluated 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 resulting spectrum. 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 due to a simple recovery of yellow pigment, but to a different type of decomposition products of the 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 part of the chromophore of the carthamin (red pigment).[5-8] Figure 4 shows the Raman spectra of the pigment film before and after the photo-illumination. The clear 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.

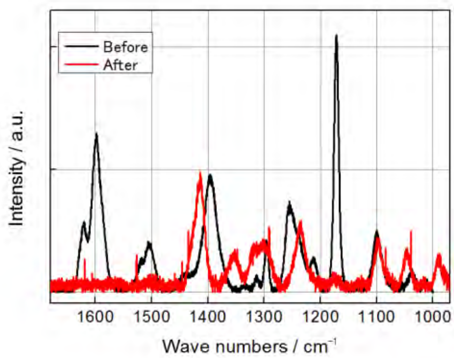


Fig. 4 Raman spectra of the pigment film (thickness : 80 nm) before and after the photo-illumination.

6. REFERENCES

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