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Original Paper

Metallic Luster from Two Organic Pigments without Metallic Elements -Relationship between Molecular Orientation by Stretching and Polarization Reflection -

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Abstract: A golden metallic luster was observed from crystal violet immobilized inside a Nafion sheet. By stretching this sheet, the degree of polarization of the reflected light was reduced. As a result of comparing the change in the degree of polarization due to stretching using different pigments, it was concluded that the reflected polarization characteristic of the crystal violet is related to the randomness of the direction of the transition dipole moment.

Key words: Metallic luster, Crystal violet, Cyanine pigment, Transition dipole moment

Introduction

In solid films of some natural or synthetic pigments or polymers, a metallic luster is observed even though the molecular structure does not contain any metallic elements. [1)2)3)4)] However, only a few of these studies have described in detail the mechanism of the metal-like luster generation. We have studied the mechanisms of the green metallic luster generating from the solid film of a carthamin pigment extracted from safflower by traditional methods. First, the reflection characteristics of the green metal-like luster were discussed, and it was found that the wavelength of the reflected light does not depend on the incident / detection angle. [5)] It was also found that the solid film of this pigment was forcibly faded by an illumination with white light, and the green metal-like luster was also weakened at the same time. [6)] These facts suggested that the reflected color of this pigment film was not due to the structural color and was based on the light absorption of the pigment. The chemical synthesis was difficult[7)] and the required amount could not be obtained by the traditional extraction method. Therefore, another pigment was explored. Since the carthamin is not industrially available, alternative pigments are required and fuchsine (fuchsin) has been used. Fuchsine is a triphenylmethane-based synthetic pigment. A metallic luster of almost the same color as the carthamin can be obtained from the solid of this pigment. Crystal violet (CV), which is often used in dyeing and medical treatment, is also triphenylmethane-based, and the solid has a luster with a color tone close to gold.[8)]

We decided to study the reflective properties of CV, which has a metallic luster with a different color tone than that of the carthamin. In discussing the model of the metal reflection, the density of free electrons is important in the Drude model. It is unclear whether it is directly related in this CV case, but in order to control the density of the CV, the pigment was dispersed in the polymer support at different ratios, and whether or not a metallic luster appeared was determined. As a result, it was found that a metallic luster appears even if it is not a solid film composed only of a pigment, and that a metallic luster begins to appear when the pigment is 30% to 40% by weight. By using this pigment dispersion film, it became possible to adjust the density of the pigment by stretching. The luster of a metal is known to have a small amount of polarized light. The reflection of these materials is electromagnetic resonance by free electrons followed by a secondary light emission, and the polarization characteristics are due to the random vibration direction of the free electrons. The reflected polarization characteristics of the CV's metallic luster were evaluated, and the effect of stretching the pigment dispersion polymer sheet on these characteristics was investigated in this study.

Experimental

Crystal violet chloride (CV), cyanine pigment, and solvent were used in the purchased state without any additional purification. The Nafion117 (thickness: 200 microns) sheet was purchased from a vendor. A ethanol solution (50 mM) of CV was prepared as a pigment solution. In addition, a Nafion sheet of 12 mm x 30 mm was soaked in the solution for 103 hours. After the sheet was taken out of the solution, the pigment on the surface of the Nafion sheet was washed off with ethanol. Finally, the sample that had been air-dried was used as a measurement sample (Nafion+CV). 3,3'-Dipropylthia dicarbocyanine iodide was used as the cyanine pigment. A ethanol solution (10 mM) of this cyanine pigment (CY) was prepared as a

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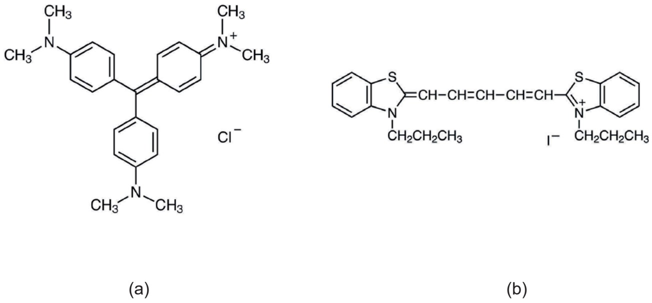

Fig. 1 Chemical structures of crystal violet chloride(a)and 3,3'-dipropylthiadicarbocyanine iodide(b).

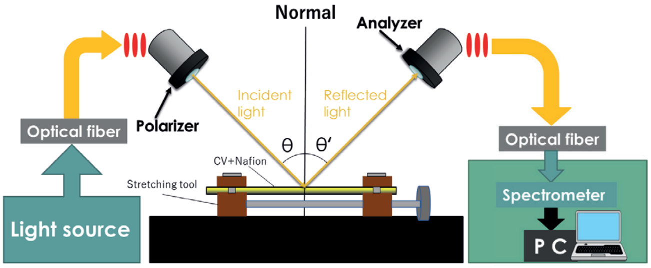

Fig. 2 Schematic diagram of reflectance measurement.

Fig. 3 Photograph of Nafion+CV.

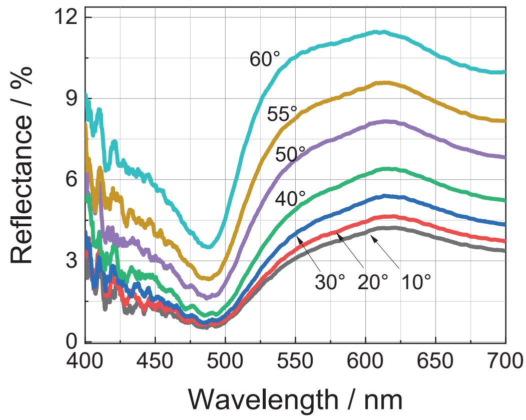

Fig. 4 Specular reflectance spectra of Nafion+CV at each angle.

pigment solution. In addition, a Nafion sheet of 12 mm x 30 mm was soaked for 167 hours. After the sheet was taken out of the solution, the pigment on the surface of the Nafion sheet was then washed off with ethanol. Finally, the sample that had been air-dried was used as a measurement sample (Nafion+CY). The chemical structures of the two pigments are shown in Fig. 1.

The apparatus shown in Fig. 2 was used to measure the reflection spectrum. The light source was a tungsten light. The sample was illuminated with incident light from a collimator lens (+polarizer) via an optical fiber, and the reflected light was condensed with a (+analyzer) collimator lens via an optical fiber, and finally the reflected light was introduced into the photodiode array spectroscopic photometer. A home-made jig was used to stretch the test sample.

Results and discussion

Because the Nafion sheet is an ion exchange resin, the CV is considered to be electrostatically immobilized in Nafion.[9] In order to confirm the color tone of the obtained sample, a photograph of the Nafion+CV is shown in Fig. 3. Because the thickness of the Nafion sheet is 200 µm, the transmitted light from the Nafion sheet (Nafion+CV) is hardly observed by the utilized light source. As shown in Fig. 3, Nafion+CV showed a metallic luster with a color tone similar to gold when illuminated with a white light source. Therefore, it is considered that this color tone is due to reflection, which is not affected by the transmitted light.

Fig. 4 shows the unpolarized reflection spectrum for each incident angle and detection angle. The 100% reflectance was corrected by the incidence beam through the direct optical path into the collimator lens on the detector side. The reflectance value of the reflection spectrum increased several times as the angle increased from 10 degrees to 60 degrees. A shoulder at the around a wavelength of 540 nm and a maximum around at the wavelength of 615 nm were observed in each spectrum. It is considered that the former corresponds to the H-dimer, which is the aggregated state of CV, and the latter corresponds to the absorption of the molecularly dispersed state. [10][11] In addition, an increase in reflectance was observed in the wavelength range shorter than 490 nm. It is considered that these reflected lights are mixed and become gold. After that, we focused on the reflection with a wavelength of 540 nm to which human vision is highly sensitive.

A polarizer and an analyzer were introduced into the optical path of the measurement system, and the reflected polarization characteristics were studied. These reflectance of the unpolarized, S and P polarized states at a wavelength of 540 nm were measured and compared for each angle. The result is shown in Fig. 5 as Fresnel reflectance. Except for the reflectance of P-polarized light, the reflectance increased with the increasing angle. With P- polarized light, the reflectance began to decrease as the angle increased from 10 degrees, reaching the minimum value (about 1%) near the angle of 55 degrees. There was no Brewster angle in this sample due to the slight residual P-polarized reflection. In the case of a colored sample, it is known that the extinction coefficient is not 0 even in the dielectric sample and there is no Brewster angle.[12]

Based on the result of Fig. 5, the degree of polarization (DOP) was calculated from the following formula using the reflectance (Rs, Rp) in the S and P polarized states of 55 degrees, which had the lowest reflectance.

$$DOP\% = ((R_s - R_p)/(R_s + R_p)) \times 100$$

The results are shown in Fig. 6. Up to 55 degrees, the DOP increased with the increase in the angle. The maximum value of Nafion+CV is 88% around 55 degrees. And, the maximum value is almost 100% for the pigment-free Nafion sheet, that is a complete dielectric in the dry state. In this state, the DOP of the Nafion+CV is very higher than the value of a real metal (ex: DOP is within 6% for aluminum).

Then, the sample was stretched to change the density of the pigment in the Nafion sheet, and the change in the DOP was discussed in the section. In this study, the stretching ratio is defined as (stretched film length / original length) x 100%, and the length of 1.8 times the original length is a 180% stretching. The relationship between the stretching ratio and the DOP is shown in Fig. 7. The DOP in the stretching direction decreased as the stretching ratio increased. This result indicated that the DOP decreased due to stretching, and the polarization state became closer to that of the real metal.

There are some reports that cyanine pigments generate a metallic luster in their solid state.[13] Next, the result of the cyanine pigment is shown for comparison of the molecular shapes. In Nafion+CY, a reddish purple metallic luster was observed as shown in Fig. 8. Fig. 9 shows the reflection spectrum in the unpolarized state at each angle. It is considered that the difference in the color tone from Nafion+CV is caused by the difference in the wavelength of the reflection minimum between two pigments. The reflectances of Nafion+CY in the unpolarized, S and P polarized states at a wavelength of 600 nm were measured and compared for each angle. The results are shown in Fig. 10. Unlike Fig. 5 (Nafion+CV), the reflectance in the P-polarized state was almost 0% near 55 degrees. At any stretching ratio, the reflectance of the P-polarized light was almost 0% and the DOP was almost 100% near 55 degrees. Using this angle, it was difficult to compare the influence in the DOP on the stretching ratios. Therefore, in Nafion+CY, the DOP by stretching was evaluated at an angle of 40 degrees at which the reflectance remained to some extent.

The results are shown in Fig. 11. It was observed that the degree of polarization tended to increase as the stretching ratio increased.

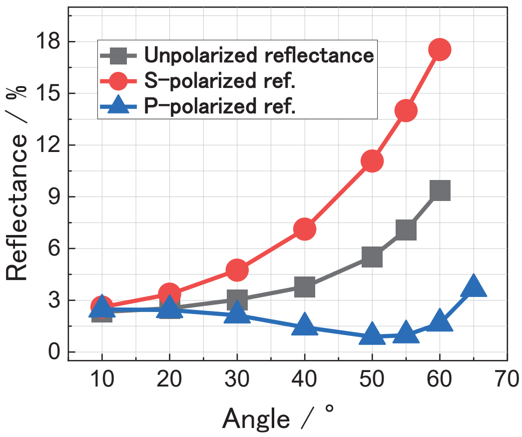

Fig. 5 Fresnel reflectance of Nafion+CV at the wavelength of 540 nm for each angle.

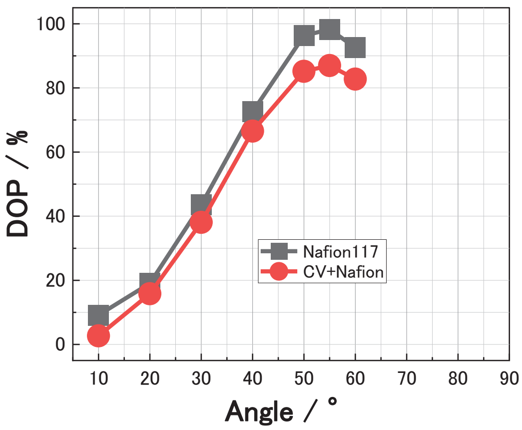

Fig. 6.Degree of polarization of Nafion+CV and Nafion117 sheet at each angle.

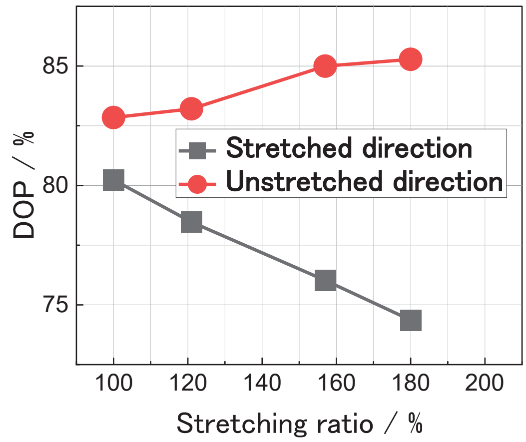

Fig. 7.Degree of polarization of Nafion+CV at each stretching ratio.

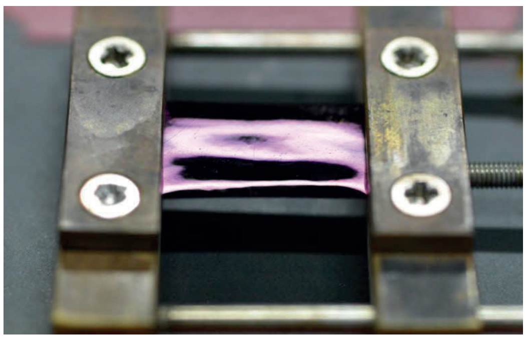

Fig. 8 Photograph of Nafion+CY.

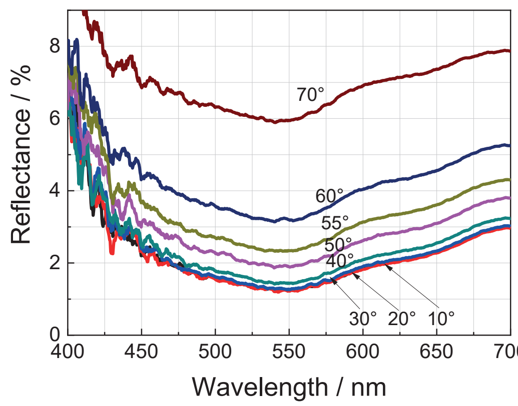

Fig. 9 Specular reflectance spectra of Nafion+CY at each angle.

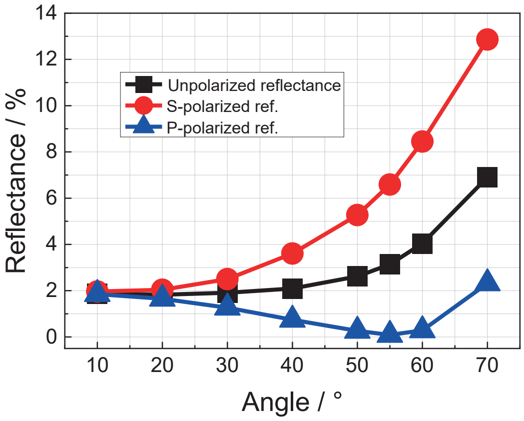

Fig. 10 Fresnel reflectance of Nafion+CY at the wavelength of 600 nm for each angle.

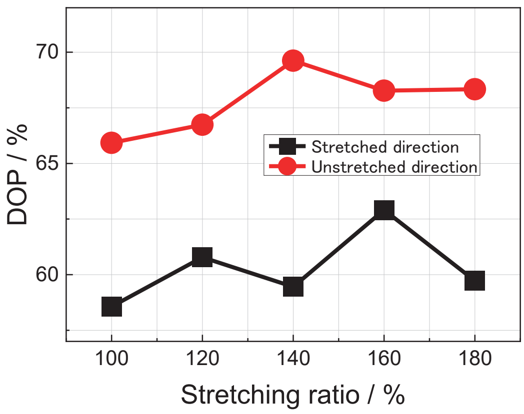

Fig. 11 Degree of polarization of Nafion+CY at each stretching ratio.

Generally, the stretching of the sample is performed to induce the orientation of the molecules. Therefore, it is expected that the polarization will become stronger when the sample is oriented by stretching. Unlike the general tendency, the result of the Nafion+CV showed that the polarization was weakened by stretching, so the cause was considered below.

The relationship between the light absorption (and reflection) of the pigment and the direction of the transition dipole moment of the pigment was investigated in the study by Mizuguchi et al. [14)] Among their papers, it is proposed that light can be absorbed with the same vibration as the direction of the transition moment of the pigment molecule. That is, it is considered that the light vibrating in the same direction as the vibration direction of the bonded electrons of the molecular structure related to the coloration of the pigment resonates, and if the secondary light is emitted, it becomes the reflected light. In such Rayleigh scattering or Thomson scattering, the wavelengths of the resonant light and the reflected light are maintained. In addition, when the properties of the material (ex. pigment) are close to those of metal, the polarized light of the reflected light becomes less polarized like Thomson scattering. The transition moment of the CV is caused by the conjugate of the central methane with the outer phenyl group, but this structure repeatedly shifts to another position at the next moment. Therefore, the direction of the transition moment of one molecule and the average molecular image in the sheet are random and always changing. In this state, it is considered that the reflected light is not very polarized. It is considered that the stretching of the Nafion sheet, which is the support, aligns the directions of the CV molecules, so that the polarization component is reduced and the DOP is also lowered. On the other hand, for the CY in the Nafion+CY, the molecular structure related to coloration almost linearly exists, and therefore, the direction of the transition moment can be determined in one direction. It is considered that the DOP of a molecule having such a transition moment increases when the molecule is oriented due to the stretching of the support.

Summary

In this study, we evaluated the phenomena that a metallic luster was observed from the solid film of a pigment having a molecular structure that did not contain metal elements, and the mechanisms that generated the metallic luster. The polarization reflection characteristics of the polymer sheet were compared using two pigments with different molecular structures. As a result, it was found that, unlike the general understanding, the DOP of CV decreases due to the stretching of the support. Since the direction of the transition dipole moment of the CV molecule is random and always changing, it is possible that the polarization component of the reflected light will decrease as the CV is oriented in a certain direction.

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