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RESEARCH ARTICLE

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Preparation and characterization of Cr_2O_3 system optically variable pigment

Abstract An optically variable pigment was produced by wet chemical method, where TiO_2-coated mica with interference colors acted as the substrate materials. The structure of the pigment was characterized by X-ray diffraction (XRD), and its optically variable effect was investigated by X-Rite MA86 II five angles spectrophotometer. The impact of different interference substrate materials for improving the color travel effect was studied, and the influence of white and black background on the hue and the color travel effect were studied. Results showed that optically variable pigments can be prepared by coating Cr_2O_3 on the surface of the pretreated TiO_2-coated mica. The color travel effect was sensitive to the change of substrate materials, and different backgrounds can influence the hue and the color travel effect of the pigment.

Keywords optically variable, pigment, Cr_2O_3, wet chemical method

1 Introduction

An optically variable pigment is an important functional material, the color and luster of which have strong dependence on the angle of lamp-house or observer. The pigment with multilayer structure is designed on the academic basis of the interferential or diffractive effect between reflective light. Because visible light can be reflected, interfered or absorbed according to the character of each layer, the color of the pigment can obviously change with the angle of viewing [1]. Interference color resulting from the substrate materials is greatly concerned with color travel effect. In case the interference color is different from the absorption color of the surface, it gives various color travel. A more ideal optically variable pigment comprises a five-layer interference structure, which possesses symmetrical distribution. The middle layer structure comprises an opaque reflecting material, and connects orderly with colorless transparent dielectric layers and semi-transparent metal layers [2,3].

Optically variable pigments are mostly made by means of physical or chemical vapor deposition in early days. However, these methods need very rigid technique and equipment, and the accurate control of the thickness and the coated density is necessary for ideal optically variable effect, which seriously holds back the wide application of optically variable pigments [3−8]. The aim of this paper is to develop a simple preparation method and to investigate the influence of different coloration layers on the color travel effect.

In this paper, wet chemical method was used to produce the optically variable pigment, where Cr_2O_3 plays the role of the semi-transparent layers. Moreover, the impact of different interference substrate materials and the influence of white and black background on color travel were analyzed. Because the technique is simple and the raw materials economical, the pigment produced by wet chemical method can hopefully be applied in the manufacture of cosmetic products, plastics, ceramics, car coating and so on.

2 Experiments and characterization

2.1 Preparation of materials

TiO_2-coated mica with different interference colors were used as substrate materials, which are called P2152, P2252, and P2352 in the following. H_3PO_4–H_2SO_4 solution or H_3PO_4–H_2NO_3 solution was added to the powder of TiO_2-coated mica (10−60 μm). The mixture was progressively heated under refluxing and stirring to 80°C for 5−6 h, and then cooled down, filtered, washed and dried [9]. The deionized water was added to the pretreated TiO_2-coated mica to form a 5% concentration serum. The mixture was heated at about 83°C under refluxing and its pH adjusted to 8.7 with NaOH solution. A 5% concentration $CrCl_3$ solution was added to the said

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mixture at certain speed and the pH was adjusted to between 8.5−9.0 with a 5% NaOH solution, resulting in the deposition of $Cr(OH)_3$ to the surface of the TiO_2-coated mica. Charging was stopped when the deposition reached the final thickness, and then aged, filtered, and washed. The coated pigment was then dried and annealed at a certain degree.

The coated card with the 300-μm thick coating was obtained by coating the emulsion at a certain concentration made from the said pigment with the preparation of wet-film.

2.2 Measurement

The structure of the pigment was analyzed by X-ray diffraction (XRD)-6000 (CuKα radiation, 40 kV, 30 mA and a scanning speed of $2.0°\cdot min^{-1}$). The pigments were also characterized by infrared (IR) spectrograph (FTIR-AVATAR 370) from ThermoNicolet Firm, using the following detecting conditions: KBr sheet formatting, scanning range 4 000–400 cm^{-1}, resolution 4 cm^{-1}, scanning times 32. The CIE-L*a*b* data from angles of 15°, 25°, 45°, 75°, and 110°, and the reflectivity of the pigments were measured using a five-angle spectrophotometer (X-Rite MA86 II).

3 Results and discussion

3.1 Structure analysis of pigment

Figure 1 shows the XRD patterns of the substrate material and the pigment, where the main diffraction peak (26.7°) of rutile type titanic dioxide can be observed. However, the diffraction peak of chromic oxide hardly appears. The result indicates that chromic oxide has low content and possesses a non crystalline state on the surface of the substrate material.

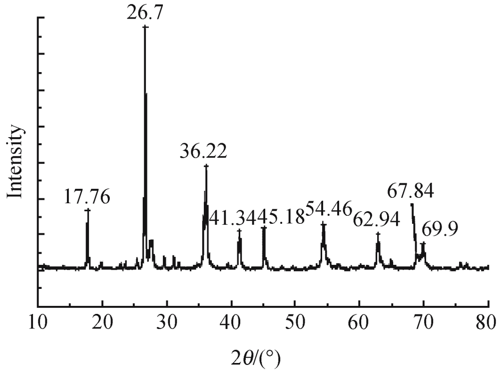

Fig. 1 XRD patterns of P2252

Figure 2 shows the IR patterns of the pigment and substrate material. Compared with the main absorption peak of the substrate material, no new peak appeared in the pigment. It is presumed that there is no chemical bond forming between the substrate material and the coloration layer of chromic oxide and the chromic oxide deposits on the surface of the TiO_2-coated mica by the physical way.

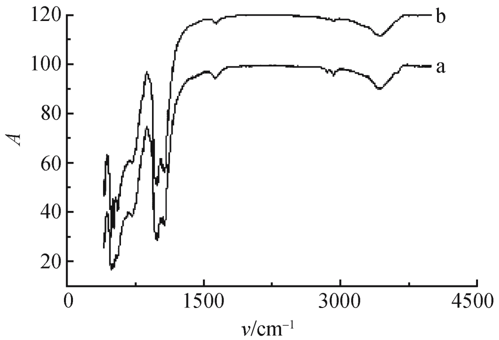

Fig. 2 IR patterns of P2352 (a) substrate material; (b) pigment

3.2 Analysis of reflectivity between white and black background

The reflectivity variations of the P2252 on white and black backgrounds are shown in Figs. 3 and 4. Similarly, in both figures, reflectivity was maximum at 15°, and decreases with angle increase. It shows that such optically variable pigment

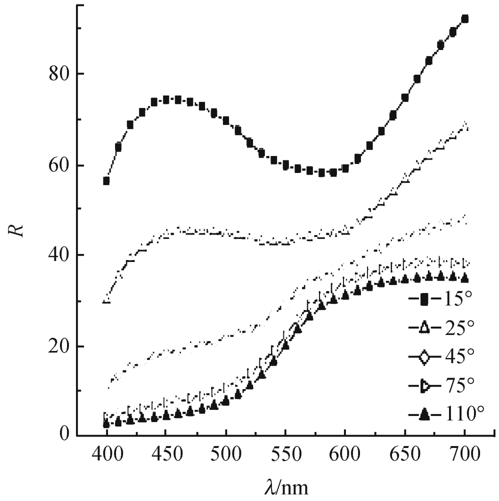

Fig. 3 Reflectivity of P2252 in white background

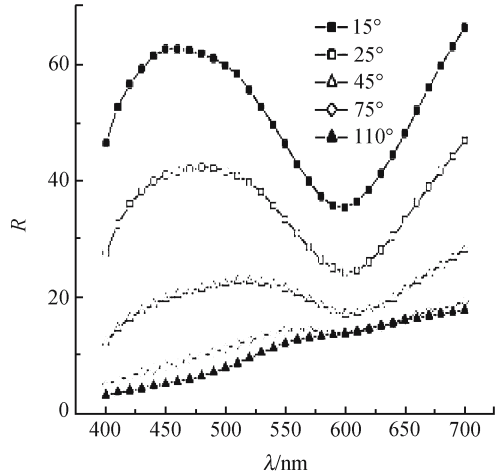

Fig. 4 Reflectivity of P2252 in black background

can display three color variations. The color and reflectivity at 75° and 110° are almost the same, and have the max color variation at 15° and 45°. Moreover, there is also an obvious discrimination in color travel effect between the white and black background. The black background offers a clearer effect on color travel.

The color variation trends of P2152, P2252, and P2352 in the same background are investigated, and the results are shown in Figs. 5 to 7. Obvious differences in reflectivity among the three products can be observed. The reflectivity maximums of P2252 and P2352 can be observed at about 450 and 550 nm, which displayed yellow-green and purple, respectively. Moreover, the P2352 possesses higher reflectivity. However, there is no reflectivity maximum observed in P2152, only a reflectivity minimum at about 500 nm. The results indicate that the interference color of the substrate material influences the color travel effect.

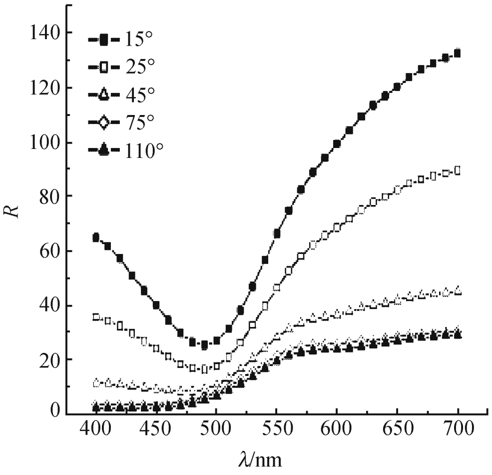

Fig. 5 Reflectivity of P2152 in white background

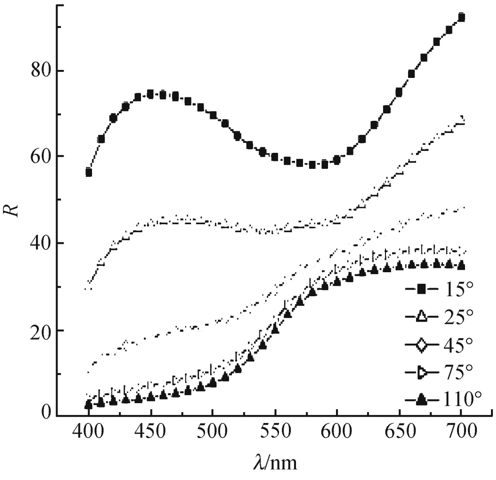

Fig. 6 Reflectivity of P2252 in white background

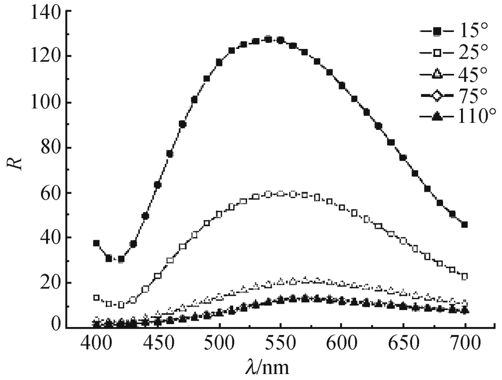

Fig. 7 Reflectivity of P2352 in white background

3.3 The analysis of the CIE chromaticity coordinates

The CIE L*a*b* data of P2252 and P2352 in white and black backgrounds at various angles are shown in Tables 1 to 4. The data indicate that the brightness of the product decreases as the angle of viewing increases, and the variation of brightness is clearer in the black background. The chromaticity coordinates (Fig. 8) show the color travel effect of P2252 in the black background, and the color travel effect from blue-green to yellow-green to orange-red is exhibited distinctly.

Table 1 The value of CIE $L^*a^*b^*$ from P2252 in white background

Angle / (°)	15	25	45	75	110
L^*	83.57	72.84	61.51	54.77	51.87
a^*	1.71	2.98	9.99	15.79	16.94
b^*	−8.72	1.36	20.48	38.14	44.39

Table 2 The value of CIE $L^*a^*b^*$ from P2252 in black background

Angle / (°)	15	25	45	75	110
L^*	74.4	64.4	52.45	43.2	40.18
a^*	−7.78	−9.43	−6.84	−0.99	3.53
b^*	−13.68	−8.94	2.1	14.87	22.01

Table 3 The value of CIE $L^*a^*b^*$ from P2352 in white background

Angle / (°)	15	25	45	75	110
L^*	104.2	83.76	60.57	50.9	49.36
a^*	−16.13	−8.78	3.87	10.81	12.46
b^*	37.36	42	43.28	44.56	46.22

Table 4 The value of CIE $L^*a^*b^*$ from P2352 in black background

Angle / (°)	15	25	45	75	110
L^*	105.59	78.95	50.39	40.78	39.5
a^*	−23.6	−15.82	−5.84	−2.62	−2.28
b^*	35.4	36.44	32.71	30.71	31.4

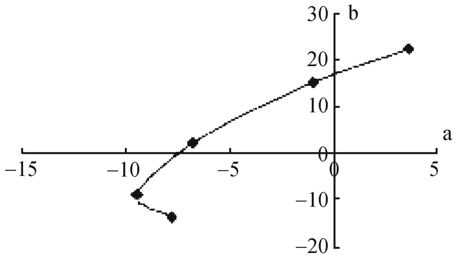

Fig. 8 The value of a*b* from P2252 in black background

3.4 The influence of coloration layers on color travel

The mechanism of exhibiting color in crystal can be summarized as follows: one is ascribed to the electronic transition of the inner crystal under activation of visible light; the other is the result of physical optical effect [10]. The color character of the chromic oxide as a coloration layer has a close relationship with the structure of substrate materials such as agglomeration degree, surface configuration, crystal shape, atomic cluster structure, and ion-coordination structure, as seen in the influence of Cr^{3+} and O^{2-} in octahedron coordination [11]. For chromic oxide crystal, the color exhibited was the result of the d to d transition or charge transfer. Cr^{3+} wavelength of absorbed light in transition is from 600 to 700 nm and from 400 to 500 nm. Therefore, chromic oxide appears green or yellow-green.

The pigment can display color travel effect after being deposited on different oxide films on the surface of TiO_2-coated mica with interference color. Due to the specular total reflection of titanic dioxide, interference color can be observed at the angle of total reflection. More incident light can come into the deeper layer as the angle of viewing shifts. Meanwhile, the reflected light becomes weaker and weaker at diffused angle, and the color becomes darker. At this time, the surface oxide color of titanic dioxide can be observed. Therefore, the hue becomes dark from bright when the angle of viewing shifts from vertical to slantwise.

Figure 9 shows the color travel effect of optically variable pigment coated chromic oxide. The incident light enters the layer of pigment in the order of total reflection, reflection, and interference. The interference color can be observed at a total reflection angle, while the color of chromic oxide can be observed at the diffuse reflecting angle.

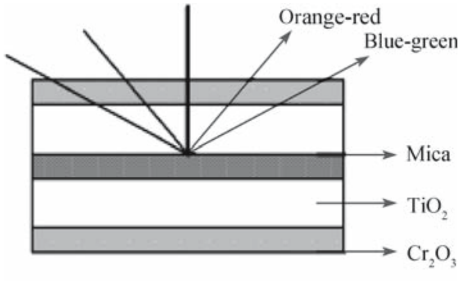

Fig. 9 The color travel effect of optically variable pigment

4 Conclusions

A wet chemical method was successfully applied to coat chromic oxide thin-films on the surface of TiO_2-coated mica with interference color, and an optically variable pigment with perfect color travel effect was produced. The IR pattern indicated that chromic oxide was deposited on the surface of the TiO_2-coated mica through the physical interaction with the substrate. The interference color of the substrate material influences the color travel effect. White and black backgrounds also have a different effect on the hue and the definition of the pigment, with the latter having a more distinct color travel effect and variation of definition.

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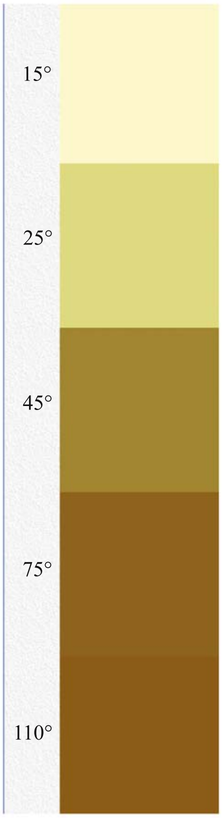
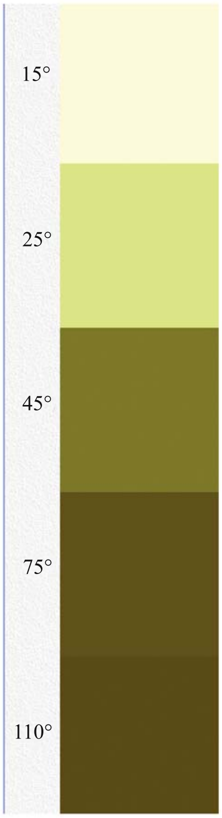
Appendix



P2352 in white background



P2352 in black background