Preparation of Composite Vivid Color Particles without Heavy Metal by Organic Yellow Pigment Coating

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Abstract

Yellow pigments with safe characters, higher chroma with vivid yellowish color, higher tinting strength, and better durability are required especially in the field of color materials. In this paper, we prepared yellow composite particles, by coating titanium dioxide submicron particles with organic yellow pigment particles, assisted by methyltriethoxysilane as an adhesive agent. TEM photographs of the yellow composite particles indicated that the organic yellow pigment particles were adhered to the surface of titanium dioxide particles and formed the shell with uneven shape. The performances such as chroma, tinting strength and durability of the composite particles prepared by organic yellow pigment coating were improved to the same or above the level of conventional inorganic heavy metal pigment particles.

Key words : *Yellow composite particles, Titanium dioxide particles, Organic yellow pigment coating, Adhesive agent*

1. Introduction

Inorganic yellow pigments containing heavy metals such as lead chromate yellow, molybdate orange, bis-muth vanadate yellow and nickel titanium yellow, have good tinting strength and durability. Therefore they have been commonly used in many applications such as paints for outdoors and road marking¹⁾. The use of those pigments is expected to shrink in the future because of the public health and environmental issues, so that alternative yellow pigments are strongly demanded.

Organic yellow pigments²⁾ such as monoazo yellow, disazo yellow, and condensed polycyclic yellow, commonly have higher chroma performance. However those organic yellow pigments have less durability and are more expensive in price compared to inorganic yellow pigment particles. On the other hand, yellow iron oxides, which are known to be superior in safety, tinting strength and durability, are weak in chroma compared

to heavy metal oxides or organic yellow pigments.

In our previous work, we have reported that the green composite particles with higher tinting strength and better durability can be obtained by phthalocyanine coating onto the yellow iron oxide particles³⁾. In this paper, we prepared yellow composite particles having higher chroma by a similar method, in which a vivid organic yellow pigment shell was adhered onto the surface of titanium dioxide core particle using a silane compound as an adhesive agent. The evaluation of the characteristics of derived yellow composite particles was also performed.

2. Experimental

2.1 Preparation and evaluation of yellow composite particles

The granular titanium dioxide (Ishihara Sangyo, Japan) used as a core particle are rutile type particles with an average cross sectional diameter of 250 nm and a specific surface area of 12.3 m²/g. It is surface treated with SiO₂ and Al₂O₃. The titanium dioxide particles were charged in an edge runner mill, and a specified amount of methyltriethoxysilane (GE Toshiba Silicone, Japan) was gradually added as an adhesive agent. The particles were then pulverized to obtain titanium dioxide particles, whose surfaces were covered by methyl-

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silane layer. The silicon content of methyl-silane coated particle was 0.16 wt%. The desired amount of the organic yellow pigment particles of PY 110 (Ciba Specialty Chemicals, Inc., Switzerland), with an average cross sectional diameter of 300 nm and a specific surface area of 45.6 m²/g, was gradually added to the methyl-silane covered particles under continuous pulverizing. The yellow composite particles, which consisted of titanium dioxide particles coated with organic yellow pigment shell, were derived. In these experiments, the coated levels of organic yellow pigment particles were varied from 40 to 120 wt% relative to the titanium dioxide particles. We also prepared physical mixtures of titanium dioxide particles and organic yellow pigment particles without an adhesive agent in the process. The ratio of organic yellow pigment particles and titanium dioxide core of physical mixtures was same as in the coating process. Color, durability and tinting strength of these physical mixtures were compared with the yellow composite particles. In another experiment, organic yellow pigment particles of PY 83 (Fu Tai Chemical Industry Co., Ltd., Taiwan), with an average cross sectional diameter of 100 nm and a specific surface area of 56.4 m²/g were used as pigment shell instead of PY 110.

The amount of organic yellow component in composite particles was measured as carbon content with a combustion-type carbon and sulfur analyzer (Model EMIA-2200, Horiba Ltd., Japan). The silicon content of particles was measured by fluorescent X-ray spectroscopy (Model 3063, Rigaku Denki Kogyo Co., Ltd., Japan) according to JIS K 0119 ("General Rule of Fluorescent X-ray Analysis," Japanese Standard Association, Tokyo, Japan). The state of the organic yellow pigment coated on the surface of composite particles was observed by TEM (Model JEM-100 S, Japan Electron Optics Laboratory, Japan). The oil absorption of particles was measured according to JIS K-5101 (1991).

2.2 Preparation of yellow paints and evaluation of coating films

Yellow paints containing yellow composite particles were prepared with the conventional paint formulation and process as described below. The yellow composite particles, solvents, and a binder resin solution consisting of 50 wt% of amino alkyd resin and 50 wt% of solvents (toluene and xylene) were mixed together. The mixture was dispersed for 45 minutes by Paint-shaker (Toyo Seiki Co., Ltd., Japan) with glass beads of 3 mm diameter. After dispersion, the additional amino alkyd resin solution was added to the mixture. The mixture was diluted and dispersed for another 5 minutes. The mixture was then passed through 0.15 mm

filter to produce the final yellow paint for the full shade enamel. The full shade enamel paint and standard white paint containing dispersed titanium dioxide particles with amino alkyd resin solution were mixed and dispersed for 15 minutes with glass beads of 3 mm diameter to prepare the final diluted yellow paint for the tint shade enamel. The white reduction ratio was 1 : 3 of yellow particles to white titanium dioxide particles. The full shade enamel paint was coated on a substrate at a thickness of 0.15 mm using doctor blade. The coated substrate was dried at 25°C in clean atmosphere and baked at 140°C for 30 minutes to derive the final coated film for several characteristic measurements.

The gloss value at an angle of 60-degree was measured using a glossmeter (Model UGV-5 D, Suga Test Instruments Co., Ltd., Japan). The hue value was measured using a spectro colorimeter (Model CM-3610, Minolta Co., Ltd., Japan) according to JIS Z 8929. The hue values were indicated by colorimetric parameters such as L*, a*, and b*. C*⁴⁾

The difference of L* values between full shade coating and tint shade coating was defined as dL*. The dL* value of yellow composite particles and the dL_s* value of the standard particle were measured in order to determine the tinting strength. The tinting strength value was simply defined by equation (1) in this paper.

$$\text{Tinting strength (\%)} = 100 + ((dL_s^* - dL^*) \times 10)$$

Eq. (1)

The durability was investigated using Super-UV tester (Model SUV-W 13, Iwasaki Electric Co., Ltd., Japan). A coated substrate was irradiated by UV light of 100 mW/cm² for 120 hours, and the hue difference between the initial value and the final value after UV irradiation was measured. The hue difference is defined by equation (2)⁴⁾.

$$dE_{ab} = ((L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2)^{1/2}$$

Eq. (2)

L*, a*, and b* describe the final hue after UV irradiation. L₀*, a₀*, and b₀* describe the initial hue respectively. The smaller dE_{ab} value indicates that the particles have a better durability.

3. Results and Discussion

3.1 Characteristics of yellow composite particles

The key physical properties of yellow composite particles and commercial lead chromate particles are given in **Table 1**. TEM photographs of uncoated titanium dioxide particles, yellow composite particles containing 60 wt% organic yellow shell onto titanium dioxide core particles, and physically mixed particles of the same ratio without adhesive agent are shown in **Figs. 1 to 3** respectively. A TEM photograph of the

Table 1 The powder characteristics of yellow composite particles.

	Yellow composite particle 1	Yellow composite particle 2	Yellow composite particle 3	Yellow composite particle 4	Yellow composite particle 5	Lead chromate particle
Core particle	TiO ₂	TiO ₂	TiO ₂	TiO ₂	TiO ₂	—
Shell material	PY 110	PY 110	PY 110	PY 110	PY 83	—
Amount of shell material relative to core particle (wt %)	120	90	60	40	40	—
Specific surface area (m ² /g)	16.8	15.1	14.6	13.2	15.5	9.1
Oil absorption (ml/100 g)	24	20	17	16	19	29
Pb content (wt %)	0.0	0.0	0.0	0.0	0.0	55.6
Cr content (wt %)	0.0	0.0	0.0	0.0	0.0	2.4
C content (wt %)	22.9	19.7	15.6	12.0	15.4	0.13

Fig. 1 TEM photograph of titanium dioxide core particles. **Fig. 3** TEM photograph of a physical mixture containing titanium dioxide and organic yellow pigment particles (PY 110). **Fig. 2** TEM photograph of yellow composite particles. **Fig. 4** TEM photograph of organic yellow pigment particles (PY 110) as shell material.

organic yellow pigment particles used for coating is shown in **Fig. 4**. The TEM photograph in **Fig. 2** demonstrates that there is almost no free organic yellow pigment particle in the yellow composite particles, which suggests that essentially almost all organic yellow

pigment particles are adhered to the surface of the titanium dioxide particles. The organic yellow pigment shell layer coated on the titanium dioxide surface is in a state of continuous uneven shape. In contrast, when no

Table 2 The colorant characteristics of yellow composite particles and physical mixtures.

	Yellow composite particle 1	Yellow composite particle 2	Yellow composite particle 3	Yellow composite particle 4	Yellow composite particle 5	Lead chromate particle
Hue L* (—)	64.6	64.8	65.2	65.6	64.8	66.5
Hue a* (—)	43.8	43.3	42.7	41.6	43.6	41.1
Hue b* (—)	70.6	68.8	65.9	61.9	69.0	66.5
60 degree gloss (%)	88	93	96	98	96	93
Durability dE _{ab} (—)	0.75	0.96	1.26	1.45	8.36	5.33

	Physical mixture 1	Physical mixture 2	Physical mixture 3	Physical mixture 4	Physical mixture 5
Hue L* (—)	65.8	66.1	65.9	66.3	66.7
Hue a* (—)	42.6	41.6	40.4	38.2	42.6
Hue b* (—)	67.3	64.2	60.9	56.8	62.5
60 degree gloss (%)	73	78	78	84	78
Durability dE _{ab} (—)	1.13	1.46	1.51	1.83	10.33

adhesive agent is used, the organic yellow pigment particles are clearly visible and are not adhered to the titanium dioxide particles.

We postulated that the agglomerated organic yellow pigment particles are broken up by the applied mechanical force and then adhered to the surface of titanium dioxide core particles to form the shell layer by an adhesive layer. It seemed that the organic yellow pigment shell enhanced its tinting strength. We think that the organic yellow pigment shell was fixed closely, and then the increase of specific surface area of the composite particles was very little. We also found that the dispersibility of the composite particles was at almost same level compared to the titanium dioxide core particles.

3.2 Estimation of the mechanism of organic yellow pigment coating

Generally, metal oxide particles, such as titanium dioxide particles, have hydroxyl groups on their surface⁵⁾. The adhesives, such as methyltriethoxysilane, can react with the surface hydroxyl group and cover the surface of the titanium dioxide particle with methyl groups by methaloxyane bonding⁶⁾. The added organic yellow pigment particles are ground by a mechanical shearing force to form clusters. We estimate that these organic yellow clusters are dispersed and strongly adhered to the methyl group.

3.3 Application of the composite yellow particles

The key properties of the coated yellow films with yellow composite particles are shown in **Table 2**. A

Fig. 5 The relation between the amount of organic yellow pigment coating and tinting strength.

second set of samples, which were made using physical mixtures of the same ratio of organic yellow particles and titanium dioxide particles, were prepared to examine the effect of organic yellow pigment coatings. These results were also given in **Table 2**.

A value of 60-degree gloss is an indicator of the dispersibility of yellow particles in paint. The dispersibility of the yellow composite particles was better than that of physically mixed particles at the same composition. **Figs. 5 to 6** indicate the change of tinting strength and chroma value when the amount of coated organic yellow pigment shell was changed from 40 to 120 wt% respectively. The tinting strength and chroma of the composite particles were enhanced compared to the physically mixed particles in all cases. Then the

Fig. 6 The relation between the amount of organic yellow pigment coating and chroma performance.

Fig. 7 The durability properties of several yellow particles.

organic yellow pigment coating was effective on the improvement of yellow colorant performances. The oil absorption levels were almost same as titanium dioxide particles, and a good wetting performance of yellow composite particles was kept in the paint vehicles. The physical mixtures and the raw organic yellow pigment particles have larger oil adsorption amount, and their dispersibilities were worse compared to yellow composite particles.

Figure 7 indicates durable properties of the yellow composite particles, physically mixed particles, and lead chromate particles. The smaller dE_{ab} indicates the better durability. The durability of yellow composite particles was strongly dependent on the type of organic yellow pigment shell. In this experiment, we examined both PY 110 and PY 83 pigment particles as shell material. PY 110 pigment particles are generally more

durable than PY 83¹⁾. As a result, the yellow composite particles made of PY 110 showed smaller dE_{ab} and had better durability compared to the composite particles made of PY 83.

Generally, if organic yellow particles become fine by crushing with higher mechanical force, their durability becomes worse⁷⁾. It is important that the durability of yellow composite particles seemed to be better than that of physically mixed particles when the type of organic pigment shell was same. This is probably because the coated organic yellow pigment shell on the particle surface may be chemically bonded with methyl silane layer and stabilized enough.

4. Conclusion

(1) We have coated organic yellow pigment shell onto titanium dioxide core particles using adhesive agent, and derived vivid yellow composite particles containing no heavy metals, such as lead and chromium.

(2) The tinting strength and chroma of yellow composite particles are better than that of physically mixed particles at the same composition.

(3) The durability of yellow composite particles is influenced by the type of organic pigment particles as shell material. However it is better than that of physical mixture when the same organic yellow pigment shell was used.

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有機黄色顔料被覆による重金属を含まない高彩色複合粒子の調製

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要 旨

近年、黄色系着色材料の分野において、安全で環境影響が少なく、優れた着色力と耐候性を併せ持つ材料が求められている。

本研究では、安全な酸化チタン粒子等の白色無機材料をコア粒子として、その黄色化および諸特性を改善するために、結合剤を使用した有機黄色顔料による表面被覆を検討した。

得られた有機黄色顔料被覆複合粒子の電子顕微鏡観察により、有機黄色顔料は変形して酸化チタン粒子表面に存在していることが確認できた。

有機黄色コーティングによって得られた複合粒子では、その彩度、着色力、および耐候性が優れており、従来の重金属系無機黄色粒子と比較して同等以上の性能が得られていた。