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The preparation and characteristics of cobalt blue colored mica titania pearlescent pigment by microemulsions

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Abstract

Blue pearlescent pigment was obtained by coating microemulsion-synthesized $CoAl_2O_4$ nanoparticles onto mica titania. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) showed that the spherical $CoAl_2O_4$ spinel was around 20 nm and dispersion of the nanoparticles on the coated surface was uniform. EDS revealed that the coating rate and coating efficiency of Co was about 3.12% and 97%, respectively. The study results indicate that the optimum technology parameters were 1:1 $CoO:Al_2O_3$ molar ratio, and the coating ratio of $CoAl_2O_4$ was 3.7–4.6% by weight.

Keywords: Mica titania pearlescent pigment; Cobalt blue; Microemulsion; Preparation

1. Introduction

A new type of pearlescent inorganic pigment, mica titania pearlescent pigment, is obtained by means of coating titania on the surface of mica to produce a more stable pigment of excellent chemical stability [1]. Furthermore, choice of suitable metal oxide to coat on the surface of mica titania will not only lead to aesthetic features but also an optimum coating may be helpful in the improvement of capability. The cobalt blue ($CoAl_2O_4$), a cobalt/aluminum mixed metal oxide, is one of the suitable metal colors. Due to incorrosion of chemical substance, even in solutions of strong hydrochloric acid and alkali, resistant to weathering, sunlight and heat, it is widely used as colorant material in high temperature-resistance paint porcelain enamel, glass, plastic and beaus-artsdyes [2,3]. This oxide colorant is stable to temperatures of 1200 °C.

To date, several methods have been employed to prepare blue mica titania pearlescent pigment. Japanese patent number 60-184570 proposes to gain blue color by reducing the TiO_2 particles on the surface of mica titania in an N_2 environment. United States patent 3,951,679 introduced the method of coating mica titania using iron blue, while Tan Junru et al. [4] adopt the liquid phase method to synthesize cobalt blue mica titania pearlescent pigment with urea as precipitant at 60–70 °C. However, these preparation methods are complicated or require specialized equipment. Microemulsion method offers several advantages: processing requires no extremely corrosive, toxic, or exotic compounds, no extreme pressure, no need for critical temperature control, easy handling, and requires no special or expensive equipment, and uniform in particle size. In general, microemulsion is an isotropic process. The reaction will occur in controlled manner in the micelles which have size in order of nanometers, resulting in formation of nanoparticles of controlled characteristics [5,6]. In this paper, cobalt blue mica titania pearlescent pigment was synthesized in a microemulsion system at room temperature. Also optimum preparation conditions would be discussed.

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2. Experimental section

2.1. Microemulsion system

Two different microemulsion systems were employed to prepare cobalt blue precursors. The first system (A) composed of oleic acid, butanol and Na_2CO_3 (1 mol L^{-1}) aimed to dissolve Co^{2+}, while the second system (B) is the mixture of oleic acid, butanol and NaOH (4 mol L^{-1}) to dissolve Al^{3+}. Oleic acid and butanol are miscible. When NaOH or Na_2CO_3 is added, the following reaction occurs:

$$CH_3(CH_2)_7{-}CH{=}CH(CH_2)_7{-}COOH + NaOH \rightarrow CH_3(CH_2)_7{-}CH{=}CH(CH_2)_7{-}COONa + H_2O$$

$$2CH_3(CH_2)_7{-}CH{=}CH(CH_2)_7{-}COOH + Na_2CO_3 \rightarrow 2CH_3(CH_2)_7{-}CH{=}CH(CH_2)_7{-}COONa + H_2O + CO_2\uparrow$$

In these microemulsion systems, sodium oleate is the surfactant, and butanol is used as oil phase. Fig. 1a and b shows the ternary phase diagrams of the above-mentioned two microemulsion systems. It suggests that the range of single-phase area become maximal when the volume ratio of oleic acid to butanol is 1:1. The maximum range will give rise to the stable single-phase preparation system.

2.2. Cobalt blue preparation

$CoCl_2$ and $Al_2(SO_4)_3$ (0.2 mol L^{-1}) were added to microemulsion systems (A) and (B), respectively. These two microemulsions were mixed and pH adjusted to 9. Then the mica titania was added. The mixture was stirred for 0.5 h. Powder samples were obtained by flocculating the colloids with acetone, followed by separation in a high speed centrifuge at 4000 rpm for 30 min. Filtrate could be collected for reusing oil phase by adding HCl. The precipitates were collected, washed with the acetone and then dried at 383 K for 3 h. The dried precipitates were calcined at 1273 K for 2 h for complete conversion into $CoAl_2O_4$.

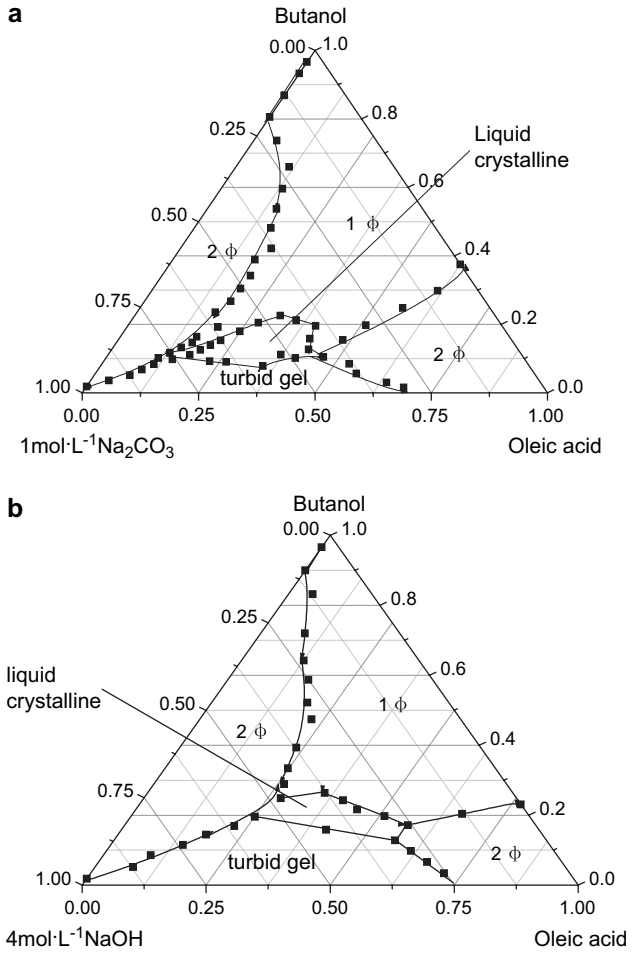

Fig. 1. Ternary phase diagram for (a) microemulsion (A): oleic acid, butanol and Na_2CO_3 (1 mol L^{-1}) and (b) microemulsion (B): oleic acid, butanol and NaOH (4 mol L^{-1}), at 303 K. 1Φ, single phase; 2Φ, biphase.

Measurement of the size of cobalt blue particles coated on the surface of mica titania was performed on a S-550 scanning electron microscope (Hitachi, Japan). The surface components of colored pigment were measured on an INCA300 energy-spectrum apparatus (OXFORD company, England). Precursor thermal behaviors were investigated at a heating rate of 10 °C/min in N_2 on an STA449C TG/DTG (NETZSCH, Germany). X-ray diffraction spectroscopy was obtained from an XRD-3A diffraction meter using Cu Kα radiation ($r = 0.154178$ nm,

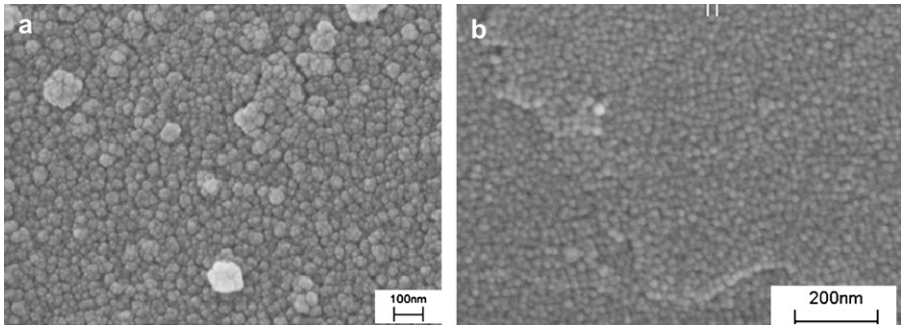

Fig. 2. The SEM micrographs for (a) mica titania pearlescent pigment and (b) cobalt blue mica titania pearlescent pigment.

Shimadzu, Japan). The spectral reflectance of the pigment was measured on color-measuring apparatus JFY-AB_1.

3. Results and discussion

3.1. Analysis of the colored pigment

Fig. 2a and b shows SEM micrographs of the mica titania pearlescent pigment and the cobalt blue colored pigment, respectively. It could be seen that the cobalt blue colored pigment displays compacted and even dispersion on the surface of mica titania. The diameter of particles is about 20 nm, suggesting that cobalt blue particles are in controlled nanosize domains, which lead to the excellent pearlescent luster of cobalt blue colored pigment, for size is threshold for coating particles to start interfering with pearlescence. The surface components of colored pigment, measured on an energy-spectrum apparatus (EDS), are listed in Table 1.

The coating ratio is also called the weight ratio of $CoAl_2O_4$ to total weight of $CoAl_2O_4$ colored pigment. In this paper, 1.0 g mica titania pigment, 3 mL 0.2 mol L^{-1} $Al_2(SO_4)_3$ and 3 mL 0.2 mol L^{-1} $CoCl_2$ in microemulsion systems were employed to prepare colored pigment. If the mica titania is colored by Co^{2+} completely, the theoretic coating ratio of Co^{2+} in the colored pigment should be:

$$\frac{0.003 \times 0.2 \times 59}{1 + 0.003 \times 0.2 \times 59 \times \frac{75}{59} + 0.003 \times 0.2 \times 2 \times 27 \times \frac{102}{54}} \times 100 = 3.20\%.$$

In this equation, numerator is the weight of Co added in the experiment, and denominator is the total weight of cobalt blue colored mica titania pearlescent pigment.

So the coating efficiency (which means the ratio of theoretic to experimental) is $(3.12/3.20) \times 100 = 97.5\%$; 3.12% is the weight ratio of Co by EDS, and 3.20% is the calculated ratio above.

Fig. 3 shows the X-ray diffraction pattern of the cobalt blue colored pearlescent pigment, where 2θ is in the range of 10–60°. The peaks near $2\theta = 36.8°$ ($d = 2.44$) and $2\theta = 31.2°$ ($d = 2.88$) are attributed to characteristic diffraction of $CoAl_2O_4$, while the peaks at $2\theta = 25.5°$ ($d = 3.52$) and $2\theta = 27.4°$ ($d = 3.25$) are due to anatase and rutile TiO_2. The results reveal that the $Co(OH)_2$ and $Al(OH)_3$ precursors convert to spinel $CoAl_2O_4$ during calcinations.

Table 1
Elements of sample by EDS

Elements	Wt%
O	31.64
Al	15.07
Si	17.24
K	13.00
Fe	1.42
Ti	18.51
Co	3.12

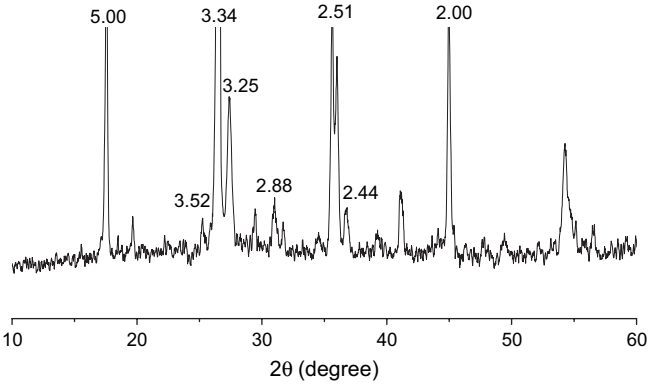

Fig. 3. X-ray diffraction patterns of the sample.

3.2. Thermal analysis of precursors

Thermal decomposition curves of the precursor in N_2 are shown in Fig. 4. The two prominent changes in the TGA curves, corresponding to the two peaks on the DTG curves, indicate that the thermal decomposition of $Co(OH)_2$ and $Al(OH)_3$ precursors is a two-step process. The first one at 0–500 °C is mainly due to removal of adsorption water, while the second at 500–1000 °C should be assigned to dehydration of $Co(OH)_2$ and $Al(OH)_3$.

3.3. Influence of experimental conditions on pigment color

3.3.1. The mole ratio of CoO to Al_2O_3

When molar ratios of Co^{2+} and Al^{3+} are varied with other experimental conditions held constant, the spectral reflectance of the resulting pigment varies greatly. As shown by the curves in Fig. 5, pigment color is mainly green when $CoO:Al_2O_3 > 1$. If $CoO:Al_2O_3 \leq 1$, the pigment color shifts to blue. The brightness of pigment will be enhanced along with an increase in the ratio of Al_2O_3. Reflectance curves also show that the pigment color is strongest as $CoO:Al_2O_3 = 1$.

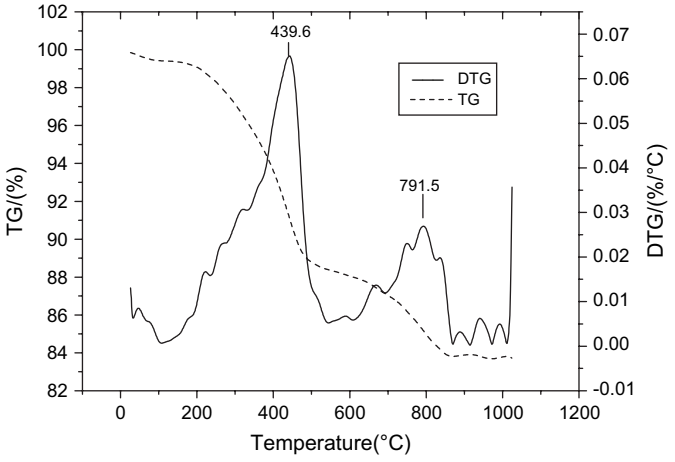

Fig. 4. TGA and DTG curves of the thermo-oxidative decomposition of precursor. Weight loss (TG%) and DTG (%/°C) are expressed on the vertical axis as a percentage of the initial weight and dw/dt, respectively, Temperature (T) is expressed on the horizontal axis in °C.

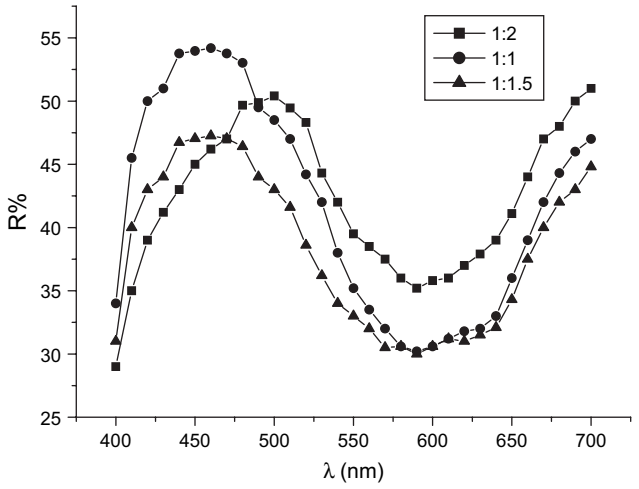

Fig. 5. The sample's spectral reflectance curves with different mole ratio of $CoO:Al_2O_3$.

3.4. $CoAl_2O_4$ coating ratio

The coating ratio of $CoAl_2O_4$ to mica titania is another important influence on pigment color. The quantity of coated $CoAl_2O_4$ on mica titania substrate will affect the hue and brightness of the pigment. The ratio of the weight of coated $CoAl_2O_4$ to the weight of pigment after coating is called the coating ratio. With other experimental conditions fixed and provided that $CoO:Al_2O_3 = 1:1$, we change the added quantity of Co^{2+} and Al^{3+} and measure the spectral reflectance of the sample. Influence of coating ratio of Co on the color of pigment is shown in Table 2. Fig. 6 illustrates pigment color variability as a function of coating ratio, colored pigment reflectance will reach the maximum in the range of blue wavelength of 400–500 nm. Accordingly, the highest reflectance is consistent with the ideal, saturated, bright pearlescent pigment.

Color results selective absorbing and reflecting to different wavelengths in the visible spectrum. The sharper the reflectance curve peaks, the brighter the color [7]. And in $CoAl_2O_4$ crystal, it is well known that the chromophore is

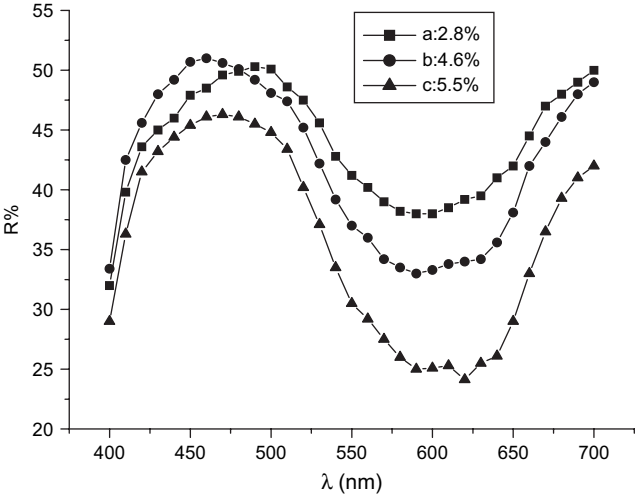

Fig. 6. The sample's spectral reflectance curves with different coating ratio of Co.

Table 2
Influence of coating ratio of Co on the color of pigment

Theoretical coating rate of Co (%)	Color
2.8	Light blue
3.7	Bright blue
4.6	Bright blue
5.5	Dark blue

not Al^{3+}, O^{2-} but Co^{2+} for the Co ion has electrons in 3d orbitals. According to crystal field theory, the coordination agent would redistribute the energy of 3d orbitals (d_{xy}, d_{zx}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2}) of Co atom or ion. The availability of electron density from the other atoms in the crystal structure lowers the d → d* bandgap to energies coincident with photons of the visible spectrum. Like in tetrahedron crystal field, the energy of d_{xy}, d_{zx}, d_{yz} would increase, while the energy of $d_{x^2-y^2}$ and d_{z^2} would decrease; the difference between them is the so-called split energy. The value of split energy is closely related to the surrounding coordination agents and the magnitude of available electron density from other crystal atoms. The mole ratios of CoO to Al_2O_3 and coating ratios would result in the magnitude of coordination agents to Co ion, which maybe due to the difference of pigment color.

4. Conclusion

Excellent blue pearlescent pigment was obtained by coating $CoAl_2O_4$ nanoparticles onto mica titania through use of a microemulsion system. Spherical spinel $CoAl_2O_4$ particles were around 20 nm, as determined through X-ray diffraction. The dispersion of the nanoparticles on the coated surface was revealed to be even by scanning electron microscopy. The results of EDS suggested that the coating ratio and coating efficiency of Co is about 3.12% and 97%, respectively.

Acknowledgements

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