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The preparation and characteristics of a multi-cover-layer type, blue mica titania, pearlescent pigment

Tan Junru*, Fu Xiansong, Hou Wenxiang, Chen Xiuzeng, Wang Li

Department of Chemistry, College of Science, Tianjin University, Tianjin, 300072, PR China

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Abstract

This paper describes an experimental method for preparing mica titania pearlescent pigments in which the substrate is coated with iron blue. The parameters that affect the pearlescence and hue of the compounds are discussed. This paper also studies the heat-resistance of the pigments and describes a method to prevent discoloration. Furthermore, the nucleation process of the iron blue precursor (i.e. white brei) is discussed.

Keywords: Iron blue; Mica titania pearlescent pigment; Homogeneous nucleation; Heterogeneous nucleation; Hue; Reflectivity

1. Introduction

A new type of pearlescent inorganic pigment, mica titania pearlescent pigment, is gaining in popularity because of its excellent chemical stability [1]. Mica titania pearlescent pigments are classified into three types according to the method of preparation used: *silver white type, iridescent type* and *coloring type* [2]. Silver white pearlescent pigments are the most common types and can be used in metal actinic lacquers. By controlling the thickness and the order of the composite oxide particle layers, iridescent pearlescent pigments can be obtained which show colour changes from gold, red, purple, blue to green. The majority of coloring pearlescent pigments are made from a coloured metal oxide coating on a mica substrate of high reflectance ratio. The blue mica titania pearlescent pigment discussed in this paper comprises mica titania as the substrate and is prepared by laying a particle layer of blue $Fe_4[Fe(CN)_6]_3$ (i.e. iron blue) on its surface. Due to the absorption and reflection of light in this layer, the pigment is termed a coloring pearlescent pigment. This pigment is widely used in many fields such as paints, resins, cosmetics, etc. This work concentrates on the method of preparing the pigment and the factors that affect its properties. Furthermore, the nucleation process of the iron blue precursor (white brei), the heat-resistance of the pigment and a means of preventing pigment discoloration during filtering and washing are discussed.

2. Experimental

2.1. Raw materials and reagents

Silver white, mica titania pearlescent pigment (70–100 μm) self-made, $TiCl_4$ industrially

* Corresponding author.
E-mail address: tjunru@yahoo.com (T. Junru).

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pure, $K_4[Fe(CN)_6]\cdot 3H_2O$, $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, $Na_2HPO_4\cdot 12H_2O$, $KClO_3\cdot 3H_2O$, $CH_3COONa\cdot 3H_2O$, NaOH, HCl chemically pure.

2.2. The preparation method

The suspending liquid was prepared by adding de-ionized water to 3.0 g mica titania at a solid: liquid ratio of 1:25, and the suspending liquid was heated to 60–70 °C in the reactor by water bath. We then added a small amount of Na_2HPO_4 and CH_3COONa as a buffering agent to keep the pH value at 5–6, and we dripped 12 ml $(NH_4)_2Fe(SO_4)_2$ liquid of 3% with certain concentration and certain volume and stirred for 10 min. After that, we dripped $K_4[Fe(CN)_6]$ liquid using the same method. The precipitate generated at this time is white $Fe_2[Fe(CN)_6]$, which is called white brei or iron blue precursor (but because Fe^{2+} is partially oxidized in the air, it appears as light blue green). Continuing to stir for 30 min, we adjusted the pH value to less than 3 by adding diluted HCl. We then added $KClO_3$ liquid of 2.4% and let it react for 1 h. After this we added a small amount of $TiCl_4$ liquid of 10% in the range of pH value 2.1–2.5. We continued to stir for 30 min. Finally, we filtered the liquid, washed the filter cake and dehydrated it at 80 °C. At this point, we got the pigment. The following were all prepared according to the method discussed earlier. The main reactions are:

$$2FeSO_4 + 2K_4[Fe(CN)_6] \rightarrow 2K_2SO_4 + Fe_2[Fe(CN)_6]\cdot K_4[Fe(CN)_6]\text{(white)} \quad (1)$$

$$3Fe_2[Fe(CN)_6]\cdot K_4[Fe(CN)_6] + 6HCl + KClO_3 \rightarrow 6KFe[Fe(CN)_6]\text{(blue)} + 7KCl + 3H_2O \quad (2)$$

$$Mica/TiO_2 + KFe[Fe(CN)_6] + TiO_2 \rightarrow Mica/TiO_2/KFe[Fe(CN)_6]/TiO_2 \quad (3)$$

2.3. Analysis

The light transmittance of filter liquor and mother liquid are measured by 721 spectrophotometer. The pigment particle surface pattern is observed by Environment Scanning Electronic Microscope XL30. The appearance and particle size of the membrane particle are observed by JEDL100cx II transmission electron microscope. The thermal decomposition of coated iron blue is studied by WCT-1 microcomputer differential thermal analytical balance and BDX3300 X-ray diffraction apparatus. The reflectivity of pigment and chromaticity coordinate is measured by a color photometer. The hue (H), brightness (V) and chroma (C) are calculated using brightness diagram of Munsell.

3. Conclusion and discussion

3.1. The color characteristics of pigment

We measured the colors' tri-stimulus values (X, Y, Z) and chromaticity coordinate (x, y, z) of the pigment using JFY-AB_1 color analysis apparatus and D_{65} illuminant, then we calculated the hue (H), brightness (V) and chroma (C) using brightness diagram of Munsell. The results are shown in Table 1.

3.2. The factors that affect the hue and pearlescent effect of pigment

3.2.1. Reaction temperature

With other experimental conditions fixed, we changed the reaction temperature and measured the average reflectivity and hue of the pigment. The results are shown in Table 2. The pigment's pearlescent effect is related with its reflectivity, the larger the reflectivity, the better the pearlescent effect. From Table 2, we can see that reaction temperature has no obvious effect to the hue of the pigment, while average reflectivity is decreased with temperature increasing, and the pearlescent effect becomes worse. This is because this reaction is a precipitation reaction, precipitation decreases with temperature increasing; when the temperature

Table 1
The characteristics of color

Lightness factors (L)	Tri-stimulus values			Chromaticity coordinate		Messell marking
	X	Y	Z	x	y	$H\ V/C$
51.30	17.28	19.52	34.67	0.2418	0.2732	8.9B 7.5/6.45

increases, the solubility of $Fe_4[Fe(CN)_6]_3$ increases relatively, the precipitate lessens and the membrane becomes uneven. The most important is that increasing temperature causes the flocculation of the colloid particle, then the particle becomes larger, and the membrane on substrate surface becomes loosen. Due to an increasing amount of holes, the reflectivity decreases and pearlescent effect becomes worse. For the above reasons, we chose reaction temperature as 60–70 °C.

3.2.2. The proportioning of materials

The proportioning of materials means the mass ratio of Fe^{2+} ion in $(NH_4)_2Fe(SO_4)_2$ and $K_4[Fe(CN)_6]$ liquids with same volume. With other conditions fixed, we changed the proportioning of materials and measured reflectivity and hues of the pigment. The results are shown in Table 3. From Table 3, it can be seen that when mass ratio of Fe^{2+} ion in two liquids is 1.2:1, the pearlescent effect and hue are the best. In the reaction process, the amount of $(NH_4)_2Fe(SO_4)_2$ is excess so that $K_4[Fe(CN)_6]$, which is very expensive, can be fully utilized and the precipitate is complete. But too much $(NH_4)_2Fe(SO_4)_2$ will cause a salt effect which can make the precipitate solubility increasing and affect the densification of membrane layer. So we chose the proportioning of materials as 1.2:1.

Table 2
The relation of reaction temperature and reflectivity and hue

Reaction temperature/°C	Average reflectivity/%	Hue (H)	Pearlescent effect
60	31.36	7.9B	Best
70	32.55	8.0B	Good
80	29.58	7.5B	Better
90	28.74	8.0B	Better

Table 3
The relation of proportioning of materials and reflectivity and hue

Mass ratio of Fe^{2+} ion	Average reflectivity/%	Hue (H)	Pearlescent effect
1.20:1	32.55	8.0B	Best
1.35:1	31.19	7.0B	Good
1.40:1	30.47	6.5B	Better

3.2.3. The amount of added materials

With other conditions fixed, we changed the amount of added $(NH_4)_2Fe(SO_4)_2$ and $K_4[Fe(CN)_6]$ (The volume of them are same). Then we measured the reflectivity and hue of the pigment, and the results are shown in Table 4. From Table 4, it can be seen that with the increase of amount of added materials, the average reflectivity of the pigment decreases, the pearlescent luster decreases, while the hue becomes darker. According to the relation among the strengths of reflecting light, transmitting light, scattering light and absorbing light, the strength of incident light $I = S + T + D + A$ [3], where S, T, D, A represent

Table 4
The relation of amount of added material and reflectivity and hue

Amount of added material/ml	Average reflectivity/%	Hue (H)	Pearlescent effect (relatively)
10	20.15	5B	Good
15	17.40	8.7B	Average
20	17.09	9.0B	Average

Table 5
The relation of stirring rate and reflectivity and color

Stirring rate (r/min)	Light transmittance of mother liquid/%	Average reflectivity/%	Messell marking *H V/C*
80	98.0	26.84	6.4B 8.0/6.00
160	97.5	25.46	6.5B 7.9/5.95
180	96.5	26.10	7.3B 7.9/6.00
250	95.0	26.68	7.3B 8.0/6.05
330	89.0	40.28	5.0B 8.6/2.80

the strength of reflecting light, transmitting light, scattering light and absorbing light respectively. When I is fixed, the thicker the membrane layer, the larger the value of A, while the smaller the values of S and T. Because T decreases, there is less incident light traveling through the membrane layer and arriving at the surface of mica substrate. Thus, the strength of reflecting light generated at the surface decreases, the reflection and interference action weaken, and the pearlescent effect becomes worse. With the thickening of the membrane layer, the strength of absorbing light increases, and the hue becomes darker.

Considering both the hue and pearlescent effect, we chose the amount of added material as 10–15 ml.

3.2.4. Stirring rate

With other conditions fixed, we changed the stirring rate, and then measured the reflectivity and the color of pigment. The results are shown in Table 5. From Table 5, the pigment's hue and chroma are worst when stirring rate is 330 r/min, and the light transmittance of mother liquid is the lowest. This shows that there is some tiny colloid micro-particle entering the solution through the filter paper rather than depositing on the surface of substrate. The fact that the average reflectivity under this condition is the largest also confirms this result. Since the coating layer is very thin, the absorbency of light decreases, while the reflectivity increases. The stirring rate affects the densification of membrane layer directly. If the stirring rate is too low, the reaction solution cannot form the turbulence [4], then the microcosmic mixture is uneven, and the generated crystal particles are of various sizes. On the other hand, if the stirring rate is too high, it will affect the growing rate of crystal nucleus, and then the tiny particles are free in the solution, which will cause the scatter to the light. Therefore, the stirring rate in this reaction should be 180–250 r/min.

3.3. The precaution to prevent discolor from washing

3.3.1. Adding $TiCl_4$

After iron blue coating, the mother liquid is almost of no color or with a little blue when filtering. But in the process of washing filter cake, the problem of discoloring of the pigment is very serious. The light transmittance of washing liquid is 65%, this means that there are coated iron blue particles falling in the solution, which makes membrane layer uneven and affects the pearlescent effect. To prevent this problem, after coating mica titania using iron blue, we adjusted pH value to 2.1–2.5 and dripped a small amount of 10% $TiCl_4$. This generated a very thin layer of TiO_2 on the surface of iron blue, which was like a barrier between iron blue coating layer and water to prevent discoloring. We measured the light transmittance of mother liquid and washing liquid, which are 80 and 65%, respectively without adding $TiCl_4$, while 98 and 100% with adding $TiCl_4$.

3.3.2. The relation of amount of added $TiCl_4$ and reflectivity and hue

After completing coating the mica titania with iron blue using the earlier optimal conditions, we changed the amount of added $TiCl_4$ solution and measured the reflectivity and hue of the pigment. The results are shown in Table 6. From Table 6, it can be seen that when we added 2 ml $TiCl_4$ of 10%, the quality of the pigment was the best.

3.4. The analysis of nucleation process of iron blue precursor and iron blue coated mica titania

Homogeneous nucleation means that, in a uniform system without phase surface, phase is changed spontaneously and crystal nucleus are

Table 6
The relation of amount of added $TiCl_4$ and reflectivity and hue

Amount of $TiCl_4$/ml	Average reflectivity/%	Hue	Light transmittance of washing liquid	Pearlescent effect
10	23.41	Blue-green	100	Bad
5	28.61	Blue-green	100	Average
3	32.47	Light blue	100	Best
2	31.75	Blue	100	Good
1.5	30.98	Blue	98.5	Better

generated [5]. When the product of square of Fe^{2+} ion and $[Fe(CN)_6]^{4-}$ ion is equal or greater than its solubility product, $[Fe(CN)_6]$ crystal nucleus are generated, while the generated $[Fe(CN)_6]$ molecule diffuses to the surface where already forms the crystal nuclei and locates on the surface of crystal nuclei according to specified crystal structure, then the precipitate motes are formed. In the following process of precipitate motes' continuing growing, the ions to form crystal generate the crystalline precipitate by directional arrangement according to certain crystal lattice [6]. This process is homogeneous nucleation. After adding mica titania, due to the existence of different phase surface, the generation of white brei is heterogeneous nucleation. Comparing homogeneous nucleation and heterogeneous nucleation, the latter is easier than the former. This can be explained by the thermodynamics of phase transformation, the new phase exists and grows stably, so when the critical nucleus is formed, the changing process of free energy of system will experience a maximum value, i.e. nuclear barrier [7]. To homogeneous nucleation, its nuclear barrier is

$$\Delta G_{\mathrm{r}}^{*} = \frac{16\pi\gamma_{\mathrm{Ls}}^{3}}{3(\Delta G_v)^2} \tag{4}$$

where $\Delta G_{\mathrm{r}}^{*}$ is nuclear barrier of homogeneous nucleation, γ_{Ls} is interfacial energy of liquid–solid, ΔG_{v} is the change of free energy per unit volume except interfacial energy when there is liquid–solid phase change. To heterogeneous nucleation, the nuclear barrier is

$$\Delta G_r = \frac{16\pi\gamma_{\mathrm{Ls}}^{2}}{3(\Delta G_v)^2} \times \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} = \Delta G_r^{*} f(\theta) \tag{5}$$

where $f(\theta) = (2+\cos\theta)(1-\cos\theta)^2/4/4$, θ is the contact angle of new phase nucleus and nucleation matrix. Forming crystal nucleus must overcome the energy of forming crystal and potential energy barrier on the surface. Comparing Eqs. (4) and (5), since $f(\theta) < 1$ the nuclear barrier of heterogeneous nucleation is small, and this is helpful for generating nucleus.

3.5. The study of the heat-resistance of the pigment

Calcining the pigment prepared under the earlier optimal conditions for 1 h at 150, 200, 250 and 300 °C in the air. The result shows that when the temperature is lower than 200 °C, there is not much change in the color of the pigment. At 250 °C, there still keeps partial color, but the blue is completely faded at 300 °C. Fig. 1 is X-ray diffraction diagram at 150, 250 and 300 °C.

In Fig. 1, the peak of diffraction (2θ) with 17.45° is the characteristic diffractive peak of $KFe[Fe(CN)_6]$. With temperature increasing, the peak value decreases until the peak disappears.

Because there was not much iron blue in iron blue coating mica titania pearlescent pigment, we did the thermogravimetric analysis of pure iron blue to study its decompose characteristics, which is shown in Fig. 2.

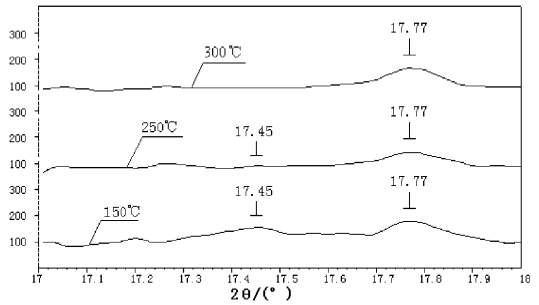

Fig. 1. X-ray diffraction diagram of blue pearlescent pigment.

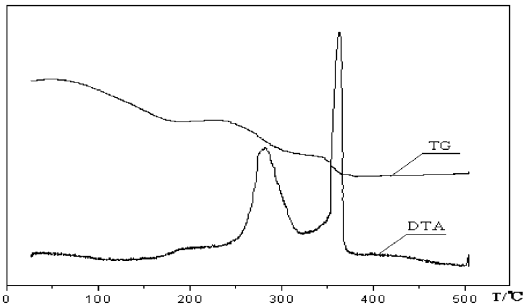

Fig. 2. TG curve of blue pearlescent pigment.

From Fig. 2, it can be seen that there are three weight loss steps. The author believes this is because CN^- is oxidized in steps. There are two strong exothermic peaks in DTA curve, and it reaches constant weight at 375 °C, the final product is Fe_2O_3, and CN^- is oxidized into CO_2 and N_2. We did the infrared absorption spectrum of calcined sample at 400 °C and found that CN^- vibrating peak disappears at 2086.03 cm^{-1}, this means that CN^- is oxidized completely in this condition. So the heat-resistant temperature of iron blue coating mica titania pearlescent pigment is 200 °C. In TG curve, the weight loss at 104–178 °C is de-adsorption water, while the weight loss happened higher than 230 °C is the destruction of iron blue structure and decomposes completely when it reaches constant weight at 375 °C. At this period, the combination and decomposition coexist. There are two exothermic peaks in DTA curve but no absorbency peak. This is because that the heat quantity of combination is greater than that of decomposition. The first exothermic peak is caused by the oxidation of part CN^-, while the second one is caused by the oxidation of the rest CN^- and the oxidation of iron. This further proves that the CN^- in iron blue is decomposed by stages. The result of thermogravimetric analysis is consistent with the result of X-ray diffraction diagram.

4. Conclusions

The optimal parameters for preparing iron blue coated mica titania pearlescent pigment using 3.0 g mica titania as raw material are: a reaction temperature of 60–70 °C, the proportion of materials is 1.2:1, the amount of added materials is 10–15 ml, adding speed of $(NH_4)_2Fe(SO_4)_2$ is 6 ml/min and adding speed of $K_4[Fe(CN)_6]$ is 1.2 ml/min, and the stirring rate is 180–250r/min. To prevent pigment's discoloring in filtering and washing, 2 ml of 10% $TiCl_4$ solution is added. The nucleation of iron blue precursor is homogeneous nucleation, while the nucleation of iron blue coating mica titania is heterogeneous nucleation. The heat-resistant temperature of the pigment is 200 °C.

References

[1] Xu Y. Mica-TiO_2 pearlescent pigments and its application in metallic paints. Paint and Coatings Industry 1995;6:24–5.
[2] Hao H., Xiong G., Tang Z. et al., Research and application of mica pearlescent pigments, Dyestuff industry, 35(6):23–26.
[3] Miller HA. optical property of pearl pigment GFR. Farbe lack 1987;12:93.
[4] Xiong Y, Zhou X, Hu L. Study on the process of the Ultrafine α-FeOOH synthesis by dripping method. Journal of East China University of Science and Technology 1996;22(5):541–7.
[5] Wei Z, Lei Y, Li X, et al. The Pilot test of nanometer-size Zinc Oxide Prepartion. Inorganic Chemicals Industry 1999;31(5):8–10.
[6] Zhang J. Study on selection of synthetic conditions of nanometer-size MgO. Inorganic Chemicals Industry 1999; 31(2):3–5.
[7] Zhejiang University, et al. Water-glass physical chemistry. Beijing: China Building Material Industry Publishing Company; 1980.