

A study on pearlescent performance of green black coating layer on micron glass

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Preparation of pearly green black pigment (micron glass/nano-Fe₃O₄) can be carried out by a green process: eroding the micron dimension glass first, then second co-precipitating ferrous and ferric ions on the eroded substrate, which should minimize long and short-term impacts on the environment. The pearly green black pigments were characterized by XRD, HRSEM and color measurement, and the content of Fe₃O₄ coating layer can be calculated by using external standard calibration method.

Keywords: Micron Glass; Fe₃O₄ Coated Layer; Green Pearlescent Pigment; Minimize Impacts on the Environment.

1. Introduction

As black perspectives for a green future, Fe₃O₄ is an important ferrite with a cubic inverse spinel structure, which makes Fe₃O₄ an important semimetal material [1]. A hypothesis is proposed which suggests pearlescent pigments with high performance could be prepared using micron dimension glass as substrate in place of the mica to develop third-generation pearlescent pigments for obtain more pearlescent luster. So in this paper, the micron dimension glass was first pretreated with sodium hydroxide solution and KF solution under ultrasonic treatment in proper order. Then the pearlescent pigment was prepared by co-precipitation of Fe₃O₄ coating on the surface of eroded micron dimension glass according to our previous work [2], the final product was filtrated and washed, following dried at 60 °C, and calcined for 3 hours at 350 °C under nitrogen in tube furnace. The results showed typically spherical micro-sized particles are generally obtained, which can be considered as green, black natural pigmen.

2. Experimental

2.1. Coating of Nano-Fe₃O₄ on micron glass

(1) Micron glass was placed into three small plastic beakers(10g each), and washed under ultrasonic treatment in NaOH solution(0.5mol/l) for 5min, 15min, 20min, respectively, and then filtrated, washed and dried at 80 °C.

(2) After surface dirt was removed from micron glass powder in the same way, KF solution (80ml, 1mol/l) and concentrated sulfuric acid (3ml) were added into the six plastic beakers each containing 10 g micron glass. Then the mixtures were stirred for 2min, 5min, 8min, 8min, 8min and 8min respectively. The eroded micron glass was filtrated, washed and dried at 80 °C, and kept until use.

(3) Synthesis of Micron Glass/Nano-Fe₃O₄

The suspension of boiled deionized water and 10 g eroded micron glass powder were formed by magnetic stirring. The typical coating experiments were performed according to our previous work [3], the specific conditions were described as following, the C_(NaOH) was 0.5 mol/L and the molar ratio of C_(Fe³⁺):C_(Fe²⁺) was kept at 1.6:1 under the conditions pH 9.2 and temperature 30°C in N₂ atmosphere, magnetic stirring at 130 r/min. Then, the final product was filtrated, washed and dried at 60 °C, calcined for 3 hours at 350 °C.

2.2. Coating layer characterization

The coating percentage of Fe₃O₄ coatings on the surface of the micron Glass were determined as previously described [3] by external standard calibration method.

3. Results and Discussion

3.1. Measurements of the coating percentage of Fe₃O₄ on surface

The XRD patterns of pure glass, pure Fe₃O₄ and sample were shown in Figure 1. As can be seen, diffraction peak of pure micro glass is only a wide peak and there is no silica crystal line, demonstrating that glass powder is just a vitreous. The diffraction peaks of the chosen in the experiment Fe₃O₄ appeared at $2\theta = 30^\circ, 35.4^\circ, 43.1^\circ, 53.7^\circ, 57.1^\circ$ and 62.8° , corresponding to 2.98\AA (220), 2.53\AA (311), 2.10\AA (400), 1.70\AA (422), 1.61\AA (511) and 1.48\AA (440) of cubic phase Fe₃O₄ respectively. After micro glass was coated by Fe₃O₄, the diffraction peaks of the sample appeared at $2\theta = 30^\circ, 35.5^\circ, 43.1^\circ, 57.1^\circ$ and 62.8° , corresponding to the characteristic diffraction peak (220), (311), (400), (511) and (440) of Fe₃O₄, indicating Fe₃O₄ has been coated on the micro glass surface.

The content of Fe₃O₄ can be calculated by using external standard calibration method [4]. H_s and H_i represent the peak intensity of glass and Fe₃O₄ respectively, C_s and C_i represent mass concentration of glass and Fe₃O₄, respectively. Related equations are as follows:

$$\frac{H_i}{H_s} = F \cdot \frac{C_i}{C_s} \quad (1)$$

Where F is the proportional coefficient,

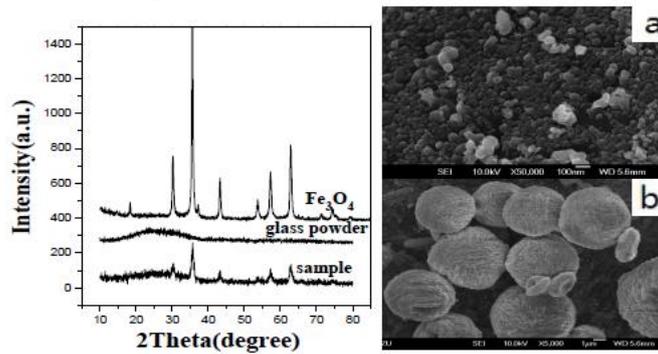


Fig. 1. XRD pattern and HRSEM of micro glass, Fe₃O₄, sample.

The corresponding peak intensity of the six standard samples was examined, using the strongest characteristic peak of Fe₃O₄ (311) as the main base peak. It is found that the normalized XRD peak (311) intensity was directly proportional to the mass ratio of pure Fe₃O₄ to micro glass, and thus the standard curve was plotted by normalized XRD peak (311) intensity versus percent of coated Fe₃O₄ to determine the percent of coated Fe₃O₄ in the sample.

The coating percent and colorimetric parameters of Fe₃O₄ prepared in experiments under different condition are given in Table 1.

Table 1. Colorimetric Parameters and Fe₃O₄ Coat Percent of the Coated Samples prepared under different eroding time of hydrofluoric acid solution, when t = 30 °C, C_(NaOH) = 0.5 mol/L, pH = 9.2, C_{(Fe³⁺)/C(Fe²⁺)} = 1.6:1, with the velocity of magnetic stirring being 113 r/min ≤ v ≤ 149 r/min in the coating process

eroding time/min	2	5	8
Colorimetric Parameters			
L*	39.18	41.64	42.14
a*	1.75	1.82	1.69
b*	3.01	2.98	3.81
ΔE* _{ab}	3.85	4.77	5.66
Mass content of Fe ₃ O ₄ /%	25.48	26.31	26.76

The standard colorimetric parameters were determined: $L^* = 38.80$, $a^* = +0.39$, $b^* = -0.57$, and colorimetric parameters of various synthesized samples determined under different conditions are listed in Table 1.

It is noted from the results of Table 1, all the luminance values L^* of Fe_3O_4 coating layer on micro glass were higher than that of the black ferric oxide pigment standard substance produced by the German Baier Pigment, Ltd. Co. The ΔE^*_{ab} value was above 3, showing obvious pearly luster effect.

3.2. Effect of eroding time by hydrofluoric acid solution on coating performance of the micron glass surface

The micron glass was treated by 0.5mol/l NaOH solution for 20 min, and following eroded by 0.1mol/L HF for 2min, 5min and 8min, respectively. The results showed the Fe_3O_4 coated layer with erosion at 8 min displays uniform packed nano-scales granular shape, with the size about 30 nm.

Pearlescent effect is also based on the “growing points” of micro glass which is affected by eroding time of HF solution; if the eroding time is short, the nano- Fe_3O_4 particles cannot deposit uniformly on the micro glass, so lead to less “growing points” serving as “crystal seed point” for Fe_3O_4 precipitation. When eroding time reached 8 min, the redness showed minimum value, while the yellowness and luminance value (L^*) showed the maximum value in the Table 1, and this led to the highest ΔE^*_{ab} value, producing obvious effects of pearly luster. The Fe_3O_4 coating content was also observed to get maximum value, because more “growing points” serve as “crystal seed point” for Fe_3O_4 precipitation.

In comparison with Fe_3O_4 coatings eroded by NaOH solution (0.5mol/l), the obvious improvements can be observed. But smoothness of coatings is not so desirable, in order to improve homogeneity and density of the coatings further, the increase of temperature for Fe^{3+} and Fe^{2+} co-precipitation must be considered first, because high temperature is beneficial to the formation of Fe_3O_4 [2].

3.3. Effect of co-precipitation temperature on coating performance of the micron glass surface

The co-precipitation temperature played important role on the pearlescent effect of samples, as shown in Table 1. With the temperature increasing, the yellowness and luminance value (L^*) decreased, and the redness showed minimum value at 90°C, this led to the highest ΔE^*_{ab} value of 9.73 and 9.21 at 85 and 90°C respectively, producing obvious effects of pearly luster. It is probable because the microspheres of Fe_3O_4 coated glass prepared at 90°C had the most smooth and compact coating.

The images recorded in Figure 1(a) showed uniform tightly packed granules

about 40 nm in diameter, and the coating layer on the micron glass surface was relatively smooth and compact. Figure 1(b) was the image of the microspheres of Fe₃O₄ coated glass at 90 °C, it can be seen that Fe₃O₄ coatings were smooth and compact, the very fine Fe₃O₄ crystals packed closely on substrates to form micro-scale spherical granules with the mean diameter about 5.8 μm, indicating the optimum coating process should be performed according to following steps. The substrates were treated by 0.5mol/L NaOH solution for 20 min, following eroded by 0.1 mol/L HF solution for 8min, and finally coated by Fe₃O₄ at 90°C. The synthetic process should minimize long and short-term impacts on the environment [5].

4. Conclusions

In this experiment, pearlescent pigment was prepared by deposition of nano-Fe₃O₄ on the micron glass surface by “crystal seed point” growing method. The effects of eroding time on micro glass surface by hydrofluoric acid, and effect of co-precipitation temperature on Fe₃O₄-coated glass morphology were discussed. The results showed when the micro glass as a substrate would be eroded by 0.5mol/l sodium hydroxide solution for 20 min and then by 0.1mol/L hydrofluoric acid for 8min, the more “growing points” for “crystal seed point” of Fe₃O₄ can be provided. XRD analysis demonstrates that the Fe₃O₄ has been coated on the micro glass surface.

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