INTRODUCTION

Mica is elastic, curving and highly resistant to abrasion and wearing, as well as heating. Moreover, mica is insoluble in acid and alkali solution, and it is chemical stable, so it is a good substrate for preparation of pearlescent pigment. At present, oxide compounds deposited on the mica surface to prepare pearlescent pigment include: TiO\textsubscript{2}, ZrO\textsubscript{2}, SnO\textsubscript{2}, Cr\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, ZnO, Fe\textsubscript{3}O\textsubscript{4}, and so on [1–4].

Usually preparation of mica/Fe\textsubscript{3}O\textsubscript{4} is under condition of certain pH value and temperature. Firstly a certain molar ratio salt solution of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} is put into the mica suspension to co-precipitate to form Fe\textsubscript{3}O\textsubscript{4}, then the resulting product is calcined in inert atmosphere to produce mica/Fe\textsubscript{3}O\textsubscript{4}. In a second method, bivalent iron salt reacts directly with certain amount of oxidant, then it is precipitated in mica suspension and calcined in inert atmosphere to produce mica/Fe\textsubscript{3}O\textsubscript{4} [2]. In another method, Fe\textsubscript{3}O\textsubscript{4} is deposited on the mica surface, then calcined to prepare mica/Fe\textsubscript{3}O\textsubscript{4} through controlling the amount of reducing gas [3, 4]. But there are problems in these methods: when using oxidant to oxidize bivalent iron, it is very difficult to control the accurate proportion, because the bivalent iron itself can be easily oxidized in the air; and when mica/Fe\textsubscript{2}O\textsubscript{3} is reduced in reducing atmosphere, the demands for equipment and operation are higher. All these limit the large-scale production and development of mica/Fe\textsubscript{3}O\textsubscript{4} composites.

Recent years, there are few researches on Fe\textsubscript{3}O\textsubscript{4} deposited on the mica surface to prepare pearlescent pigment in China. Comparing to separate Fe\textsubscript{3}O\textsubscript{4} or mica, mica/Fe\textsubscript{3}O\textsubscript{4} has one or more layers of mica. When the light shines on the surface of Fe\textsubscript{3}O\textsubscript{4}, it is partially reflected and partially penetrates into mica, then reflected again, resulting in one more mica reflecting light, which will further penetrate into the surface layer of Fe\textsubscript{3}O\textsubscript{4} and interfere with the reflecting light of Fe\textsubscript{3}O\textsubscript{4} surface. Owing to different colors and sizes, mica/Fe\textsubscript{3}O\textsubscript{4} not only features a graceful gloss, but also possesses colour sensation, gentle or twinkle appearance, which help it to gain more and more applications in industries. In this paper co-precipitation method was used to produce pearlescent pigment by depositing the newly-formed nano Fe\textsubscript{3}O\textsubscript{4} particles onto mica surface under controlled pH conditions, the effects of pH values, temperatures, sodium hydroxide concentrations, molar ratios of C\textsubscript{Fe\textsuperscript{3+}}/C\textsubscript{Fe\textsuperscript{2+}}, on the smoothness, compactness and colour deepness of the coating were determined.

EXPERIMENTAL

Instruments and Equipments

Constant-flow pump, peristaltic pump BT50-1J, pH controller DICAWOP24000G210E, temperature
indicating controller WMZK-01, tubular resistance furnace SK2-2-12, electric vacuum drying oven, Color i5 type color measurement device.

Preparation of mica/Fe$_3$O$_4$

All reagents were analytically pure, and the distilled water used was boiled for five minutes to eliminate oxygen. mica/Fe$_3$O$_4$ was synthesized as follows: first, by 100 ml of boiled distilled water and 10 g of mica were put into a beaker, and then the suspension was made by magnetic stirring. In the atmosphere of nitrogen, a certain molar ratio of the mixed solution of FeCl$_3$·6H$_2$O and FeCl$_2$·4H$_2$O was put into the beaker with a peristaltic pump, then a certain amount of sodium hydroxide solution was dropped into the beaker under controlled pH conditions by using pH controller. After all reactants were added, the suspension was stirred for half an hour to complete the reaction. Then the product was filtered, washed and dried at 60°C in vacuum, then the dry product was calcined in tube type electric-resistance furnace at 350°C for 3 h in nitrogen gas flow.

In the experiment the co-precipitation method was used to coat one layer of nanometer Fe$_3$O$_4$ on the mica surface. The experimental principle is described by the following reactions:

$$mica/Fe^{2+}/Fe^{3+} + OH^- \rightarrow mica/Fe(OH)_2/Fe(OH)_3,$$

$$mica/Fe(OH)_2/Fe(OH)_3 \rightarrow mica/FeOOH,$$

$$mica/FeOOH + Fe^{2+} \rightarrow mica/Fe_3O_4 + H^+.$$  

In an ideal situation the ratio of Fe$^{3+}$ to Fe$^{2+}$ should be 2 : 1, but in actual operation Fe$^{2+}$ is easily oxidized in the air, therefore, for obtaining the mica surface coated with highpurity Fe$_3$O$_4$, the oxidation of Fe$^{2+}$ should be taken into consideration, and the ratio of Fe$^{3+}$ to Fe$^{2+}$ should be smaller than 2 : 1 [5].

Determination of Percent of Coated Fe$_3$O$_4$ in the Sample

Structure analyses. As seen from Fig. 1, the mica diffraction peak appears at 17.5, 26.5, 35.8, and 45.1°.

The Fe$_3$O$_4$ coated mica sample was prepared under the condition of pH 9.2, $C_{NaOH}$ equals to 0.5 mol/l, $C_{Fe^{3+}}/C_{Fe^{2+}}$ at 1.6 : 1, and $\nu$: 138~151 r/min at the temperature of 75°C, corresponding to the 2M1 white mica (001) reflection peak: 5.06 (004), 3.36 (006), 2.51 (008), and 2.01 Å (0010), respectively [6]. All (001) reflection peaks intensity are strong in Fig. 1, moreover, the peak shape is sharp and symmetrical, indicating that the crystallinity of the chosen in the experiment mica was high. The diffraction peak of the chosen in the experiment Fe$_3$O$_4$ appeared at 20 = 30, 35.4, 43.1, 53.7, 57.1 and 62.8°, corresponding to 2.98 (220), 2.53 (311), 2.10 (400), 1.70 (422), 1.61 (511), and 1.48 Å (440) crystal face of cubic phase Fe$_3$O$_4$, respectively [7]. After mica surface was coated by Fe$_3$O$_4$, the diffraction peaks of the sample appeared at 20 = 17.5, 26.5, and 45.1°, corresponding to the characteristic diffraction peak of mica; while weak diffraction, peaks appeared at 20 = 35.4, 43.1, 57.1, and 62.8°, corresponding to the characteristic diffraction peak (311), (400), (511), and (440) of Fe$_3$O$_4$, indicating that Fe$_3$O$_4$ has been coated the mica surface.

Determination of Fe$_3$O$_4$ Coating Rate on the Mica Surface

The external standard method [8] was used to calculate the content of Fe$_3$O$_4$ coated the mica surface, which is described as follows:

$$C_a = f_s H_s,$$

$$C_i = f_i H_i,$$

then (1) : (2) and obtains:

$$\frac{H_s}{H_i} = F \frac{C_i}{C_s},$$

where $H_s$ and $H_i$ are peak intensity of mica and Fe$_3$O$_4$, $C_s$ and $C_i$ are mass concentration of mica and Fe$_3$O$_4$ respectively, and $F$ is a proportional coefficient.

In this study analytical pure Fe$_3$O$_4$ and dry mica were mixed uniformly with mass ratio of 9 : 1, 8 : 2, 6 : 4, 4 : 6, 2 : 8, and 1 : 9, respectively, and the mixed samples were determined by XRD. The peak intensity corresponding to Fe$_3$O$_4$ was determined, using the strongest characteristic peak (311) as main base peak. It is found that the normalized XRD peak (311) intensity was directly proportional to the mass ratio of pure Fe$_3$O$_4$ to mica, and thus the standard curve was plotted by normalized XRD peak (311) intensity versus per-