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Effect of synthesis parameters on a hematite–silica red pigment obtained using a coprecipitation route

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Abstract

The morphology and the dimensions of the hematite particle influenced the shade of the red pigments obtained; both fine (<30 nm in length) spherical and long (>250 nm in length) acicular shapes gave poor red shades. The morphology of the hematite particles depends on the precipitant used; ammonia provided spherical, whereas NaOH produced acicular hematite particles. The dimensions of the hematite particles depended on the mineralisers used; while the silica structure did not influence pigment shade, the use of mineralisers promotes tridymite structure crystallization.

Keywords: Ceramic; Inclusion pigment; Non-toxic red pigment; Hematite–silica

1. Introduction

Inorganic natural and synthetic pigments produced and marketed as fine powders are an integral part of many decorative and protective coatings and are used for the mass coloration of many materials, including glazes, ceramic bodies and porcelain enamels. In these applications, the pigments disperse in the media, forming a heterogeneous mixture. The powders used to color ceramics must possess thermal and chemical stability at high temperature and must be inert to the action of molten glass (frits or sintering aids) [1]; these characteristics limit the number of available ceramic pigments [2–12]. The need for high chemical and thermal stabilities has dominated research and development in recent years, especially as regards new red or pink pigments. In particular, interest has focused on the development of inclusion pigments which are not tolerant of the high thermal and chemical environment, but which can be occluded in a stable glassy or crystalline matrix (heteromorphic pigments). The inclusion or encapsulation of a reactive, coloured or toxic crystal inside a stable crystalline or amorphous uncoloured matrix, provides protection to the chromophore; in this way, the crystal is inactivated inside the matrix.

Hematite–silica, heteromorphic pigments are popular despite the fact that the traditional preparation method yields powders that are unable to tolerate neither the glazing composition nor the sintering temperature. To achieve high-efficiency chromophore encapsulation, the temperature of the matrix sintering and crystallization must synchronize with the temperature of nucleation and growth of the occluded chromophore phase. The crystallization, sintering and inclusion processes must take place simultaneously and, consequently, control of the particle size and the choice of mineraliser are major parameters that need to be controlled [6].

In this work, a coprecipitation route, employing two precipitant agents, ammonia and sodium hydroxide, was used to include hematite in a silica matrix so as to control the microstructural

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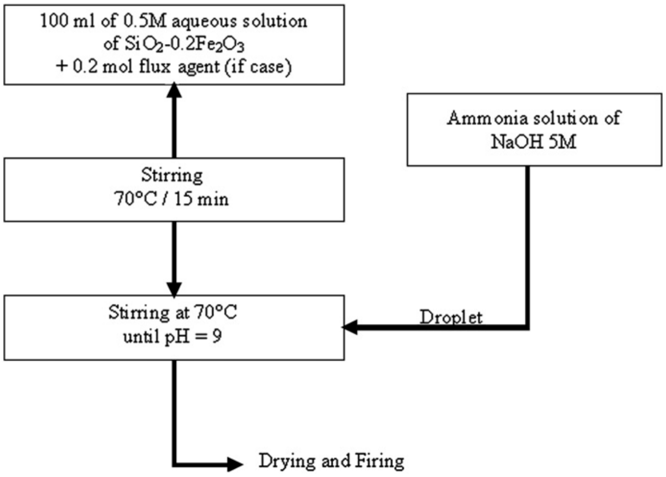

Fig. 1. Flux diagram of coprecipitation method used.

characteristics and particle morphology [1,3,6]. The effect of the mineralisers, NaF and NaCl, was investigated in order to optimize the pigment calcination temperature and secure control over the color obtained in an industrial glaze.

2. Experimental procedure

Samples of SiO_2–$0.2Fe_2O_3$ were prepared using the coprecipitation (P) route shown in Fig. 1. A 0.5 M aq solution was prepared by adding iron sulphate ($Fe_2SO_4 \cdot 7H_2O$, Aldrich) in the required mole ratio to an aqueous suspension of colloidal silica (Ludox). The precursors used are reported in Table 1. In mineralized samples, 0.2 M NaF, NaCl, NaF·NaCl or NaF·2NaCl (Sigma–Aldrich) was added to the aqueous solutions before reaction. Drops of concentrated ammonia solution (PI) or 5 M aq sodium hydroxide solution (PII) were then added to the mixture, which was continuously stirred and kept at 70 °C until the pH stabilized at 9. The resulting dark green coprecipitate was dried at 110 °C and fired. In order to determine the effects of firing temperature and mineraliser composition, the powders were fired at temperatures ranging from 800 to 1100 °C in an electrical furnace with a soaking time of 3 h. The fired samples were micronised, wet milled in water and finally dried at 110 °C.

To identify the crystalline phases present in the raw and fired samples, X-ray diffraction patterns were collected using a conventional powder technique in a Siemens Diffractometer (D500 mod) employing Cu Kα Ni-filtered radiation. To define the color developed by the samples, a Gretag Macbeth, *Color-Eye 7000*, was used, employing a 10° Standard Observer. The powder's microstructure was characterised using scanning electron microscopy (Philips XL-30) and by transmission electron microscopy (Jeol JEM 2010 equipped with a GIF Multiscan Camera 794).

Table 1
Precursors used to prepare $0.2Fe_2O_3$–SiO_2 samples

Sample	Method	Si precursor, Fe precursor and precipitant agent
PI	Coprecipitation	Ludox (30% in SiO_2), $FeSO_4 \cdot 7H_2O$ and NH_4OH
PII	Coprecipitation	Ludox (30% in SiO_2), $FeSO_4 \cdot 7H_2O$ and NaOH

Table 2
Crystalline phases and CIELab values of PI samples as a function of calcination temperature

Mineraliser	*T* (°C)	Phase composition (XRD)	Color *L**/*a**/*b**
Without	Raw	Ma	Maroon
	900	H	45.8/27.2/23.4
	1000	H, C(w)	43.5/26.6/23.1
	1100	H, C(s)	41.9/25.6/22.8
NaF	Raw	Ma	Green-yellow
	900	H, C(w)	45.1/26.2/21.3
	1000	H, C, T(w)	43.0/25.2/20.1
	1100	Local melting H, C(w), T_m	Brown
NaCl	Raw	Ma	Green-yellow
	900	H, C(w)	44.9/26.5/21.1
	1000	H, C(w), T	42.5/25.7/19.4
	1100	Local melting, H, T_m	Brown
NaF·NaCl	Raw	Ma, N(w), S, T_H	Light green
	800	N(w), H, T_m(w)	46.4/26.6/22.1
	900	N(w), H, T_m(s)	44.8/25.2/20.3
	1000	Local melting, H, T_m	Brown
NaF·2NaCl	Raw	Ma, N, S, T_H	Brown
	800	N(w), H, T_m	43.2/28.9/24.1
	900	N(w), H, T_m(s)	44.2/28.6/23.1
	1000	Local melting, H, T_m	Brown

Ma: $(NH_4)_2SO_4$ (mascagnite 00-001-0363); H: hematite (00-033-0664); C: cristobalite (01-076-0937); N: Na_2SO_4 (01-075-1979); T_m: tridymite-monoclinic (01-071-0197); T_h: tridymite-hexagonal (01-089-3141); S: NH_4Cl (00-001-1037); w: weak; s: strong.

Table 3
Crystalline phases and CIELab values of PII samples as a function of calcination temperature

Mineraliser	*T* (°C)	Phase composition (XRD)	Color *L**/*a**/*b**
Without	Raw	N	Dark brown
	900	N, H, C(w)	42.9/28.9/24.9
	1000	N, H, C(s)	41.7/27.9/19.8
	1100	Local melting, H, C	Red brown
NaF	Raw	N	Green
	900	N, H, T_o(w)	43.9/27.1/21.5
	1000	N, H, T_o(s), C(w)	42.7/25.8/21.6
	1100	Melting, H, T_o(w)	Brown
NaCl	Raw	N	Green-yellow
	900	N, H, T_o(w)	44.4/27.5/20.9
	1000	N, H, T_o(s), C(w)	43.0/26.2/19.7
	1100	Melting, H, T_o(w)	Brown
NaF·NaCl	Raw	F, N	Yellow-brown
	800	N, H, T_o(w)	46.1/26.5/19.8
	900	N, H, T_o(s), C(w)	43.6/25.9/18.6
	1000	Local melting, H, T_o	Brown
NaF·2NaCl	Raw	F, N, NaCl(w)	Light brown
	800	N, H, T_o(s), C(w)	45.9/26.9/24.2
	900	Local melting, H, To	52.8/26.3/23.1
	1000	Melting, H, T_o(w)	Brown

N: Na_2SO_4 (01-075-1979); H: hematite (00-033-0664); C: cristobalite-tetragonal (01-076-0937); T_o: tridymite-orthorhombic (00-002-0242); F: FeOOH (00-034-1266); w: weak; s: strong.