CHEMICAL NATURE OF THE IRON-SILICA PIGMENT

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1. INTRODUCTION

The iron-silica ceramic pigment is widely used in porcelain tile through-body colouring. Lahuerta [1] considers this pigment to be similar to the natural colouring agent 'Gres de Thiviers', which is a mixture of quartz and goethite (FeO(OH)), which contains around 10% Fe_2O_3. Lahuerta observes that with the calcination, goethite changes to hematite and quartz to cristobalite. Monros [3], using the sol-gel process in aqueous media, controlled the material's synthesis conditions, evidencing an inclusion of hematite with a particle size of about 200 nm in the sintered granules of silica particles of about the same size, postulating a model of sintering- crystalline growth in this system.

In the present study, the effect is analysed of the type of crystalline phase associated with the pigment (alpha/beta cristobalite or quartz), the crystallite size (Scherrer method) or the dimensions of the elemental cell on the CIEL*a*b* values of through-body coloured samples in porcelain tile, obtained from colloidal silica or quartz with the addition of mineralisers such as KNO_3 or NaF.

2. EXPERIMENTAL PART AND DISCUSSION OF RESULTS

Mixtures were prepared by the traditional method mixing quartz with an average particle size of 3 μm (Sibelco S.A), iron oxide (III) (Panreac S.A.) and, where necessary, fluxing agents (KNO_3 or NaF supplied by Panreac S.A.) in a ball mill in acetone. Mixtures were also prepared using colloidal silicas and iron salts of red iron-silica pigments [2].

The mixtures with quartz were subjected to isothermal calcination in order to monitor the cristobalite formation process in these mixtures. The samples were characterized by X-ray diffraction, measurement of lattice parameters through the software, measurement of the CIEL*a*b* parameters with a C illuminant (samples of porcelain tile to which the through-body colouring materials were added in 3%) and scanning electron microscopy (SEM) with associated energy-dispersive X-ray analysis (EDAX).

Table I presents the evolution of the intensity of a representative peak and the CIEL*a*b* results of the samples with quartz. Figure 1 shows micrographs of the samples mentioned with related EDAX analysis.

According to classic studies on the subject [3], the transformation of quartz into cristobalite occurs through the formation of amorphous and glassy phases. Indeed, the addition of a fluxing agent with a low melting point allows the crystallization of cristobalite in isothermal treatments at 1000ºC of only two hours. A fluxing agent like NaF with a relatively high melting point induces this after 8 hours; if no fluxing agent is added, the cristobalite does not transform with 12-hour treatments, though an incipient crystallization is seen in the treatment at

1100ºC/6h. The CIEL*a*b* data of table 1 indicate that the colouring induced by the samples in the porcelain tile body is independent of the presence of cristobalite (a* values of about 10 in all cases). It should be noted that the initial cristobalite crystallizations are cubic or β-cristobalite. Later thermal treatments indicate a transformation to the tetragonal or α-form. The SEM-EDAX studies in figure 1.a indicate the presence of clearly differentiated hematite particles in the samples with quartz.

In the colloidal samples, the level of red of the through-body colourings in porcelain tile is much higher (a* about 17: L*a*b* = 52.8/16.8/14.1 for COL2). Also, the crystalline phase detected is α-cristobalite (800 cps for peak º2Θ=22) along with hematite (100 cps for peak º2Θ=33.2) and quartz (50 cps for peak º2Θ=21). The SEM-EDAX studies in figure 1.b show the presence of clearly differentiated hematite particles in the samples with quartz, as well as much smaller colloidal size particles. Indeed, the studies of the cristobalite crystallite size measured using the Scherrer method (4) do not exceed 50 nm (49.4 and 41.2 nm respectively for COL 1 and COL 2). The cell size values do not indicate a significant change and it the reverse in the two samples analysed (173.5±0.1 Å COL1 and 174.16±0.05 Å COL2 in comparison with 173.39 Å of the cristobalite card 01-077-1317), which rules out the solid solution model of iron in silica.

3. CONCLUSIONS

The model of hematite inclusion in colloidal or glassy silica is confirmed for the iron-silica pigment, the colour being independent of the presence of cristobalite in the system, which always appears with sub-micrometric size, however, in the system as a product of the transformation of the colloidal silica.

SAMPLE	1000ºC/2h	1000ºC/4h	1000ºC/8h	1000ºC/12h	1100ºC/6h
0,1Fe-Q	H(300) Q(2200) 52.1/9.7/11	H(300) Q(2200) 51.9/9.6/11.2	H(300) Q(2000) 50.1/9.8/9.1	H(350) Q(2000) 48.7/10.2/9.3	C(50) H(300)Q(2500) 48)10.3/6.2
0,1Fe-Q 5%KNO_3	**C(250)** H(250)Q(700) 47.7/9.9/7.1	**C(380)** H(250)Q(600) 48.1/9.7/6.8	**C(400)** H(300)Q(650) 49/9.7/6.8	**C(370)** H(210)Q(450) 49.3/9.5/6.3	C(200) H(250)Q(1100) 49,.7/10/7
0,1Fe-Q 5%KNO_3	H(200) Q(1500) 50.9/9/8.1	H(250) Q(1400) 47/10/7	**C(50)** H(300)Q(1500) 48.7/10.1/6.7	**C(100)** H(250)Q(1250) 52.1/9.7/11	C(200) H(250)Q(950) 47.6/10.1/6.1

CRYSTALLINE PHASES AND MEASURED PEAK (cps):
C (cristobalite, º2Θ=22), H (hematite,33.2), Q (quarz,21).

*Table 1. Evolution of the intensity of a representative peak and CIEL*a*b* results.*

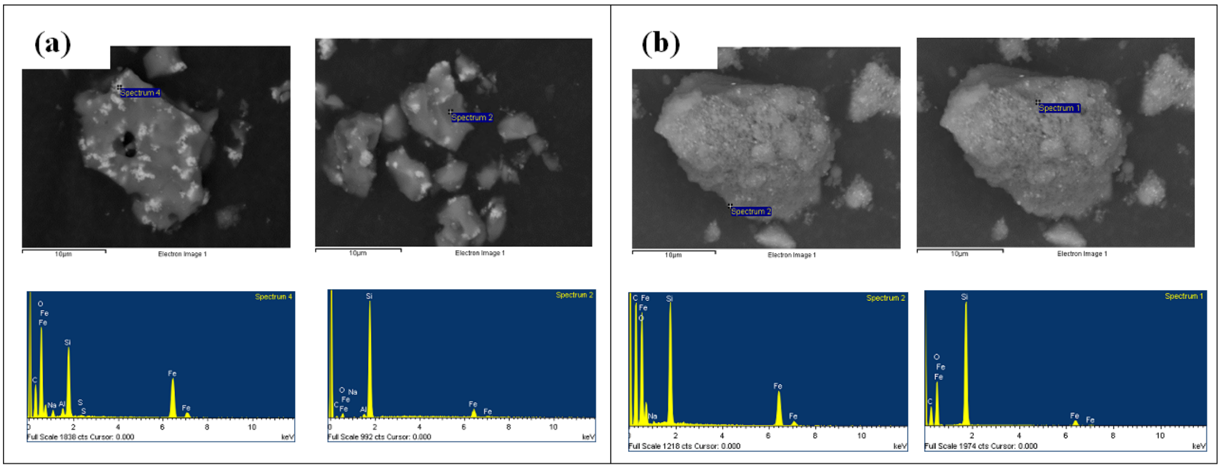

Figure 1. SEM micrographs of the samples: (a) 0.1Fe-Q-5%KNO_3 100ºC/12h, (b) colloidal sample COL1.

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