RUTILE-BASED NANOSTRUCTURED PIGMENTS

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1. INTRODUCTION

In the traditional preparation of ceramic pigments, the raw materials are homogenised and calcined to obtain the pigmenting system, which is washed and micronised to avoid incompatibilities with the matrices to be coloured and to optimise the particle size in order to obtain the best colouring yield: large sizes produce defective colorations, while particle sizes that are too fine are dissolved and degraded by the matrix[1]. However, in new colour applications, such as the inks for ink-jet applications, it is necessary to operate in a solution or with nano-scale sizes. Yet, the nanoparticles obtained by mechanical procedures are usually excessively agglomerated or are dissolved by the ceramic glazes, and need an appropriate stabilization in emulsions or suspensions[2]. This study presents a synthesis strategy based on the development of nanoparticles that form nanostructured aggregates, either of the pigmenting system or of mesoporous mixtures of the precursors, with an appropriate size in order to remain stable under the action of the glazes in the ceramic firing or to react during that action in order to produce, in a self-generated way, the pigmenting particle for three rutile-based pigmenting systems $(AB)_xTi_{2-x}O_2$: pink AB=CrSb, yellow AB=NiSb, and blue-black AB=VW.

2. EXPERIMENTAL

The pigments of optimised composition[2,3] $(VW)_{0,1}Ti_{1,8}O_2$ (System VW), $(NiSb)_{0,1}Ti_{1,8}O_2$ (System NiSb), and $(CrSb)_{0,06}Ti_{1,88}O_2$ (System CrSb) were obtained by hyperacid hydrolysis of titanium alkoxides and subsequent ammonia digestion at pH 8. The hydrolysed powders were dried in an oven at 110ºC and screen printed with a 48 mesh thread in diethylene glycol medium in a vehicle:powder ratio =5:2 on a porcelain tile glaze that was fired at 1200ºC in conventional cycle of 54 minutes. The dry powders were directly used, after calcining at 500, 1000, 1100 y 1200ºC for 1 hour, and used in the coloration at 5% in the porous single-fired wall tile frit.

The materials were characterised by X-ray diffraction, as well as by scanning electron (SEM) and transmission microscopy (TEM) with a view to analysing the microstructural characteristics. The glazed materials were characterised by UV-Vis-NIR spectroscopy by diffuse reflectance and measurement of the colorimetric coordinates CIE L*a*b*.

3. DISCUSSION AND RESULTS

The results indicate the obtainment of nanostructured powders with good pigmenting results in self-generation on the porcelain tile cycle: orange (L*a*b*=74/18/41), yellow (83/-6/30) for systems CrSb and NiSb, respectively, in the case of VW pink-yellow (82/3/23) colorations are obtained instead of the dark blue colorations (Fig. 1.a, b, and c), The raw powders and the powders calcined at 500, 1000, 1100 and 1200ºC for 1 hour were added in a 5% in a porous single-fired wall tile frit, and developed pink (67/10/15 at 1000ºC), yellow (78/0/30 at 1100ºC) and intense blue colorations (49/-2/13 at 1200ºC) for the systems CrSb, NiSb, and VW, respectively (Fig. 1. d, e, and f).

The X-ray diffraction studies (not shown) indicate the crystallisation of anatase and ammonic salts from the ammonia digestion of the green materials. At 500ºC anatase and rutile crystallised in all samples. At higher temperatures only rutile was detected. The dry samples displayed particle microaggregates measuring between 4 and 20 µm (Fig. 1.g, h, and i). The particles making up the microaggregates are nano-aggregates of particles between 3 and 10 nm, both in the dry materials and in those stabilised at 500ºC (Fig. j, k, and l).

$(VW)_{0,1}Ti_{1,8}O_2$ $(NiSb)_{0,1}Ti_{1,8}O_2$ $(CrSb)_{0,06}Ti_{1,88}O_2$

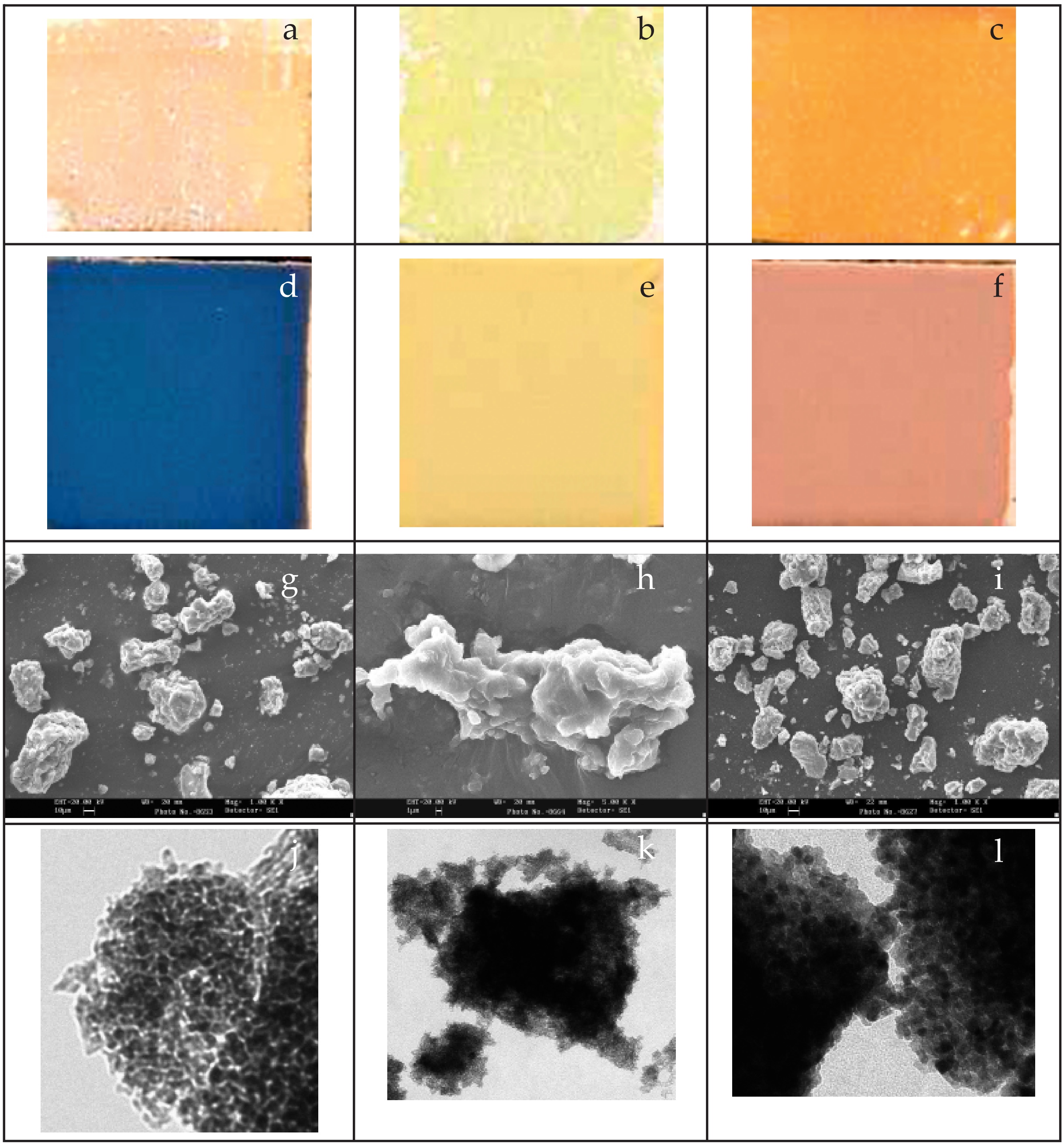

Figure 1. (a, b, and c) Photograph of the screen printed powders on porcelain tile body, (d,e,f) Photograph of the glazed samples in conventional porous single-fired wall tile frit powders fired at the indicated temperature, (g,h,i) SEM micrographs of the dry green (j,k,l). TEM micrographs of samples stabilised at 500ºC (j and l) or dry samples (k).

4. CONCLUSIONS

Rutile-based pigments have been developed made up of nanostructured microaggregates with nanoparticles between 3-10 nm both in the green materials and in those stabilised at 500ºC. The materials can be used as self-generating screen printing ink in the substrate firing with pink, yellow, or orange colorations for the chromophore systems V-W, Ni-Sb, and Cr-Sb respectively. The calcined materials produce pigments of relatively high intensity in the optimised compositions developed of blue, yellow and orange colorations for the chromophore systems V-W, Ni-Sb, and Cr-Sb respectively.

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