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Blue cobalt doped-hibonite pigments prepared from industrial sludges: Formulation and characterization

A. Leite [a], G. Costa [b], W. Hajjaji [a], M.J. Ribeiro [b], M.P. Seabra [a], J.A. Labrincha [a,*]

[a] *Ceramics and Glass Engineering Department, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *ESTG, Polytechnic Institute of Viana do Castelo, 4900-348 Viana do Castelo, Portugal*

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ABSTRACT

The structural stability of the pigment was investigated using X-ray diffraction coupled with SEM and UV–vis–IR analysis, as a function of the relative Co content and calcination temperature. A standard formulation prepared from commercial reagents was also prepared and characterized for the sake of comparison. The pigment was added to a transparent glaze and to a porcelain stoneware body. Since the relative amount of cobalt was low and the sintering temperature of the pigment was not too high (1350–1400 °C), the new pigment system offers an interesting alternative to spinel, olivine and willemite commercial blue pigments. Moreover, the use of several wastes in the pigment formulation does not diminish its colouring performance.

1. Introduction

With the exception of vanadium–zircon (14-42-2 DCMA), traditional blue inorganic pigments are based on cobalt-doped structures [1] namely, Co_2SiO_4 olivine (5-08-2 DCMA) $(Co,Zn)_2SiO_4$ willemite (7-10-2 DCMA), blue or blue green spinels, such as: $CoAl_2O_4$ (13-26-2 DCMA), Co_2SnO_4 (13-27-2 DCMA), $(Co,Zn)Al_2O_4$ (13-28-2 DCMA) and $Co(Al,Cr)_2O_4$ (13-29-2 DCMA). Cobalt aluminate is widely preferred to olivine, since a navy blue hue can be obtained using ~ 50% cobalt content (33.3% in $CoAl_2O_4$ against 56.1% in Co_2SiO_4), as well as differences in chroma [1,2]. In these formulations, the Co^{2+} ions are situated within non centrosymmetric sites (e.g. tetrahedronally) and offer the highest colouring efficiency among crystal-field transitions [2]. However, the above formulations contain relatively high amounts of cobalt which is not only expensive but also is a toxic component [3]. Hence, attention has foccussed on alternative pigmentary systems that contain lower amounts of cobalt [4,5].

Calcium hexaluminate ($CaAl_{12}O_{19}$ or $CaO \cdot 6Al_2O_3$), which occurs in nature as the mineral *hibonite*, possesses the magnetoplumbite-type structure (space group $P6_3/mmc$, $Z = 2$) of general crystallochemical formula: A [12] M1 [6] M2$_2$ [5] M3$_2$ [4] M4$_2$ [6] M5$_6$ [6] O$_{19}$. Calcium occurs in 12-fold coordination (site A), whereas the Al^{3+} ions are distributed over five different coordination sites, including three distinct octahedra (M1, M4 and M5), one tetrahedron (M3) as well as an unusual trigonal bipyramid (M2) providing five-fold coordination by oxygen ions [6,7]. Of significance herein, is the tendency of the M^{2+} ions to be hosted at the M3 site, while M^{4+} and M^{5+} ions are preferentially accommodated at the M4 site [8]. Magnetoplumbite-group minerals may contain significant amounts of divalent as well as tetravalent and pentavalent cations occupying interstitial M sites [8]. The marked preference of divalent cations for the M3 site occurs because these substitutions are electrostatically more favourable than incorporation of highly charged cations. The ions of different charges tend to improve the local charge balance in the crystal structure. Therefore, the introduction of divalent ions is thought to be achieved by coupled incorporation of tetravalent or pentavalent cations which are mainly ordered over the octahedral sites in the face-sharing interlayer doublet [8].

This ability to accommodate such a wide variety of ions, with different valences and coordinations, makes the hibonite structure very interesting to be used as a pigment. The electroneutrality of the hibonite lattice was eased by making available a tetravalent ion in order to get a coupled substitution Co^{2+}–Al^{3+} and Ti^{4+}–Al^{3+}. Any excess of titanium oxide is not detrimental for the overall pigment performance, since it ensures increased brightness. However, the temperatures required for the synthesis make its application difficult [6]. To overcome kinetic hindrances, batch formulation might be adjusted introducing anorthite into the system, which contributes to lower the synthesis temperature of hibonite, allowing its application as pigment [9]. The use of wastes or by-products in the

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* Corresponding author. Tel.: +351 234370250; fax: +351 234370204.
E-mail address: jal@ua.pt (J.A. Labrincha).

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Table 1
Components and relative codes of synthesized pigments.

Pigment code	Alumina	AS	Calcite	MS	Silica	FS	Co_3O_4/TiO_2	n(Co) (mol)[a]
0.45Co/Ti-H_1400 °C	63.5		18.6		11.2		3.4	0.45
0.45Co/Ti-H_1350 °C								
0.3Co/Ti-H_1400 °C	65		19		11.4		2.3	0.3
0.3Co/Ti-H_1350 °C								
0.15Co/Ti-H_1400 °C	66.5		19.5		11.7		1.2	0.15
0.15Co/Ti-H_1350 °C								
0.45Co/Ti-H/3S_1400 °C		79.98		12.86		4.16	3.4	0.45
0.45Co/Ti-H/3S_1350 °C								
0.3Co/Ti-H/3S_1400 °C		80.8		13		4.2	2.3	0.3
0.3Co/Ti-H/3S_1350 °C								
0.15Co/Ti-H/3S_1400 °C		81.64		13.13		4.25	1.2	0.15
0.15Co/Ti-H/3S_1350 °C								

H: hibonite. 3S: with anodizing (LS) and marble (MS) sludges and foundry sand (FS).

[a] n_{Co} (Mol) = n_{Ti}(Mol).

formulation of hibonite might also improve the sintering process since they might contain mineralising/fluxing agents [10]. In fact, one of the current trends in pigments' production are the search for alternative and less expensive raw materials and wastes that might act either as colouring agents or as hosts for diverse colouring species, so they can be looked as supplementary raw materials for pigments' production [11–13].

2. Experimental

Hibonite-based pigments, doped with cobalt, were synthesized by the conventional ceramic route, designing a batch composition in the Al_2O_3–CaO–SiO_2–TiO_2 system (Table 1). The following precursors were used in batch formulations: calcite (Calcitec M1), silica sand (Sibelco P500), alumina (Alcoa, CT 3000), titanium dioxide (Kronos) and Co_3O_4 (Panreac). Alternative raw materials were used to formulate similar compositions.

(i) Aluminium anodising sludge (AS) of mass% composition: 36.36 Al_2O_3, 1.23 SiO_2, 3.08 CaO, 0.05 TiO_2, 40.0 (LOI) replacing the pure alumina above;
(ii) foundry sand (FS) of mass% composition: 0.20 Al_2O_3, 97.74 SiO_2, 0.20 CaO, 0.20 TiO_2, 0.2 (LOI) as the source of silica;
(iii) marble sawing sludge (MS) of mass% composition: 0.14 Al_2O_3, 0.64 SiO_2, 55.51 CaO, 0.02 TiO_2, 43.0 (LOI) replacing calcite.

Each was disintegrated or milled (<100 μm) and dried at 100 °C. Their full characterisation is given elsewhere [13].

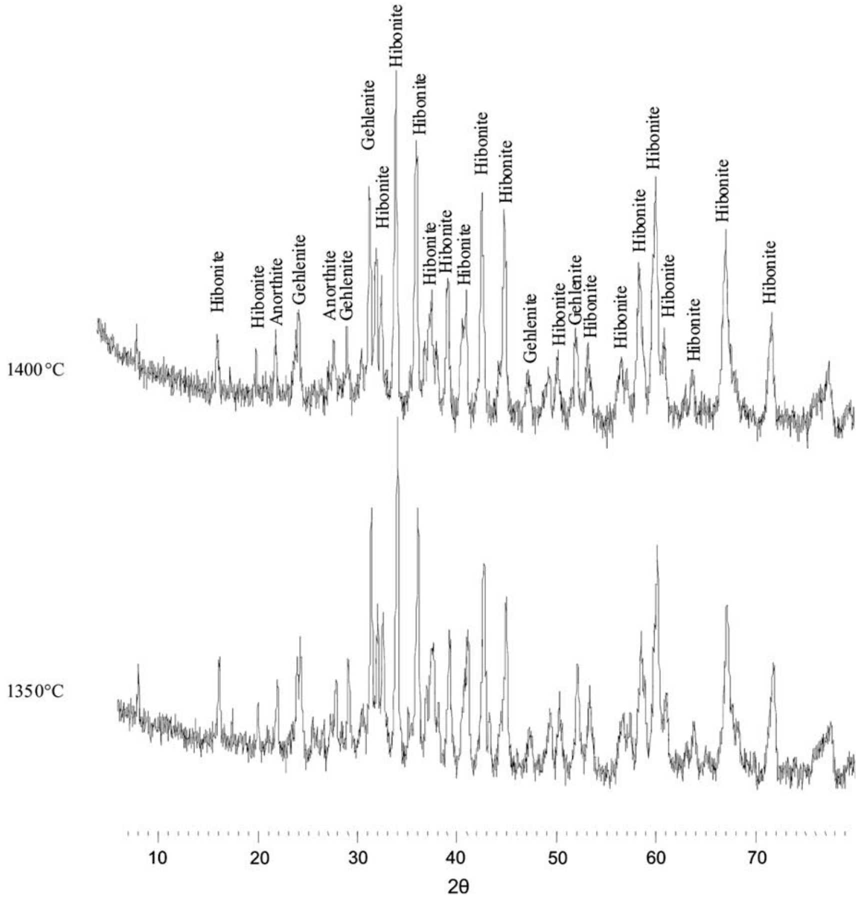

Fig. 1. X-ray diffraction patterns of 0.3Co/Ti-H/3S pigments calcined at 1350 °C and 1400 °C.