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Recycling of solid wastes in the synthesis of Co-bearing calcium hexaluminate pigment

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ABSTRACT

Cobalt doped calcium hexaluminate was firstly synthesized using pure reagents; subsequently, the pure reagents were substituted with industrial wastes, the composition of which had been characterized using X-Ray diffraction and X-Ray fluorescence namely, Al-anodising sludge replaced pure aluminium whilst marble cutting rejects and foundry sand were employed as sources of calcite and silica, respectively. As expected, cobalt doped hibonite was the major phase present in calcined powders and displayed an intense blue coloration due to the incorporation of cobalt in tetrahedral positions, as confirmed by transitions from $^4A_2(F)$ to the excited $^4T_1(F)$ and $^4T_1(P)$ states observed from UV–Vis–NIR absorption spectra. The novel waste-derived hibonite pigment showed strong and stable colouring potential when applied in different ceramic supports.

1. Introduction

Although many chemical compounds are effectively applied as pigments there is still a need to find new mixtures combining colour efficiency and lower cost. As blue inorganic pigments, cobalt doped olivine – Co_2SiO_4 (5-08-2 DCMA), spinel – (Co, Zn)Al_2O_4 (13-28-2 DCMA), and willemite – $(Co, Zn)_2SiO_4$ (7-10-2 DCMA) are commonly used [1–4]. In all cases, it is easy to see that the relative amount of cobalt is high (>30 wt.%), increasing their price and environmental health risks, since cobalt is toxic. A potential alternative for these pigments was found by preparing cobalt bearing hibonite [5]. This calcium hexaluminate rarely occurs in the earth, shows the aptitude to incorporate distinct sized ions in five different lattice sites. It might be represented by the general formula $(A^{XII})(M^{IV;V;VI})_{12}O_{19}$, with A: K, Ca, Sr, Ba, Pb, REE (Rare Earth Elements) and M: Mg, Al, Ti, Cr, Mn, Fe, Co, Zn, Ga [6–10]. This mineral exhibits hexagonal symmetry with $a = b = 5.613$ Å, $c = 22.285$ Å and belongs to the space group $P6_3/mmc$ [6]. The incorporation of chromophor ions is allowed by substitution of tetrahedral Al^{3+} in larger (M3) sites, what explains the affinity of divalent cations like Co^{2+} to this position occupancy. The expectable high structural stability of hibonite and the need of much lower amount of cobalt to get intense blue coloration are arguments in favour of its use as promising candidate as a ceramic pigment.

The selective use of industrial wastes replacing primary/pure reagents could help to reduce the pigments price, as proved in previous trials [5,11]. In addition, the presence of impurities, in controlled amounts, in such secondary raw materials might act as mineralising/fluxing agents, then helping to decrease the sintering temperature. Besides this, in the actual processing conditions the co-formation (equimolar) of anorthite ($CaAl_2Si_2O_8$) was promoted, in order to decrease the required temperature for hibonite development [5].

2. Experimental

The oxide composition of used raw materials is given in Table 1, as obtained by X-ray fluorescence using an Axios Wavelength Dispersive XRF spectrometer. Excepting cobalt, tin oxide and titanium which total amounts are less then 3 wt.% of the total mixture, alternatives for pure reagents where found by using rejects from distinct industries. Progressively, alumina (Alcoa CT300), calcite (Calcitec M1) and silica sand (Sibelco P500) were replaced by Al-anodising sludge, marble sawing sludge and foundry sand, respectively. In fact, each waste shows composition close to the pure reagent that it will replace and slight differences were accomplished and corrected in the prepared batches. The mixtures were encoded as:

- Hb–Co/Ti: obtained using pure reagents,
- Hb–Co/Ti _1S: Al-anodizing sludge, calcite (Calcitec) and silica (Sibelco),

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Table 1
Compositions of used raw materials and formed pigments (in wt.%).

	Alumina (Alcoa CT)	Al-anodising sludge	Calcite (Calcitec)	Marble sludge	Silica (Sibelco)	Foundry sand	Cobalt II (Panreac)	Cassiterite (CCT)	Rutile (Kronos)
Al_2O_3	98.7	35.3	0.10	0.14	0.10	0.20	–	–	–
SiO_2	0.20	1.19	0.10	0.64	99.0	97.7	–	–	–
Fe_2O_3	0.37	1.41	0.07	0.24	0.06	1.12	–	–	0.03
CaO	0.10	2.99	55.6	55.5	0.10	0.20	–	–	–
Na_2O	0.01	0.35	0.01	–	0.05	–	–	–	–
K_2O	0.04	0.07	0.01	0.11	0.10	0.26	–	–	–
MgO	0.01	0.34	0.22	0.31	0.07	–	–	–	–
TiO_2	0.06	–	0.01	0.02	0.01	0.20	–	–	99.3
SnO_2	–	–	–	–	–	–	–	99.9	–
Co_3O_4	–	–	–	–	–	–	99.9	–	–
Cr_2O_3	–	–	–	–	–	0.20	–	–	–
SO_3	–	16.7	–	–	–	–	–	–	0.02
P_2O_5	–	–	–	–	–	–	–	–	0.02
LOI	0.50	40.0	43.9	43.0	0.50	0.20	–	–	0.10
Hb-Co/Sn	63.7	–	18.6	–	11.2	–	2.2	4.2	–
Hb-Co/Sn_1S	–	80.2	12.8	–	4.1	–	1.0	1.8	–
Hb-Co/Sn_2S	–	80.2	–	12.8	4.1	–	1.0	1.8	–
Hb-Co/Sn_3S	–	80.2	–	12.8	–	4.2	1.0	1.7	–
Hb-Co/Ti	65.0	–	19.0	–	11.4	–	2.3	–	2.3
Hb-Co/Ti_1S	–	80.9	12.9	–	4.2	–	1.0	–	1.0
Hb-Co/Ti_2S	–	80.9	–	13.0	4.1	–	1.0	–	1.0
Hb-Co/Ti_3S	–	80.8	–	13.0	–	4.2	1.0	–	1.0

- Hb–Co/Ti _2S: Al-anodizing sludge, marble sludge and silica (Sibelco),
- Hb–Co/Ti _3S: Al-anodizing sludge, marble sludge and foundry sand.

A similar nomenclature was used for cobalt-tin doped pigments namely, Hb–Co/Sn, Hb–Co/Sn_1S, Hb–Co/Sn_2S and Hb–Co/Sn_3S.

The batches were formulated aiming to generate 1 mol hibonite + 1 mol anorthite, corresponding to the theoretical composition (wt.%): 65–63.7 Al_2O_3; 11.4–11.2 SiO_2, 19–18.6 $CaCO_3$, 2.3–2.2 Co_3O_4 and 2.3 TiO_2 (or 4.2 SnO_2), in which $n(\mathrm{Co}) = n(\mathrm{Ti}) = n(\mathrm{Sn}) = 0.3$ mol (see Table 1). Tin or titanium was added to assure structural charge electroneutrality and also to highlight the blue hue [5].

The pigments were produced by the conventional ceramic route. The starting slurries were wet-milled for 1 h, dried at 98 °C (overnight) and calcined in an electric kiln at 1350 °C (3 h dwell time and 5 °C min^{-1} heating rate). To better define the sintering cycle, the thermal behaviour of mixed reagents was studied by performing simultaneous differential (DTA) and gravimetric (TG) analyses, in a Setaram apparatus (in air atmosphere with 10 °C min^{-1} heating rate).

The qualitative analysis of formed phases was performed by X-ray powder diffraction, using a Rigaku Geigerflex diffractometer with Cu Kα radiation in the 2θ range 4–80°. The microstructural characterization was conducted by scanning electron microscopy (SEM – Hitachi, SU 70) and energy dispersive X-ray (EDS – EDAX with detector Bruker AXS, software: Quantax).

The optical properties of the pigments were determined by absorption spectroscopy in the 350–1700 nm range using a Shimadzu UV-3100.

The $L^*a^*b^*C^*$ and $h°$ colorimetric parameters of the pigments and coloured products were measured using a Konica-Minolta Chroma Meter CR-400, employing illuminant D65, specular component included and 2° standard observer [12–14].

Selected pigments were then tested with respect to colouring common ceramic products, under firing trials performed in an industrial furnace (Revigrés, PT). Glazes (transparent bright, opaque bright, and transparent mate) were coloured by adding 3.7 wt.% of each pigment, while only 3 wt.% was added to porcelain stoneware bodies. For the coloured glazes the homogenization process was performed by wet-mixing before application on the ceramic tiles, as uniform layers that were fired following a fast firing scheme (50 min and a maximum temperature of 1130 °C). The porcelain stoneware coloured powders were obtained by wet-mixing followed by drying (110 °C). The powders were then used to press pellets which were fired at a maximum temperature of 1200 °C being the total cycle 60 min.

3. Results and discussion

3.1. Thermal analysis

Coupled differential thermal and thermogravimetric analyses, shown in Fig. 1, were conducted to distinguish the differences between pure and waste-based similar formulations. Total weight loss of wastes-based pigment upon firing reaches approximately 38%, mostly concentrated in two regions: (i) up to 500 °C, due to dehydration and dehydroxylation reactions, basically occurring in the anodizing sludge; (ii) above 1000 °C, as a possible result of sulphates decomposition in the same sludge (see Table 1) [15–17]. As expected, changes on TG curve of Hb–Co/Ti formulation are less

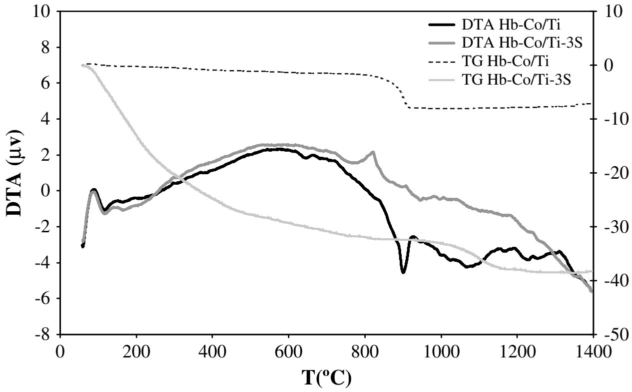


Fig. 1. Coupled DTA–TG curves of pigment mixtures obtained for pure and waste reagents.

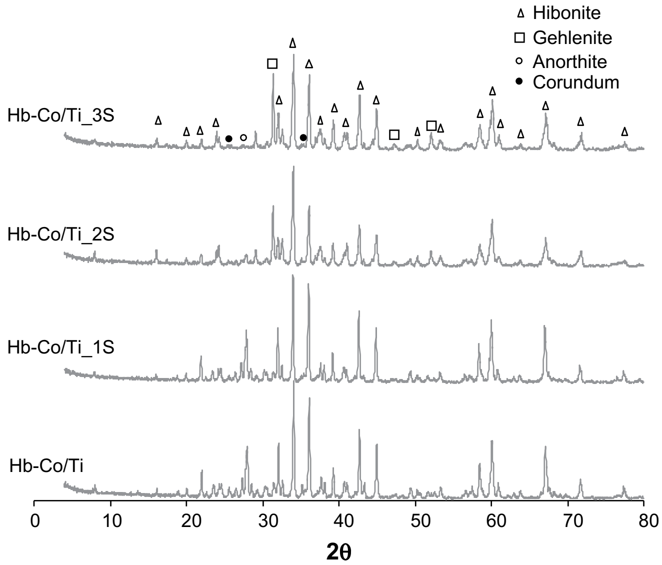


Fig. 2. X-Ray diffraction patterns of Co/Ti-doped powders calcined at 1350 °C.

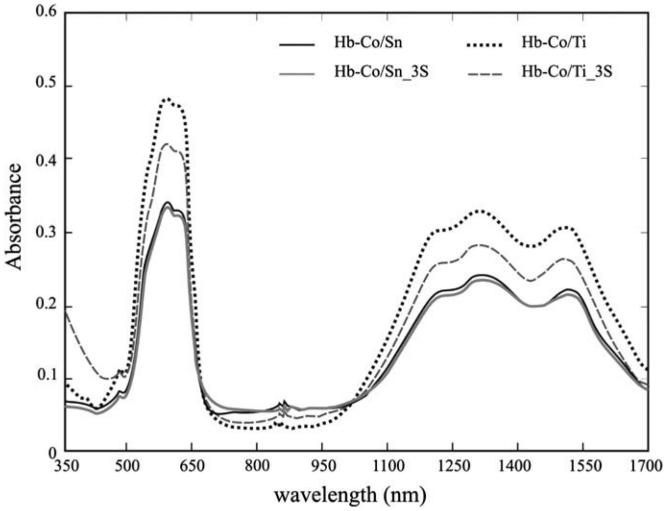


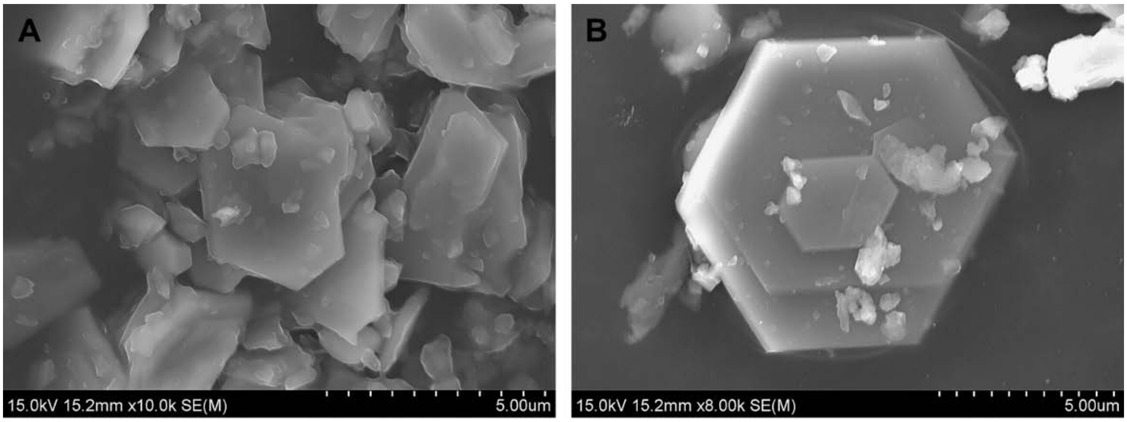
Fig. 4. Optical absorption spectra of selected pigments.

significant. Now, the total mass loss is about 7%, and is basically due to decarbonation of calcite at 875 °C, as revealed by the endothermic peak in DTA. In this region, polymorphic transformations can take place conducing to anorthite or gehlenite ($Ca_2Al_2SiO_7$) [17]. The hibonite progressive crystal growth seems to happen after 1200 °C once finished the ultimate desulphuration reaction. Nevertheless, the selected sintering temperature was higher (1350 °C), to promote an intense formation of the desired structure.

3.2. XRD and SEM analyses

Fig. 2 shows the X-ray diffraction data of powders calcined at 1350 °C. In all cases hibonite is depicted as main phase. A divergence from the initial prediction (1 mol hibonite + 1 mol anorthite) is denoted by the appearance of gehlenite and corundum peaks. This deviation is more accentuated with the progressive use of wastes in the pigment mixtures. The anorthite seems to disappear when gehlenite emerges, and this happens by adding marble sawing sludge, so exclusively in Hb–Co/Ti_2S and Hb–Co/Ti_3S formulations. The co-existence of gehlenite and anorthite with the hibonite phase is predicted by looking to the Al_2O_3–CaO–SiO_2 ternary diagram [5,18].

The EDS micropunctual analysis (see Fig. 3) confirmed that selected grains A and B, respectively on pure and waste-based pigments, correspond to hibonite phase. In them, cobalt and titanium contents are close to the predicted values (0.3 mol) in the initial formulations. The amount of Si is also very low. The SEM micrographs (Fig. 3) also reveal that Co-bearing hibonite particles



Elements (at.%)	Particle A	Particle B
Calcium	3.49	3.48
Aluminium	35.39	36.35
Titanium	1.28	0.81
Cobalt	1.21	0.75
Silicon	0.29	0.35
Oxygen	58.35	58.25

Fig. 3. SEM/EDS analyses of Hb–Co/Ti (A) and Hb–Co/Ti_3S (B).

Table 2
CIELab parameters of pigments and respective glazes (3.7 wt.% of pigment) and porcelain stoneware (3 wt.% of pigment) applications. TM: Transparent Mate glaze, OB: Opaque Bright glaze, TB: Transparent Bright glaze; and PS: Porcelain Stoneware.

References	Pigments	TM	OB	TB	PS
	*L**/*a**/*b**/*C**/*h*°	*L**/*a**/*b**/*C**/*h*°			*L**/*a**/*b**/*C**/*h*°
Hb-Co/Ti	59.8/10.9/−48.1/49.0/282	70.0/3.0/−19.0/17.8/279	72.3/2.4/−14.2/14.0/280	47.9/7.7/−28.9/31.2/288	58.0/−1.5/−2.2/3.2/235
Hb-Co/Ti_1S	60.4/7.9/−38.9/39.5/281	74.0/2.2/−15.5/14.6/277	75.6/2.0/−13.5/12.0/278	51.7/6.6/−27.7/27.5/285	58.2/−0.5/−6.8/7.5/262
Hb-Co/Ti_2S	56.2/8.9/−40.5/41.1/282	72.0/2.9/−19.4/18.5/278	74.8/2.1/−14.3/13.7/277	48.8/8.8/−37.4/35.8/286	57.0/−0.3/−6.7/7.4/263
Hb-Co/Ti_3S	46.7/13.3/−53.8/55.6/283	70.1/3.0/−21.5/20.6/279	73.7/2.0/−16.9/16.4/277	45.1/10.0/−42.1/40.3/287	56.5/−0.5/−5.7/6.4/264
Hb-Co/Sn	66.2/3.5/−27.2/27.4/277	73.4/2.4/−16.0/15.5/278	74.0/2.2/−13.5/13.3/279	49.6/6.5/−24.5/25.6/287	58.2/−1.7/−4.7/5.4/246
Hb-Co/Sn_1S	65.7/2.5/−21.9/22.0/276	76.5/1.5/−13.5/13.1/276	76.9/1.3/−10.4/10.3/276	58.1/3.6/−16.4/17.5/283	59.8/−1.6/−2.4/3.4/234
Hb-Co/Sn_2S	65.0/2.7/−24.4/24.5/276	76.0/1.7/−14.2/13.8/276	76.5/1.4/−10.7/10.5/276	56.4/4.0/−18.5/18.2/283	60.4/−1.5/−1.2/2.4/212
Hb-Co/Sn_3S	65.7/3.4/−25.9/26.0/275	75.8/1.8/−16.1/15.4/276	77.2/1.4/−10.7/10.5/276	56.4/4.4/−21.3/21.9/283	59.9/−1.6/−2.7/3.7/236
PGE 5104	63.4/−7.9/−14.4/16.3/241	71.4/−7.3/−17.1/18.2/244	74.4/−7.7/−16.5/18.0/243	52.2/−9.7/−26.6/28.5/246	–
PGE 5101	52.2/11.1/−9.7/14.3/318	39.1/8.5/−28.5/30.5/290	44.8/7.9/−28.1/29.1/288	16.7/9.4/−19.8/27.1/301	–
CP AZ 51	40.9/2.8/−32.4/32.6/274	–	–	–	33.1/3.1/−22.9/25.0/279.6

have a hexagonal shape being its morphological definition higher in the waste-based pigments, as a probable result of fluxing/mineralizing action of some impurities present on industrial wastes upon pigment sintering.

3.3. Optical characterization and colour development

Fig. 4 shows the UV–Vis–NIR absorption spectra of the Co-doped pigments. The general aspect was similar for all the pigments insofar as a wide band was obtained that was composed of three emissions in the NIR region, at ~1200, 1300 and 1500 nm. These seem to be attributable to spin forbidden transitions of tetrahedrally coordinated Co^{2+} ions from $^4A_2(F)$ ground state to the excited $^4T_1(F)$ state [19–23]. In the visible region, four bands of distinct intensities are noticed. This multiple excitation reflected at 471, 544, 580 and 610 nm is assigned to $^4A_2(F) \rightarrow {}^4T_1(P)$ forbidden d–d transitions of Co^{2+} ($3d^7$) in a tetrahedral field (T_d) [19–23]. The exhibited colour is interpreted by the first reflected band at 471 nm in the range of blue visible light interval (490–450 nm) [23]. In this zone, the spectra (Fig. 4) reveal differences in pigment's absorbance intensities. Weaker bands are observed when tin is added instead of titanium to compensate the charge unbalance created by the

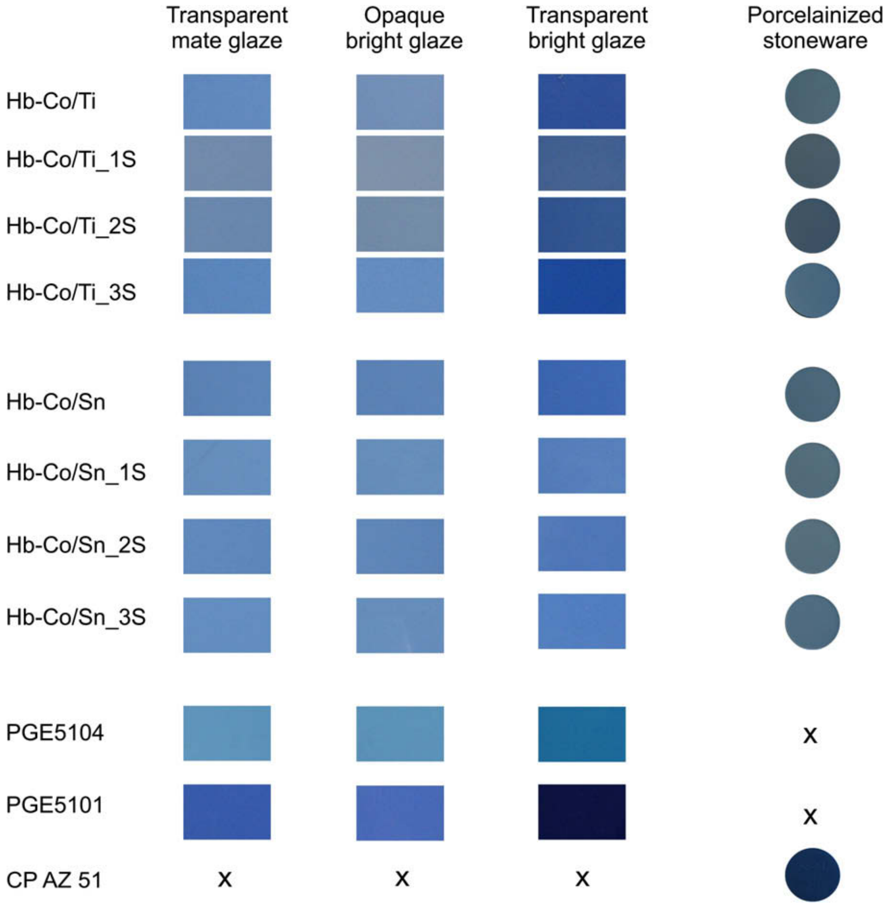


Fig. 5. Schematic view of coloured glazes and porcelain stoneware bodies after firing in industrial trials.

substitution of Al^{3+} by Co^{2+}. Focusing on the effect of reagents nature, the replacement of pure components by industrial wastes is more distinguished in Co/Ti formulations. In fact, the absorbance of the Hb–Co/Ti_3S pigment tends to be lower and it could also affect its colouring performance on distinct applications. For Hb–Co/Sn and Hb–Co/Sn_3S pigments band intensities are closer, revealing that tin tends to minimize colour changes and to partially hide the blue hue.

The colorimetric parameters of the pigments, both as powder and when dispersed in ceramics are displayed in Table 2. The blue colour of the colorants is clearly indicated by the negative b^* values and positive a^* values; the high C^* values is indicates their high intensity. Hence, the titanium doped pigments were superior to their tin doped counterparts, in agreement with previous UV–Vis–NIR observations (Fig. 3). The colorimetric differences between Ti-doped and Sn-doped pigments are directly translated to the applications, and then Ti-doped pigments tend to show better colour development than Sn-containing ones. With fixed cobalt amount and by doping with 0.3 mol of tin (Hb–Co/Sn) or titanium (Hb–Co/Ti), we observed that the first one (SnO_2) acts as a stronger opacifying agent [3]. This compound exalted when pigments were applied to different glaze supports. The trend is clearly denoted by the negative $-b^*$ *values* and high chroma (C^*) values.

The chemical and electronic stability of these pigments on distinct environments is easily confirmed by colour development on different glaze types and ceramic bodies, in which a strong and stable blue hue is dominant. This is true either with the use of pure reagents as with wastes. In fact, Hb–Co/Ti_3S and Hb–Co/Sn_3S pigments tend to show the darkest blue colorations, probably as a consequence of the mentioned mineralising action of some impurities. This is confirmed by the higher chroma values (C^*) obtained even though the hue angle (h°) was reduced, corresponding to an interesting light violet component. Visually, these observations are noticed in Fig. 5. It seems that final substitution of pure silica by foundry sand in 3S pigments is responsible for exalting the blue color in comparison to the 1S and 2S products. The explication could be provided by the iron amount (1.12 wt.%) present in the waste sands and by knowing the sensibility of such ceramic applications to this element. On the other hand, this factor might correct the small degradation originated by addition of Al-anodising and marble cutting sludges already noticed in XRD patterns by a deviation in the mineralogical composition.

For sake of comparison, distinct commercial pigments were tested. Olivine (PGE5101-Colorobbia) and willemite (PGE5104-Colorobbia) cobalt containing pigments were added to glazes, while Co-doped spinel (CP AZ 51-Itaca) was used to colouring stoneware bodies, according their normal use in industry. Preparation and firing conditions were similar to those used with the new pigments. The relative higher amount of Co in olivine (73 wt.%) and spinel (44 wt.%) based pigments in comparison to hibonite (olivine > spinel > willemite > hibonite) gives darker and stronger blue colorations, while willemite develops light (sky) blue (see Fig. 5). These differences are clearly transmitted by the L^* and h° values.

Anyway, the new waste-based Co-doped hibonite pigments show competitive colouring performance, especially in glazes (see Table 2). Their measured $L^*a^*b^*C^*h^\circ$ values are closer to those achieved by olivine-based pigments. This is confirmed by the low displayed brightness achieved by comparing commercial pigments with those formulated by us using pure reagents, while differences to willemite are stronger, particularly in the green component ($-a^*$). The colouring of porcelain ceramic bodies is somewhat poor when compared with that assured by the spinel (CP AZ 51), specially developed for this matrixes, suggesting the need of using higher Co percentages in the hibonite or increasing the added amount to the paste. In fact, hibonite pigments have a relatively low cobalt amount (1.8 wt.%).

4. Conclusions

The industrial tests performed showed that the development of a new blue solid solution pigment with Co(II) ions in tetrahedral coordination as chromophore element was well succeeded. The calcium hexaluminate proved to be a suitable host structure and relatively low cobalt amounts (1.8 wt.%) are required to develop good chromatic properties. The prepared pigments are especially interesting for colouring glazes being the results comparable to those assured by the commercial ones. Their performance in colouring porcelain ceramic bodies was not so promising. Moreover, the replacement of pure reagents by industrial wastes is also feasible, which is attractive from environmental and economical points of view. The blue hue of the wastes-based pigment is stronger and it might sintered at lower temperature than the one formulated with pure reagents. Titanium co-doping is preferable to tin, based on the colour characteristics and also on economical aspects. However, future trials will be focused on the preparation of Ti and Sn-free formulations.

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