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Synthesis and characterization of hematite pigment obtained from a steel waste industry

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ABSTRACT

Pigments that meet environmental and technology requirements are the focus of the research in the ceramic sector. This study focuses on the synthesis of ceramic pigment by encapsulation of hematite in crystalline and amorphous silica matrix. Iron oxide from a metal sheet rolling process was used as chromophore. A different content of hematite and silica was homogenized by conventional and high energy milling. The powders obtained after calcinations between 1050 and 1200 °C for 2 h were characterized by X-ray diffraction and SEM analysis. The pigments were applied to ceramic enamel and porcelain body. The effect of pigment was measured by comparing $L^*a^*b^*$ values of the heated samples. Results showed that the color developed is influenced by variables such as oxide content employed, conditions of milling and processing temperature. The results showed that the use of pigment developed does not interfere in microstructural characteristics of pigmented material. The best hue was obtained from samples with 15 wt% of chromophore, heated at 1200 °C in amorphous silica matrix.

1. Introduction

Metal industries contribute significantly to the generation of waste. Thus, these industries show growing support for studies that research the use of these materials for applications in other processes, adding value to materials that are treated as waste [1].

The production of iron oxide pigments might become one approach for reducing the problem of these industries because they generate waste with high content of iron in the form of oxides and metals in their processes.

The use of these iron-rich materials is essential due to growing demand for new pigments, driven by the increase in construction activities. The importance of iron oxide pigments is also based on their non-toxicity, chemical stability, durability, variety of colors and particularly their low cost for emerging markets and a growing concern about the use of heavy metals in pigment production [2].

This environmental awareness is regarded with great interest by the industry, leading to the development of ceramic pigments with high stability and intense hues. These pigments will also meet technological and environmental requirements. In turn, this might lead to the development of more economical and efficient processes thus allowing for the production of new pigments with intense hues. These results might take place mainly by improving the characteristics of the pigments already used [3]. Many of the studies developed to reuse industrial wastes as ceramic pigments include the reuse of waste from the process of electroplating. Examples of these applications are reported in studies by Ferreira and Castanho [4], Milanez [5], Gomes [6], Costa et al. [7] and Casagrande et al. [8]. Additionally, studies on the incorporation of other typos of waste from iron and steel have been carried out [9,10,2].

This paper aims to investigate the possibility of reuse of the waste from the rolling industry in the production of ceramic pigments.

2. Experimental

2.1. Pigment synthesis

The waste employed in this investigation was obtained from metal sheet treatment process (ArcelorMittal). This waste was used in the same condition as when collected. Crystalline (quartz) and amorphous silica was employed as raw material for the matrix.

In the formulation of pigments, the content of hematite added was of 5–15 wt%. These samples were subject to wet milling (alcohol), using conventional and high energy (300 rpm) milling for 4 h for both methods of milling. After that, the mixtures were calcined for 2 h in porcelain crucibles at 1050–1300 °C. Then the products were sifted through a 325 mesh screen.

The powders obtained were characterized and tested as ceramic pigments. A ceramic enamel and a porcelain body, composition

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Table 1
Base glase formula (Portobello, 2009).

Raw material	Descrição	Enemal (wt%)	Porcelain (wt%)
Refractors	Alumina and Zirconium silicate	5.00	–
Hues	Wollastonite and Dolomite	11.50	–
Additives	Glue and Deffloculant	0.50	–
Frits	Ca and Zn mattes	57.00	–
Suspension agents	Kaolin and Bentonite	12.00	40
Feldspats	Potássim and Sodium	14.00	60

(Table 1), was used for the application of pigment. The pigments content added to the composition of 2 wt% for ceramic enamel and 3 wt% for porcelain body. These were fired at 1188 °C for 39 min for enameled and 1214 °C for 50 min for porcelain pieces, in accordance with industrial cycles.

2.2. Characterization techniques

In order to evaluate the thermal stability of the residue, a differential thermal analysis (TG-DTA) was perfomed on the iron oxide in oxidizing atmosphere.

The morphology of the samples of the pigments was examined by scanning electron microscopy (SEM). The samples were prepared in ultrasound (mod. C/T, Thonson) using alcohol as dispersant.

In order to examine the crystalline phases present, X-ray diffraction measurements were carried out on the calcined powdered samples using a conventional diffractometer. The interpretation of the diffractogram was done using the ICDD database (International Centre for Diffraction Data).

Color measurements were performed in fired pieces by colorimeter using the solf-spectr Magic software in a Spectrophotomer (model CM 3600d, Minolta) using the CIELab method. The color is defined through the parameters $L^*a^*b^*$, where a^* represents the change from green (negative values) to red (positive values); b^* represents the change from blue (negative values) to yellow (positive values). The parameter L^* define the brightness. The tests were performed at the Portobello company.

3. Results and discussion

3.1. Hematite characterization

The chemical analysis is described in Table 2. The results show that hematite contains a high percentage of Fe_3O_2, indicating that this waste is an important low-cost raw material for the preparation of ceramic pigments.

Table 2
Chemical composition of Hematite.

Oxide	Wt (%)
Al_2O_3	0.25
CaO	0.02
Fe_2O_3	97.3
K_2O	0.05
MgO	0.08
MnO	0.25
Na_2O	0.03
P_2O_5	0.03
SiO_2	0.87
TiO_2	0.04
BaO	0.74
Co_2O_3	N.D.
Cr_2O_3	<0.1
PbO	N.D.
SrO	N.D.
ZnO	N.D.

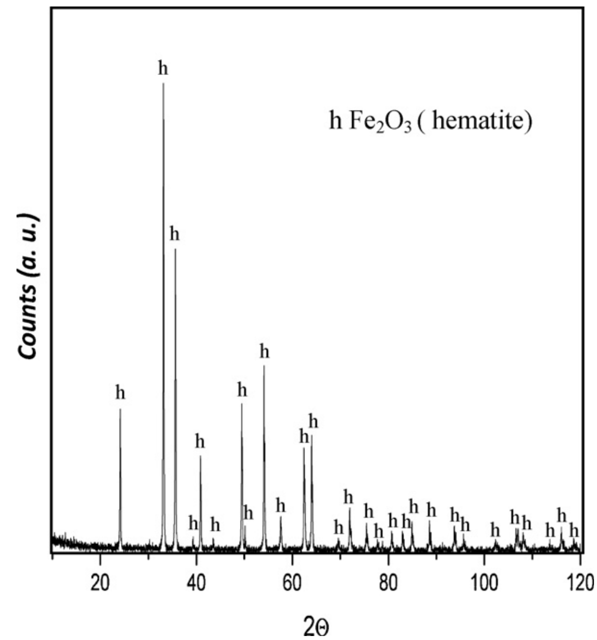

Fig. 1. XRD patterns of the hematite.

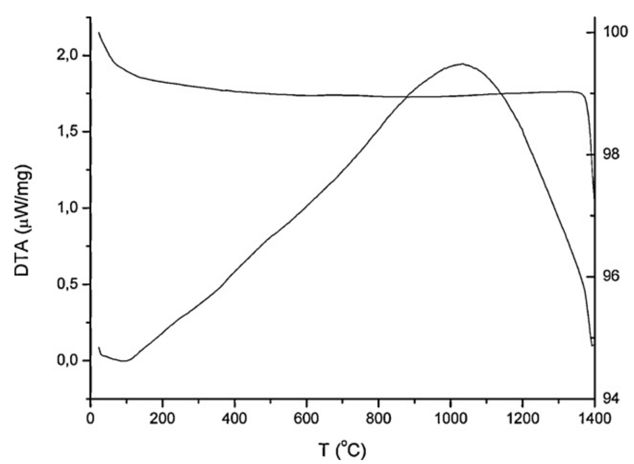

Fig. 2. DTA curve of the hematite.

Fig. 1 shows the XRD patterns of hematite present only iron oxide, in the shape of hematite (ICDD, 73-0603). Its low particle size, typical of materials from a chemical process of precipitation, favors the formation of the oxide.

The differential thermal and gravimetric analysis of hematite was performed in an oxidizing atmosphere. The purpose of performing the analysis was to identify the possible presence of phase other than hematite, as this would be subjected to oxidation process, with consequent effects associated with weight gain. The results showed that in range between 200 and 1350 °C the effect of weight gain was not identified (Fig. 2).

3.2. Pigments characterization

In order to evaluate the effect of the percentage of hematite in the thermal behavior of mixtures (quartz-hematite) the phases present after milling and sintering were analyzed. The limit of 15 wt% of chromophore added was defined based on literature [6,10–12]. The increase in the percentage of hematite had no influ-