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Synthesis of black pigments containing chromium from leather sludge

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Abstract

The black ceramic pigments with spinel structure have been prepared by using Cr-rich leather sludge in this paper. The washed Cr-rich leather sludge calcined at 1100 °C for 1 h as chromium oxide precursor (named as CA) was mixed with an appropriate proportion of other industrial metallic oxides, followed synthesizing black ceramic pigment by sintering. Both non-washed and washed sludge fired at 1100 °C were characterized by X-ray fluorescence (XRF) in order to determine their chemical compositions and X-ray diffraction (XRD) analysis to confirm that CA mainly contains Cr_2O_3 crystal phase. The results show that CA could be used as a source of chromium to prepare black pigment. The crystalline phases of obtained pigments were characterized by XRD. Furthermore, the morphology as well as the composition of pigments was investigated by scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS). The color coordinates of pigments were examined and compared with the commercial pigments based on CIE-L^* a^* b^* values measured using UV–vis spectroscopy. The obtained pigments sintered at 1200 °C with 35–55 wt% content of CA possess the excellent black spinel structure and color effect. Under optimized conditions, the pigment has low average spectral reflectance (7%).

Keywords: Leather waste; Chromium oxide; Black pigment; Spinel structure

1. Introduction

A chrome tanning method to produce leather is comparatively traditional and common today. However, this method generates a large amount of organic waste, wastewater and sludge containing chromium. For example, processing one metric ton of raw hide generates 200 kg of final leather, 200 kg of tanned waste (containing 3 kg of chromium), 250 kg of non tanned solid waste, and 50,000 kg of wastewater (containing 5 kg of chromium). More than 60% of the trivalent chromium is left in the solid and liquid waste [1], which will be easily oxidized to hexavalent chromium in typical oxidation conditions [2]. Studies have proved that hexavalent chromium compounds have greater toxicity, which can generate toxic effects on living tissue through the cell membrane, making carcinogenic or teratogenic diseases. Moreover, hexavalent chromium can easily be absorbed by human through the skin, digestive and respiratory system, etc [3]. Therefore, chromium pollution severely affects the hostility of human physiology and other biological systems when it exceeds the tolerance levels [4]. Several methods, such as ionic adsorption [5–8], ion exchanging [9], chemical precipitation [10–12] etc, were used for the treatment of liquid waste containing chromium. However, for the Cr-rich solid waste, the methods adopted in actual production are usually the ways of burial or incineration, which do not really solve the problem, and easily cause secondary pollution. It is very necessary to find out an effective method, which not only solves the environmental pollution of Cr-rich sludge precipitated from tanning liquid waste, but also re-uses waste sludge saving chrome resources.

In the present ceramics industry, inorganic black pigments are largely applied as colorants either for ceramic bodies or for glazes [13]. Black pigments with its pure and dignified decorative effect are heavily favored by more people and regarded as high-grade treasures. Nearly 25 wt% of the total consumption of commercial formulations of black pigments are based on the spinel structure, i.e., (Ni, Fe)(Fe, Cr)$_2$O$_4$, (Fe, Co)(Fe, Cr)$_2$O$_4$ and

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(Fe, Mn)(Fe, Mn)$_2$O$_4$ [14,15]. Most of the synthetic pigments are prepared with certain salts or metallic oxides of the desired metals with high purity which results in high cost [14]. Therefore, searching for the alternative less expensive natural raw materials or industrial wastes is the trend to prepare the ceramic pigments. For this purpose, metal-rich sludges to produce black or other color pigments have been reported [14–20]. For leather solid waste, the studies on the preparation of green and pink pigment have already existed [21,22]. However, it was not reported to prepare black ceramic pigment by utilizing tanning chromium-rich sludge.

On the other hand, Co-free black spinel structure in which chromium is the main base, has been widely studied as ceramic pigments because of excellent properties including high-temperature chemical stability and coloring capacity. In this paper, the Co-free black spinel pigment synthesized from the tannery sludge is provided, which discovers a new way to control and reduce tannery heavy metals chromium pollution and significantly to decrease the cost of black ceramic pigment.

2. Experimental

The Cr-rich leather sludge generated from tanning procedure which was collected by alkali precipitation method from the local leather factory was planetary ball milled for 1 h and washed to remove the vast majority of water-soluble inorganic components such as sulfate and chlorate, then dried at 105 °C. The dried sludge was calcined at 1100 °C in a tube furnace with nitrogen as protective gas for 1 h to remove all organics including skin proteins, hair, fat, and other organic components which were decomposed into oxycarbide, water and some of nitrogen oxide gas, and part of inorganic impurities easily volatilized at high temperature. The protective gas prevented Cr^{3+} from being oxidized to Cr^{6+} [23]. Meanwhile, these organic matters in sludge have other benefits because they can react as a Cr(VI) reductant in the mixture. When Cr(VI) came in contact with organic substances or biomaterial, Cr(VI) could be not only bound on the surface but also reduced to Cr(III) [24]. Finally, the sludge raw material was obtained and named as CA. In order to test the stability of CA, leaching experiments with 10% hydrochloric acid solution (liquid/solid ratio 20:1) were carried out at room temperature for 24 h with magnetic stirrer.

In the preparation of pigments, the as-prepared CA material with the content of 35–55% was mixed with other different components of metallic oxides, such as Fe_2O_3, Ni_2O_3, and CuO as present formulations in Table 1 by wet ball-milling for 30 min to obtain very homogeneous slurries and the slurries were dried at 105 °C. The dried slurries were followed by calcination firstly at 1200 °C with a heating rate of 5 °C/min for 1 h dwell time. In order to examine the effect of calcination temperature on reaction products, a selected composition was also calcined at 900–1300 °C for the same dwell time. The calcined products were ground by planetary wet ball milling for 30 min and washed with water to eliminate undesirable soluble salts that had negative effects during glazing, and dried at 105 °C in an oven. Finally, in order to examine the application results, the as-prepared and commercial pigments were added (3%) to commercial transparent glaze.

Table 1
The composition proportion of raw materials used for the preparation of black ceramic pigments.

Sample	Chromium source(CA)/wt%	Fe_2O_3/wt%	CuO/wt%	Ni_2O_3/wt%
BC1	35	30	10	25
BC2	45	20	15	20
BC3	55	15	10	20

The thermal behavior of the washed Cr-rich sludge was characterized by differential thermal analysis (DTA) and thermogravimetry (TG) carried out from room temperature to 1200 °C. The chemical compositions of the non-washed Cr-rich sludge calcined at 1100 °C for 1 h were determined using an X-ray fluorescence spectrometer (ZSX Primus II). The crystalline phases were characterized by XRD on a Rigaku D/Max2200PC X-ray diffractometer using Cu Kα radiation ($\lambda=0.15418$ nm) with 2θ of 10–90° at 40 kV and 20 mA. The morphology and elementary composition of products were examined by scanning electron microscopy (SEM) (SUPRATM55), equipped with an energy dispersion spectroscopy (EDS) (SUPRATM 55) equipment to analyze the elements of the samples. The color coordinates of the pigments were measured using UV–vis spectroscopy (UV-2550, Shimazduo) in the range of 300–800 nm and the CIELab method was used to obtain $L*$, $a*$ and $b*$ values. Using ultraviolet spectrophotometer determines the color of pigments under different visible light wavelength (380–780 nm). The curve reflected the color properties of the pigment directly or indirectly. These color parameters were measured for an illuminant D65, following the CIE-$L*$ $a*$ $b*$ colorimetric method recommended by the CIE (Commission Internationale del'Eclairage). In this system, $L*$ is the degree of lightness and darkness of the color extending from white ($L*=100$) to black ($L*=0$). Positive $a*$ values correspond to red color; negative values to green. Positive $b*$ values correspond to yellow color; negative values correspond to blue.

3. Results and discussion

The XRD pattern shown in Fig.1 evidences that the as-prepared CA material primarily contains Cr_2O_3 as well as part of $MgCr_2O_4$ and Mg(FeAl)O_4 crystalline phase. In TG-DTA (TGA/SDTA851e) curves (Fig. 2), the strong endothermal DTA peak around 178 °C indicates that from the beginning of the test physical water weight loss, due to the evaporation of moisture remained in chromium sludge, as well as the loss of crystal water of certain compounds. Both peaks at around 390 °C and 473 °C are the exothermal characteristic behavior of the organic matter burnout present in the waste associated with a significant weight loss (20 wt%) in the TG curve. In addition, chromium hydroxide in waste possibly is pyrolysised into chromic oxide. There is no significant weight loss up to around 975 °C. In the range from 1000 °C to 1200 °C, there is a significant weight loss of almost 10%, approximately due to the decomposition of certain salts