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Encapsulated carbon black prepared by sol–gel-spraying: A new black ceramic pigment

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Abstract

As a new black ceramic pigment, encapsulated carbon black pigment has been prepared by a sol–gel-spraying method. The obtained pigment sintered at 900 °C for 2 h in air has a deep black hue ($L^* = 19$), indicating carbon black can be fully covered. In the pigment, a dense coating layer on carbon black is formed due to the fast transformation from sol into gel by rapid extraction of solvent. The transparent silica phase spaces out the fine crystalline (zirconia or zircon), which permits to display the color of carbon black. This preparation method provides a way to prepare the encapsulated pigments. It will provide more colorful ceramic pigment applied in ceramic decoration by encapsulating.

Keywords: Ceramic; Pigment; Encapsulated; Carbon black; Sol–gel-spraying

1. Introduction

Inkjet printing using the Cyan–Magenta–Yellow–blacK (CMYK) printing system has become the tendency of industrial ceramic decoration over the last decade. Black pigment is more important because it has the dual actions: to act as a basic color and to change the brightness of the printing. Nowadays, the ceramic pigment with deep black hue can only choose the cobalt-containing pigment. This kind of pigment is expensive and might be environmentally harmful.[1] More importantly, the cobalt-containing pigment cannot provide the pure black hue because cobalt ion has to cooperate with the other ions, such as iron ion, manganese ion, to absorb jointly the visible light, which is sensitive to the crystal structure of pigment.[2] Carbon black (CB) is a very well black pigment ascribing to its high tinting ability and low cost. Unfortunately, it is impossible that CB is used directly as ceramic pigment because it can be oxidized in air above 800 °C. Coating an oxidation protection layer on carbon black has been suggested.[3–5] However, two obstacles still exist in literature: (1) to obtain a dense coating with an out-and-out coverage of carbon black. Carbon black must be covered completely, or else, the pigment will become gray or white due to the oxidation of carbon black, and thus cannot be used in CMYK system and (2) to obtain a transparent coating avoiding concealing the color of CB. To solve them, sol–gel method is generally suggested, by which the perfect core-shell particles can be prepared.[6] However, the obtained encapsulated carbon black pigment is gray in color ($L^* = 53.73$) after calcination in air.[3] It may be explained that the evaporation of solvent which is consolidated in the gel results in the coating is porous. Some of CB is burnt. To avoid this case, the combustion of solvent is chosen to fasten the transformation of SiO_2 from sol to gel.[4] The obtained SiO_2 encapsulated carbon black pigment keeps black even sintered at 1300 °C in air indicating carbon black has a perfect coverage. However, the key is that the pigment cannot be used in most of the glazes because the coating will be damaged due to the reaction SiO_2 with the other oxides in glaze, especially at high temperature (>1200 °C). Zircon is stable in glazes and is regarded as the best coating material for encapsulated pigment.[1] However, zircon is white. The zircon coating needs

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the special structure which permits the light to penetrate it, and thus displays the color of carbon black. Otherwise, the higher the coverage of zircon is, the whiter the encapsulated carbon black pigment is.

In the present work, zircon encapsulated carbon black was prepared by a sol–gel-spraying method. This method might give the high coverage of carbon black and the special structure to show the color of carbon black. The pigments were characterized by XRD, TEM, SEM, TG/DTA, etc.

2. Materials and methods

2.1. Preparation of pigments

Tetraethylorthosilicate ($Si(OC_2H_5)_4$, TEOS, 104 ml), alcohol (170 ml), and water (40 ml) were mixed in a flask, and then dilute HNO_3 (40 ml, 1 ml concentrated HNO_3 dissolved in 39 ml water) was dropped into the above-mentioned mixed solution. The solution was reflux in a water bath for 8 h at 85 °C. SiO_2 sol can be obtained.

$ZrOCl_2{\cdot}8H_2O$ (99.82 g) was dissolved into 200 ml of alcohol–water solution (1:1 volume ratio). Hexamethylenetetramine ($C_6H_{12}N_4$, 34.72 g) was dissolved into another 200 ml of alcohol–water mixed solution. Hexamethylenetetramine solution was dropped into $ZrOCl_2$ solution under vigorous stirring at 10 °C. And then aging for 3 h at room temperature, ZrO_2 sol can be obtained.

Carbon black suspension (14.4 g) was prepared by mixing of carbon black (2 g, with 20 nm in particle size), Arabic gum (used as dispersant, 0.1 g) and water (12.3 g) by ball milling.

Finally, SiO_2 sol, ZrO_2 sol and carbon black suspension were directly mixed together. In the mixture, the molar ratio Si:Zr was 1.5:1; weight ratio carbon black:zircon was 2.5:1. Three kinds of preparation methods could be chosen:

(A) Normal sol–gel method. The mixture is stood undisturbed until the gel was formed.
(B) Combustion method. The mixture was poured into an evaporating dish, heated until alcohol burns completely. The obtained dried gels were crushed by mortar.
(C) Sol–gel-spraying method. The mixture was sprayed into a tube furnace. The temperature of the furnace is 600 °C. The spraying condition is air pressure: 1.5 bar, air flow: 200 $cm^3\ min^{-1}$.

The gels prepared by (A), (B) or (C) were collected and calcined at 1150 °C for 3 h in Ar, and then calcined at 900 °C for 2 h in air. The encapsulated pigments were obtained. The calcination at 900 °C in air is not required for the preparation of the pigments, which just removes the uncoated carbon black.

To characterize the microstructure changes caused by the calcinations temperature, the encapsulated pigment prepared by sol–gel-spraying method was calcined at 1300 °C for 2 h in air.

The encapsulated pigment (3 g) was mixed with the transparent glaze (10 g, with the melting temperature of 900 °C) and water (20 g). The obtained suspension was brushed on the porcelain and calcined at 900 °C for 10 min.

2.2. Characterization

To measure the coverage of carbon black, the obtained pigment (without calination at air atmosphere) was characterized by TG/DTA using a thermal analyzer (NETZSCH STA 449C) from room temperature to 1200 °C at a constant rate of 10 °C min^{-1} in Air using α-Al_2O_3 as a reference. The mass lose above 800 °C was considered as the mass lose of carbon black.

The mixtures with different molar ratio of Si:Zr of 1:1, 1.2:1 and 1.4:1 were prepared. No carbon black suspension was added. The other preparation processes were the same to molar ratio of Si:Zr of 1.5:1. The encapsulated pigments were characterized by XRD. The XRD data for the pigments were collected on a Rigaku D/max-(β) X-ray diffractometer using a graphite monochromator and Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) with the scanning range (2θ) of 10–70°. The effect of carbon black on the crystal structure of the pigments is also characterized by XRD.

TEM imaging observation was carried out on the transmission electronic microscope (JEOL-2010, Japan).

CIE lab parameters L^*, a^*, b^* was measured by a spectraphotometer (HunterLab Miniscan MSXP 4000, 400–700 nm, white glazed tile reference $x = 31.5$, $y = 33.3$). In this way, L^* is the lightness axis (black (0) ∼ white (100)), b^* is the blue (−) ∼ yellow (+) axis, and a^* is the green (−) ∼ red (+) axis.

The UV-visible spectroscopy was performed by diffuse reflectance with integrating sphere (Perkin-Elmer, USA) in the 200–900 nm range, step 0.3 nm, using $BaSO_4$ as a reference.

3. Results and discussion

3.1. Effect of the prepared methods on the microstructures of pigments

Fig. 1 shows the TEM images of the pigments prepared by different preparation methods. Pigment prepared by the normal sol–gel method is porous, as shown in Fig. 1(a). Comparing to the TEM image of carbon black shown in Fig. 1(d), it can be seen that most of carbon black are naked. Obviously, even if carbon black is covered, such a loose structure of the coating cannot prevent carbon black from being oxidized.

However, the dense structure still can be found in small parts of the pigment, which maybe generated by aggregation of the sol particles in the fabrication process. Carbon black embedded in this structure can be protected. In a whole, the pigment has a relatively low coverage. This may be the reason that carbon black pigment prepared by normal sol–gel method is gray.[3] Both the pigment prepared by combustion and that by spray drying are fully dense. The difference is that the pigment prepared by combustion method is irregular caused by the grinding of gels and the pigment prepared by spraying is global. In both the preparation processes, alcohol is evaporated very quickly and the sol particles aggregate together and transfer into the gel in a short time. No solution is consolidated into the gel, thus, no pores can be remained in the dried gel in this