Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 5503–5511

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of the milling process on the properties of $CoFe_2O_4$ pigment

Hasan Yüngevis[a], Emel Ozel[b,*]

[a]Karamanoğlu Mehmetbey University, Department of Material Science and Engineering, Konya, Turkey
[b]Anadolu University, Department of Material Science and Engineering, Eskişehir, Turkey

Received 22 October 2012; received in revised form 18 December 2012; accepted 18 December 2012
Available online 28 December 2012

Abstract

In this study, $CoFe_2O_4$ pigments were synthesised using both co-precipitation and conventional ceramic methods. Pigment particles prepared using the conventional ceramic method were subsequently milled to submicron size. The effects of the solvent, dispersant and milling type in the milling process were investigated. This study showed that planetary milling in a diethylene glycol (DEG) medium with sodium tripolyphosphate (STPP) was an effective method for producing submicron-sized pigment powders from pigments synthesised using the conventional method. With this method, submicron-sized pigment particles (approximately 190 nm) were obtained after milling for 4 h. Planetary milling was more efficient in reducing particle size compared to attrition milling. Co-precipitated pigment had a more intense black colour, due to the nanoscale particle size (< 100 nm). However, conventional ceramic pigments also had an adequately intense black colour that increased after milling compared to unmilled conventional pigments. When considering production of industrial scale submicron-sized pigments, the milling of these pigments to submicron size can be a good alternative method for the production of ink colourants.

Keywords: A. Milling; $CoFe_2O_4$ pigments; Co-precipitation method; Conventional ceramic method

1. Introduction

Due to society's increasing degree of aesthetic awareness, digital printing has become a widespread technology, offering such advantages as high-quality decoration, a continuous process, and achieving accurate direct reproduction of patterns or pictures stored digitally [1].

Colourants used in digital printing can be divided into five groups: soluble salts, micronised pigments, colloidal metals, nanopigments, and precursors for synthesis in situ of nanopigments or colloidal metals [2]. Among these colourants, nanopigments can be produced by various methods, such as co-precipitation [3,4], hydrothermal synthesis [5], and sol–gel auto combustion [6]. These methods have certain advantages, such as the preparation of powders without calcination or at a low calcination temperature, synthesising narrow particle size distributions and controlling particle morphology and size. However, these methods are complex, expensive and inappropriate for mass production. Conversely, an alternative method for the production of submicron pigments is the synthesis of micron-sized pigments using conventional methods and reducing the size of the larger particles by milling. Thus, the objectives of this study are synthesising $CoFe_2O_4$ using the conventional ceramic method, milling it to submicron size (in 100 nm–1 μm range), examining the milling parameters and comparing the colour properties of milled pigments with co-precipitated pigments. $CoFe_2O_4$ pigments are widely utilised in the ceramics industry as black colouring agents, due to their superior properties, such as chemical, thermal and colour stability. The $CoFe_2O_4$ pigments were synthesised using both co-precipitation and conventional ceramic methods in this study. Pigment particles were prepared using the conventional ceramic method and milled to obtain a submicron size, and the effects of solvent and dispersant on the milling process

*Corresponding author. Tel.: +90 222 3213550x6347; fax: +90 222 3239501.
E-mail address: eozel@anadolu.edu.tr (E. Ozel).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.12.062

were later investigated. Finally, the colour properties were discussed based on the present experimental results.

2. Experimental procedure

2.1. Synthesis of $CoFe_2O_4$ black pigments by the conventional ceramic method

$CoFe_2O_4$ black pigments were produced using the conventional ceramic method. For this purpose, reagent grade raw materials Co_3O_4 (Merck) and Fe_2O_3 (Merck) were mixed with water and ground for homogenisation using a planetary ball mill (Pulvarisette 6 Fritsch, Germany) for 1 h at 150 rpm. Next, slurry was dried at 100 °C for 24 h, the dried mixture was pulverised and the powder was calcined at 1200 °C for 3 h. Calcinations were performed at different temperatures between 800 and 1300 °C at the start of the study, and a calcination temperature of 1200 °C was chosen because of the complete transformation of the Co_3O_4 and Fe_2O_3 phases to the $CoFe_2O_4$ spinel phase.

2.2. Pigment characterisation

After calcination, the mineralogical composition of the calcined pigments were characterised by X-ray diffraction (XRD, Rigaku Rint 2200, Japan) using CuKα radiation. Chemical analysis of the synthesised pigments was conducted using an X-ray fluorescence spectrometer (XRF, Rigaku RZS Primus). The mean specific surface area of the pigments was measured by the Brunauer–Emmitt–Teller (BET) technique (Quantochrome Autosorb-1 C, USA). The average diameter of a spherical particle (D_{BET}) was calculated according to the following equation [7,8]:

$$D_{BET} = \frac{6000}{\rho S} \text{ (nm)} \quad (1)$$

where S represents the measured surface area of the powder (m^2/g), and ρ is the theoretical density (g/cm^3) [7,8]. The density of the $CoFe_2O_4$ pigment powder (ρ) was taken to be 5.29 g/cm^3 [9].

The morphology and particle size of the powders were characterised using a scanning electron microscope (SEM, EVO-50 VP, Carl-Zeiss, Germany) and a transmission electron microscope (TEM, JEOL-2100F). The pigment powder's primary particle size was measured using secondary electron SEM images and an Image J programme.

2.3. Suspension characterisation

For zeta potential measurements, the synthesised $CoFe_2O_4$ pigment suspensions were prepared by adding 1 g of the pigment powder to 100 cm^3 of distilled water. All of the suspensions were homogenised by magnetic stirring and ultrasonication. Zeta potential measurements were performed with laser Doppler velocimetry (Zetasizer NanoZS, Malvern, UK)as a function of pH to determine the isoelectric point (IEP) of the $CoFe_2O_4$ pigments. These measurements were performed in the pH range of 2–11.To decrease the solution pH, 0.25 M and 1 M HCl solutions were added, whereas 0.5 M and 1 M NH_4OH solutions were used to increase the pH of the pigment–water solution.

The sedimentation method was used for determination of an adequate dispersion to improve the milling efficiency. The powders were mixed with different solvents (distilled water, isopropanol (IPA), diethylene glycol (DEG) or 60% DEG—40% IPA mixture by volume) in volumetric solid ratio (ϕ) of 0.01. The suspensions were transferred to cylindrical glass tubes (diameter ~15 mm, height ~150 mm). The glass tubes were capped to minimise water evaporation and left undisturbed for the gravity sedimentation. The top interface that separates the supernatant from the sediment was measured. After the determination of the most adequate solvent, four kinds of dispersants (sodium tripolyphosphate (STPP), fumed silica, stearic acid and ammonium polymethacrylate (Darvan-C)) were added to the pigment–solvent mixture at different ratios (0.1–3 wt%) to obtain better-dispersed suspension.

2.4. Milling

Milling was performed using both a planetary mill and an attrition mill to investigate the effect of the milling type on the final particle size. The parameters, such as ball type and size (3 mm diameter yttrium stabilised zirconia balls) and milling speed (300 rpm), were kept constant. The pigment/ball ratio was 1/10 by weight, and the pigment/solvent ratio was 1/10 by volume. An yttrium-stabilised zirconia-milling bowl was used for planetary milling, while a Kestamid (cast polyamide) bowl was used for attrition milling. Samples were obtained on an hourly interval to determine the particle size. Two particle size characterisation techniques were used in this study: (i) the BET technique (BET, Quantachrome Autosorb 1) and (ii) scanning electron microscopy (SEM, EVO-50 VP, Carl-Zeiss, Germany). The BET technique measures the specific surface area of a particle sample, rather than the particle size distribution; the BET measurements are valid for submicron particles, as well as larger particles. Using an Image J programme on secondary electron SEM images, this technique provides both morphological and particle size information. Contamination caused by the milling balls and/or vial was evaluated by weighing them both before and after the milling process and by XRF analysis.

2.5. Colour measurements

To understand the effect of the milling process on the colour properties of the pigment powders, $L^*a^*b^*$ colour parameters and spectral reflectance curves of pigments were measured with an UV–vis spectrophotometer (Konica Minolta CM3600 d, Japan, illuminant D_{65}, 10° observer, following the CIE-$L^*a^*b^*$ colourimetric method