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

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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

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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]:

$$D_{\mathrm{BET}} = \frac{6000}{\rho S}\ (\mathrm{nm}) \tag{1}$$

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 recommended by the CIE (Commission Internationaled-el'Eclairage). In this system, L^* is the degree of lightness and darkness of the colour in relation to the scale extending from white ($L^*=100$) to black ($L^*=0$). a^* is the scale extending from green (a^*) to red ($+a^*$) axis and b^* is the scale extending from blue ($-b^*$) to yellow ($+b^*$) axis.The colour properties of the milled pigments were compared with those of the unmilled pigments in the form of ΔE^*_{ab}. The total colour difference between the two samples (ΔE^*_{ab}) is a measurement used to indicate how much the measured colour deviates from a standard and is given by [10]

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{2}$$

The colouring performances of the unmilled pigment and the pigment milled with planetary milling for 4 h were assessed by two different methods: (i) dropping the pigment suspensions containing 5 wt% pigment and DEG on unfired ceramic substrates and firing at 1000 °C and (ii) adding 5 wt% pigment into different glassy coatings (Frit A and Glaze A) and firing 1000 °C for Frit A and 1200 °C for Glaze A. The pigment addition into commercial Frit A (zinc containing transparent frit for wall tiles) and Glaze A (porcelain stoneware glaze) was carried out by dry mixing, hand palletisation (6 wt% moisture), uniaxial pressing (30 MPa) of 13 mm-diameter disk, drying in oven and firing at 1000 °C for frit A and 1200 °C for glaze A in electric kiln.

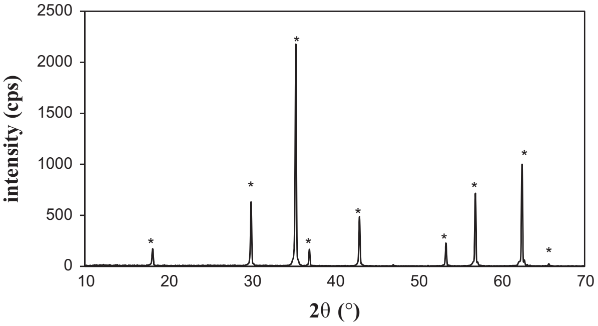

Fig. 1. XRD pattern of the $CoFe_2O_4$ pigments synthesised at 1200 °C by the conventional method (*JCPDS Card no.: 22-1086).

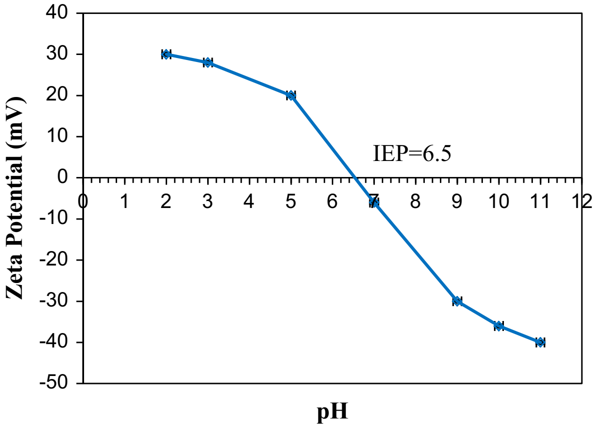

Fig. 2. Electrokinetic studies of the $CoFe_2O_4$ particles as a function of pH.

2.6. Synthesis of $CoFe_2O_4$ black pigments by the co-precipitation method

Iron chloride ($FeCl_3 \cdot 6H_2O$;TEKKIM, 95% purity) and cobalt chloride ($CoCl_2$; Lobal Chemie, 99% purity) were dissolved in distilled water, and 100 ml of 0.1 M $FeCl_3 \cdot 6H_2O$ and 100 ml of 0.05 M $CoCl_2$ solutions were prepared. These solutions were later added drop by drop into a hot and vigorously stirred 100 ml 0.8 M NaOH

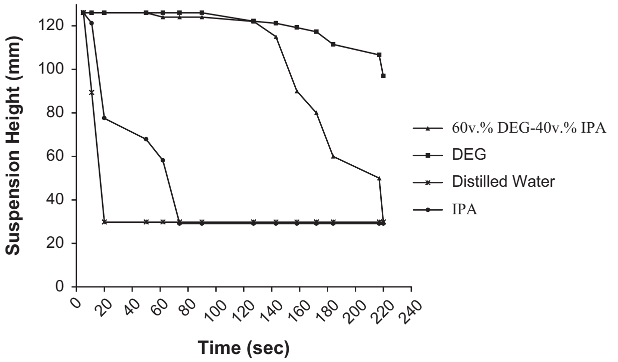

Fig. 3. Suspension heights of the $CoFe_2O_4$ pigment particles as a function of time for different media.

Table 1
Physical properties of the used solvents.

Name	Density (g/cm^3)	Viscosity (cP)
Water at 25 °C [19]	0.997	0.891
Isopropanol 25 °C [19]	0.781	2.073
DEG at 25 °C [20]	1.118	35.70

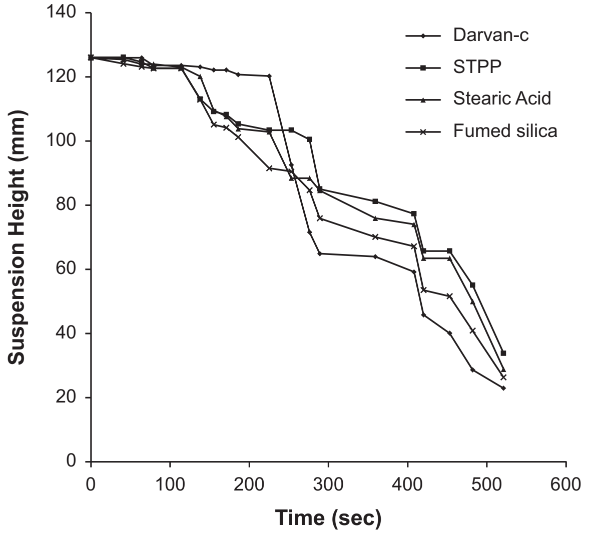

Fig. 4. Suspension heights of the $CoFe_2O_4$ pigment particles as a function of time for different dispersants.

aqueous solution at 80 °C for 2 h to complete the reaction. Black precipitates were formed. After the precipitates were washed by distilled water many times until the pH value becomes 7, the black precipitates were dried at 100 °C and calcined at 800 °C for 6 h.

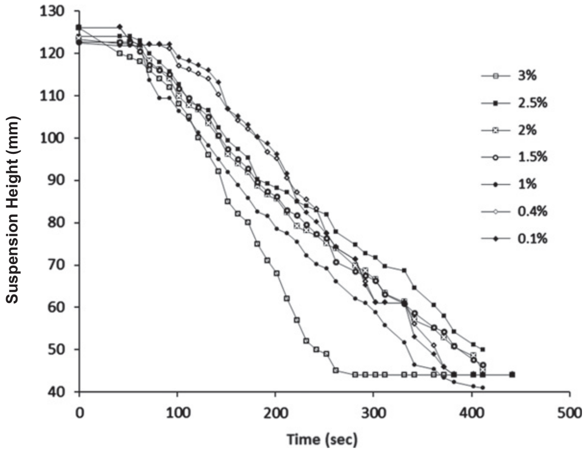

Fig. 5. Suspension heights of the $CoFe_2O_4$ pigment particles as a function of time for different amounts of STPP.

3. Results and discussion

3.1. *Characterisation of pigment powder*

The XRD pattern of the $CoFe_2O_4$ pigments synthesised using the conventional ceramic method is shown in Fig. 1. The synthesised $CoFe_2O_4$ pigment powders consisted of only the spinel $CoFe_2O_4$ phase (JCPDS Card no. 22-1086). In addition, no residue phases including starting oxides were detected. Therefore, these results indicate that calcination is successfully completed at 1200 °C for 3 h.

3.2. *Characterisation of pigment suspensions*

Fig. 2 shows the electrokinetic behaviour of the $CoFe_2O_4$ pigments synthesised using the conventional ceramic method as a function of pH. The IEPs of the $CoFe_2O_4$ pigment were found to be pH $\cong 6.5$. This result is in good agreement with previously reported data [11]. The surface of oxide particles generally become negatively charged above the IEP and positively charged below the IEP. Particles with low zeta potentials ($< \pm 30$ mV) have

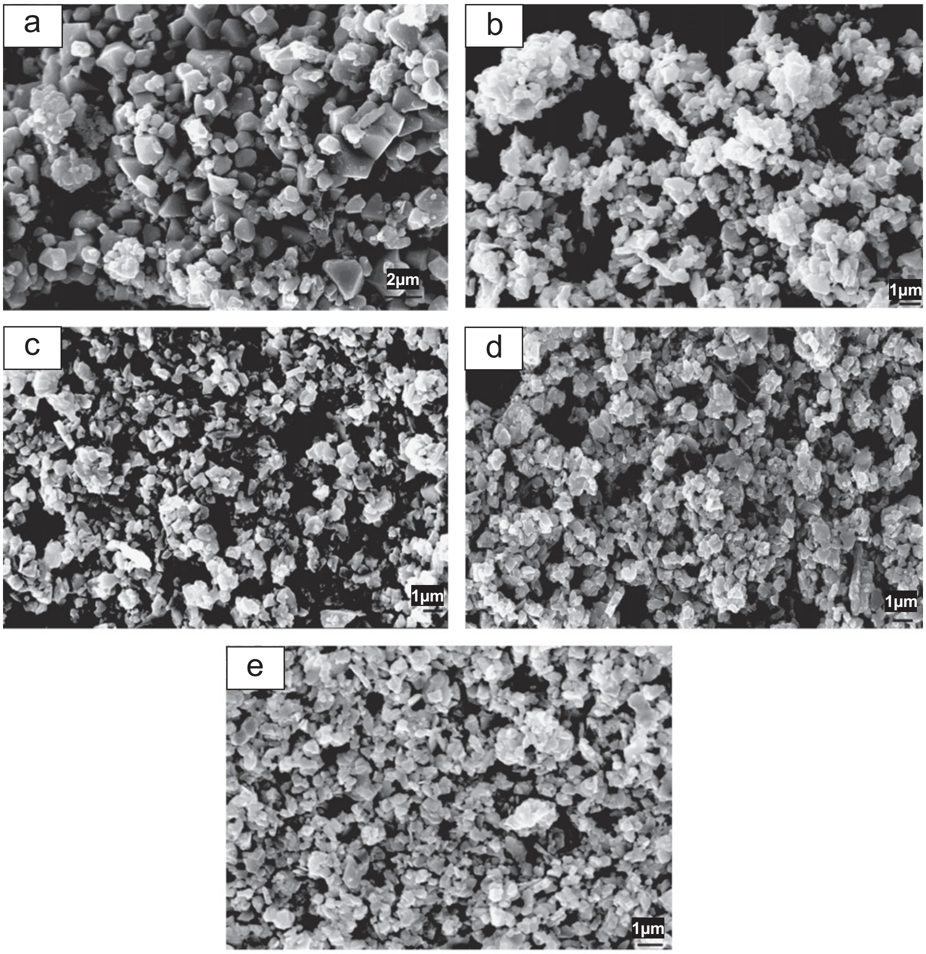

Fig. 6. SEM images of the planetary milled pigments: (a) before milling and after (b) 1 h of milling, (c) 2 h of milling, (d) 3 h of milling, and (e) 4 h of milling.

minimal electrostatic repulsion between particles, making the suspension unstable [12–15]. In the suspension containing $CoFe_2O_4$ particles, a stable system is hard to form because an additional magnetic attraction exists in addition to London–Vander Waals attraction [11]. Because of the existence of strong interactions between these particles, such interactions may affect both the rheology and colloidal stability of the suspensions. However, it is stated in a previous study that the stability of the $CoFe_2O_4$ particles can be improved by changing the pH values of solution [11]. According to the obtained results, it can be concluded that the $CoFe_2O_4$ particles are more stable below pH 4 and above pH 8 when the particles have high surface charges.

In this study, the stability of the $CoFe_2O_4$ suspensions was evaluated by the settling of powder in different types of medium. Distilled water and isopropanol were not suitable media for the stabilisation of $CoFe_2O_4$ pigments because of sudden sedimentation of the pigment powder in these media (Fig. 3). This behaviour can be explained by the physical properties of the solvent. The viscosity and density values of the DEG at 25 °C are higher than water and isopropanol (Table 1). If the particles settle in the viscous fluid through gravitational means alone, then the settling velocity is reached when this frictional force combined with the resistant force exactly balance the gravitational force. The resulting settling velocity is given by the following equation [16], known as Stokes law, for laminar flow and spherical particles

$$\upsilon = 2R^2(\rho_p - \rho_f)g/9\mu, \tag{3}$$

where υ is the particles' settling velocity (m/s) (vertically downwards if $\rho_p > \rho_f$, upwards if $\rho_p < \rho_f$), μ is the dynamic viscosity (N s/m^2), g is the gravitational acceleration (m/s^2), ρ_p is the mass density of the particles (kg/m^3), and ρ_f is the mass density of the fluid (kg/m^3) [16]. Fig. 3 shows that the settling behaviour of the $CoFe_2O_4$particles was strictly dependent on the viscosity and density of the solvents used in the experiment. Therefore, it can be concluded that the sedimentation velocity of the $CoFe_2O_4$

Table 2
Comparison of specific surface areas and grain sizes obtained by BET and SEM for different milling conditions.

	Milling time (h)								
	Planetary milling					**Attrition milling**			
	0	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
BET surface area (m^2/g)	1.70	3.93	4.69	5.18	5.83	2.00	2.23	2.37	2.43
BET particle size (nm)	670	280	250	220	190	560	507	477	465
SEM particle size (nm ± 20 nm)	760	310	270	230	220	580	550	530	480

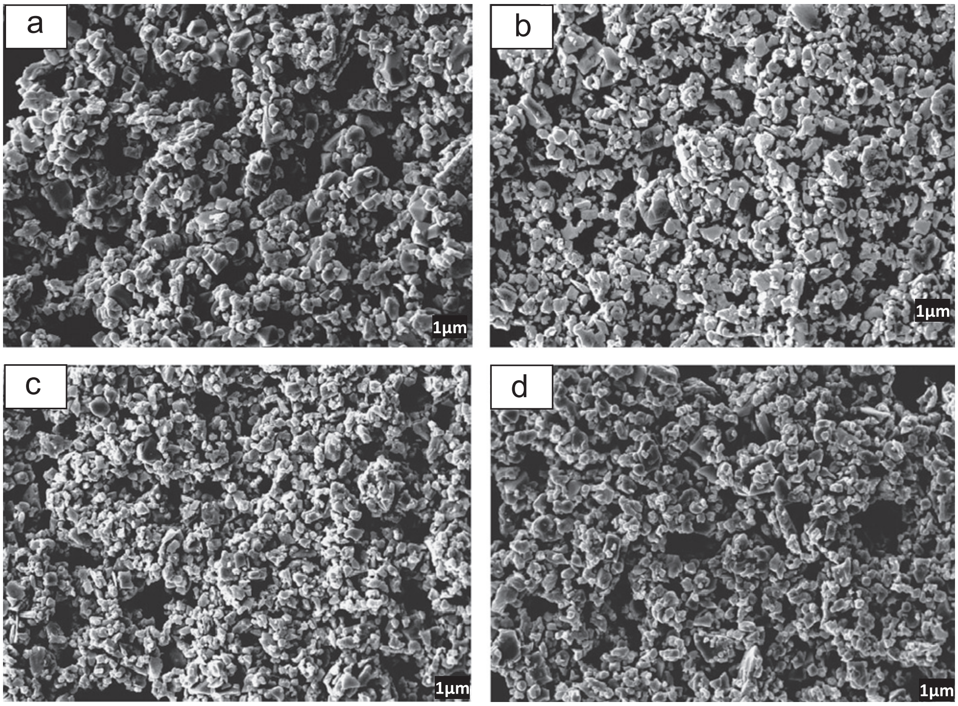

Fig. 7. SEM images of the attrition milled pigments after (a) 1 h of milling, (b) 2 h of milling, (c) 3 h of milling, and (d) 4 h of milling.

particles in DEG is lower than in water and isopropanol, due to the higher viscosity and density of DEG compared to the other solvents.

In Fig. 4, although there was no sedimentation in the tube that contained Darvan-C for nearly 200 s, particles started sedimentation rapidly after 200 s. With STPP addition, the maximum suspension height and the most stable sedimentation were observed. Therefore, STPP was found to be the best dispersant for improving milling efficiency. The stability of pigments increased as the amount of STPP increased, with a maximum suspension height being obtained after the addition of 2.5 wt% STPP (Fig. 5). After adding 2.5 wt% STPP, the sedimentation time increased up to 400 s, which is a longer sedimentation time than that of a previous study [11]. As a consequence, DEG was chosen as the milling medium and 2.5 wt% STPP as the dispersant for the milling studies.

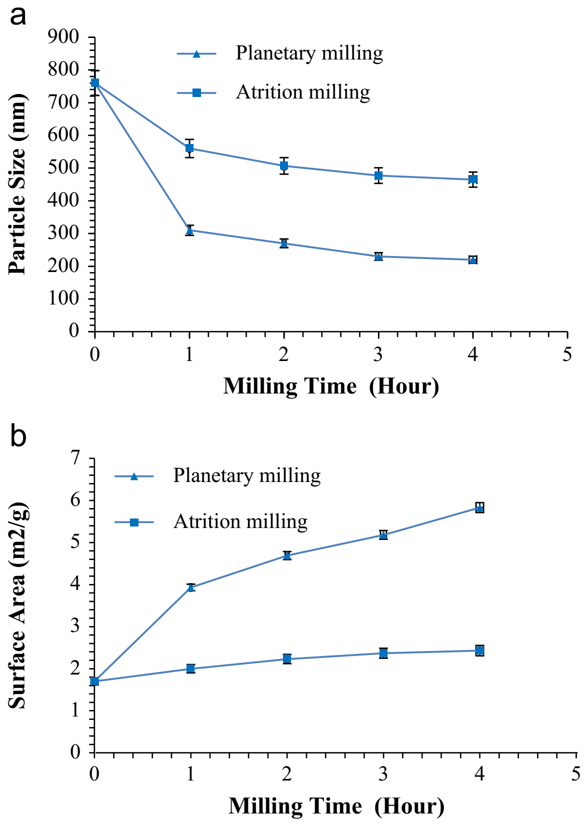

Fig. 8. Evaluation of the specific surface area and particle size versus milling time for different milling conditions.

3.3. Planetary milling of the $CoFe_2O_4$ pigments synthesised using the conventional ceramic method

The morphology and grain size of the $CoFe_2O_4$ pigments before and after milling were evaluated by SEM (Fig. 6). Before milling, pigment particles were generally smooth geometrical shape with an average grain size of 760 nm. In addition, the BET particle size was calculated as 670 nm from the specific surface area of the pigments, which was found to be 1.7 m^2/g. The difference between the calculated particle size and that observed from the SEM images can be explained by the approximation of the particles as spherical in shape. The grains of powder obtained after milling for 1 and 2 h were not spherical and exhibited rough shapes compared to the more spherical grains of powders milled for 3 and 4 h. The powders that were milled for 3 and 4 h had 220 nm and 190 nm average BET particle sizes, respectively (Table 2). Because pigments used in digital printing have a particle size of between 200 and 600 nm [2], further milling over 3 h is pointless because of the decrease in the rate of particle size reduction and the probability of further contamination from the milling bowl and balls.

3.4. Attrition milling of $CoFe_2O_4$ pigments synthesised using the conventional ceramic method

To investigate the effect of mill type on the milling performance of the $CoFe_2O_4$ pigments, attrition milling was also performed. As shown in Table 2, the BET particle size changed from 670 nm to 560 nm and 465 nm after 1 h and 4 h of milling, respectively. The SEM images of the attrition milled pigments are presented in Fig. 7. After 1 h

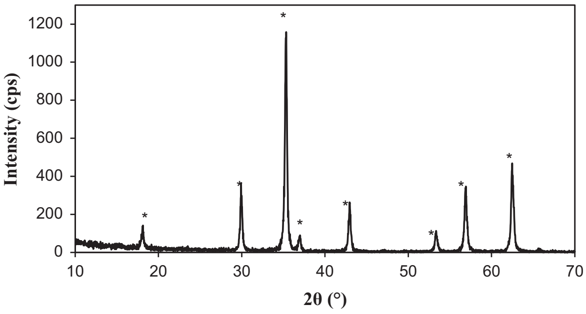

Fig. 9. XRD pattern of the $CoFe_2O_4$ pigments synthesised at 800 °C by the co-precipitation method (*JCPDS Card no.: 22-1086).

Table 3
Chemical analysis of pigment powders with XRF before and after milling for 4 h.

	Oxides (wt% ± 0.02)								
	Co_2O_3	Fe_2O_3	MnO	CaO	SiO_2	Al_2O_3	ZrO_2	Na_2O	MgO
Calcined pigment	32.60	66.50	0.18	0.05	0.23	0.11	–	0.24	0.09
Planetary milled	33.40	65.60	0.14	0.07	0.26	0.09	0.05	0.30	–
Attrition milled	33.90	64.80	0.13	0.08	0.32	0.30	0.09	0.20	–

of milling, the particle size dropped to 560 nm with a notably broad particle size distribution (Fig. 7a). Although the milling time was increased to 4 h, the particle size of the pigment powder could not be reduced to less than 300 nm. Therefore, it can be concluded that the attrition milling was less effective compared to planetary milling, due to a lower particle size reduction for the same milling time under the same circumstances.

Fig. 8 shows both the specific surface area and particle size versus milling time. The specific surface area increased dramatically with planetary milling and depended on the milling time to slow reductions in particle size. When the milling time was increased, the decrease in particle size slowed because it was more difficult to grind finer particles [13]. Generally, for a variety of milling types, it has been observed that the mean powder particle size decreases exponentially over time. However, planetary milling was more efficient than attrition milling for $CoFe_2O_4$ pigments, due to the greater particle size reduction for the same milling time interval.

3.5. Powder contamination

Powder contamination was evaluated by chemical analysis of the powders using XRF before and after the milling process. Before milling, the $CoFe_2O_4$ pigment powder

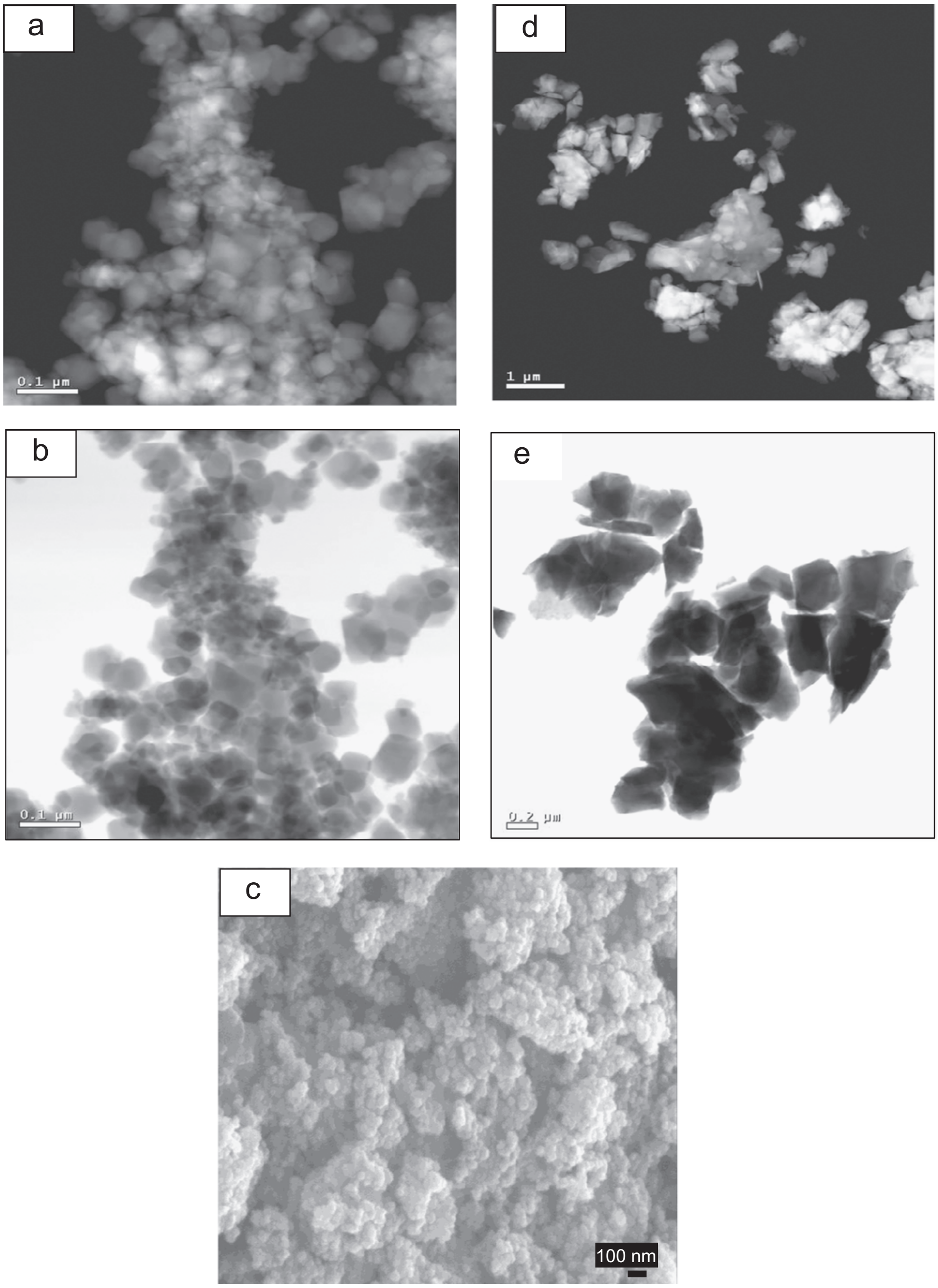

Fig. 10. HADF (a), BFTEM (b) and SEM (c) images of the co-precipitated pigments; HADF (d) and BF TEM (e) images of the milled pigments for 4 h.

Table 4
CIE lab values of the pigments produced by different methods.

	Pigment powders synthesised by conventional method (unmilled)	**Pigment powders milled by planetary milling**	**Pigment powders milled by attrition milling**	**Pigment powders synthesised by co-precipitation method**
L	29.76 ± 0.01	27.84 ± 0.01	31.43 ± 0.01	22.72 ± 0.01
a^*	0.23 ± 0.01	0.62 ± 0.01	0.16 ± 0.01	0.86 ± 0.01
b^*	-1.01 ± 0.01	-0.46 ± 0.01	-1.13 ± 0.01	1.29 ± 0.01
ΔE^*	–	2.07	1.65	7.46

contained 32.60 wt% Co_2O_3, 66.50 wt% Fe_2O_3 and reagent level of impurity (Table 3). After planetary and attrition milling for 4 h, it was observed that the ground pigments contained 0.05 wt% and 0.09 wt% ZrO_2 contaminations, respectively. Conversely, by weighing the milling bowl and the ball, the wear loss was determined to be 0.007% after planetary milling for 4 h. There was a negligible amount of change in the weights of the balls and the milling bowl. It is well-known that Y-doped zirconia balls exhibit a higher milling efficiency because of their specific gravity (6.05) [17]. Therefore, the lower contamination could be attributed to the higher solidity of the Y-doped zirconia balls.

3.6. Comparison of the co-precipitated $CoFe_2O_4$ and milled pigments for 4 h.

To determine the consequences of milling on the pigment properties, the $CoFe_2O_4$ pigments were also synthesised using the co-precipitation method. The XRD patterns of the co-precipitated $CoFe_2O_4$ pigments are shown in Fig. 9. The co-precipitated $CoFe_2O_4$ pigment powders consisted of the spinel $CoFe_2O_4$ phase (JCPDS Card no. 22-1086).

The morphology, particle size and distribution of the pigment powder were also examined by TEM. High angle annular dark field (HADF) and bright field (BF) TEM images of the co-precipitated pigments are shown in Fig. 10a and . The TEM images clearly show that the pigment particles have a regular and almost spherical shape. The particle size examined by TEM was nearly 60 nm, which is in accordance with the result of the calculated D_{BET} value (58 nm) from the BET method. In addition, the SEM image in Fig. 10c shows that the pigment particles are homogeneous and have a narrow particle size (approximately 60 nm) distribution.

TEM images of milled particles for 4 h (Fig. 10d and e) illustrate various structures of the pigment particles, including irregularly shaped primary particles with sharp edges, as well as agglomerates. Based on the BF TEM image, the average grain size of the milled particles was approximately 200–300 nm,while for the agglomerates, the average grain size was approximately 1 μm (Fig. 10d). These agglomerates seem to cluster or fuse at their faces, which is possibly due to the sintering of individual crystals during calcination at 1200 °C.

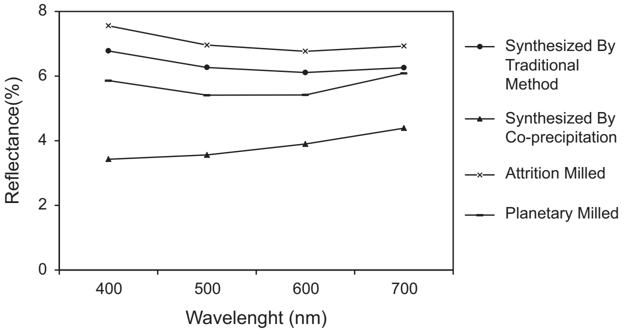

Fig. 11. Reflectance curves of the pigment powders.

The co-precipitated pigments represented the most intense black colour with $L^*a^*b^*$ values of 22.72/0.86/1.29 (Table 4). The $CoFe_2O_4$ particles intensely absorbed all wavelengths of visible light and led to a black colour. The intense colour performance can be attributed to the lower particle size because the pigments with particle size (<100 nm) in nanoscale have a higher number of reflectance points [2].

To show the consequences of milling on the colour properties of the milled pigment powder for 4 h, its $L^*a^*b^*$ values and reflectance curves were evaluated by comparison with unmilled pigment powder synthesised by conventional method. Attrition milling led to lower colour differences of $\Delta E^*_{\mathrm{ab}}=1.65$, but higher L^* values led to decreased pigment colour intensity, as seen in Fig. 11. Pigment powder milled with a planetary ball mill had a lower reflectance curve than unmilled pigment powder, indicating an intense black colour in comparison. This unmilled pigment powder had $L^*a^*b^*$ values of 29.76/0.23/-1.01 (Table 4). After milling, the $L^*a^*b^*$ values were obtained as 27.84/0.62/-0.46 with a colour change $\Delta E^*_{\mathrm{ab}}=2.07$. Although the results show that the colour change after milling is visually distinguishable, these results are acceptable because of the increased colour intensity and their proximity to tolerance limits ($\Delta E^*_{\mathrm{ab}}=1$). The interatomic distances in the crystal structure affect the colour properties of transition metal ions. An increase in interatomic distances decreases the interaction between electrons, leading to weak electron excitation and resulting in a change in colour intensity [18]. Therefore, small colour variation can be attributed to an alteration in crystal structure during milling. With improved colour properties, milled submicron scale black pigments may be a promising

Table 5
CIE lab values of the unmilled pigment and pigment milled with planetary ball mill for 4 h after firing.

	Pigment powders synthesised by conventional method (unmilled)			**Pigment powders milled with planetary ball mill for 4 h**		
	As droplet (1000 °C)	**In Frit A (1000 °C)**	**In Glaze A (1200 °C)**	**As droplet (1000 °C)**	**In Frit A (1000 °C)**	**In Glaze A (1200 °C)**
L	32.00 ± 0.01	27.79 ± 0.01	49.56 ± 0.01	29.79 ± 0.01	26.23 ± 0.01	47.55 ± 0.01
a^*	1.19 ± 0.01	0.39 ± 0.01	−2.50 ± 0.01	1.01 ± 0.01	0.23 ± 0.01	−2.10 ± 0.01
b^*	1.48 ± 0.01	0.05 ± 0.01	3.13 ± 0.01	1.16 ± 0.01	−1.01 ± 0.01	4.0 ± 0.01

colourant in digital printing inks, due to their simple and cheap production using the conventional method.

The colouring performances of unmilled and pigment milled with planetary ball mill for 4 h were assessed by considering the chromatic changes in different matrices and temperatures (Table 5). $CoFe_2O_4$ black pigments were stable at 1000 °C and the more intense black colours were obtained with milled pigments compared to unmilled pigments. However, the colours of pellets containing unmilled and milled pigments changed from black to dark brown in Glaze A at 1200 °C. The thermal stability of black $CoFe_2O_4$ pigments reduced in Glaze A due to the increasing aggressive chemical attacks at 1200 °C [21,22].

4. Conclusions

This study shows that planetary milling in a DEG medium with STPP is an effective method for the production of submicron-sized pigment powders from pigments synthesised by the conventional method. Using 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 in the same milling time compared with attrition milling. The co-precipitated pigment had a more intense black colour due to its nanoscale particle size (<100 nm). However, conventional ceramic pigments also had an adequately intense black colour, and its intensity increased after milling compared to unmilled conventional pigments. When considering production of industrial scale submicron pigments, the milling of these pigments to submicron size could be a suitable alternative method to produce ink colourants.

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