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Comparative Study on the Effect of Heat Treatment Temperatures on Colorimetric Properties of $CoFe_2O_4$ Nanoparticles and $CoFe_2O_4/SiO_2$ Nanocomposites

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ABSTRACT

In this paper, a comparative study on the effect of different heat treatment temperatures, i.e., 400, 500, 600 and 700 ºC on colorimetric properties of $CoFe_2O_4$ nanoparticles has been done for the first time. Then, the mentioned Co-Fe mixed oxide pigments are dispersed in an amorphous silicon oxide matrix to form $CoFe_2O_4/SiO_2$ nanocomposites. In the next step, the optical properties of nanocomposites treated at different temperatures are investigated and compared with those of nanoparticles. Results show that increasing the treatment temperature from 400 ºC to 700 ºC leads to more neutral nanoparticles and nanocomposites, while the lightness attributes of them behave reversely. Besides, the gradient of lightness variation in nanoparticles is higher than that of nanocomposites. Meanwhile, regarding to the calculated color difference values, it is found that the colorimetric variations between nanoparticles and nanocomposites increase by increasing the treatment temperature. Prog. Color Colorants Coat. 8(2015), 37-45© Institute for Color Science and Technology.

1. Introduction

Among different techniques including XRD, TG-DTA, IR, UV–Vis, DRS, etc., used to characterize the physical and chemical attributes of materials, the colorimetry method is capable of representing the color of objects [1-3]. The technique will be so important when the colorimetric attributes [4] of materials is concerned. Various parameters, i.e. synthesis procedures, components ratio, process factors, size and shape of components, etc can influence the colorimetric properties of materials [1-3]. Karmaoui *et al.*, reported the chemical synthesis of cobalt aluminate nanopigments by a non-aqueous sol-gel route. They

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showed that the low average size of $CoAl_2O_4$ nanoparticles as well as their colorimetric attributes could be controlled by the synthesis temperature applied in the range of 150 to 300 ℃. For example, they achieved the specific blue color of $CoAl_2O_4$ pigments for specimens constructed at synthesis temperatures higher than 200 ℃ [1].

In other work, the colorimetric attributes of $CoAl_2O_4$, Au, (Ti, Cr, Sb)O_2 and $CoFe_2O_4$ ceramic nano-pigments were investigated and compared with those of conventional micro-pigments while the nano sized pigments were dispersed in different ceramic glazes as well as glassy coatings. Results showed that in spite of very small particle size of nano-pigments (smaller than 50 nm) they provide more intense colors rather than micro-pigments. Besides, the chroma of pigments influenced by their particle size and in comparison to micro-pigments, the nano-sized pigments show less saturated hues [2]. Souza *et al.,* investigated the colorimetric properties of $Co_xZn_{1-x}Al_2O_4$ spinels synthesized by the polymeric precursor method while different component ratio (x = 0; 0.1; 0.3; 0.5; 0.7; 0.9 and 1) and various heat treatment temperatures (600, 700, 800 and 900 ℃) were applied. Results show that the lightness attribute (L*) of $Co_xZn_{1-x}Al_2O_4$ spinels decreases while the Co content increases. In addition, increase of heat treatment temperature of $Co_{0.5}Zn_{0.5}Al_2O_4$ spinels from 600 to 900℃ leads to high negative values of b* that indicated to the formation of blue pigments can be used for obtaining the ceramic blue pigments. Meanwhile, it was found that the absorption attribute of $Co_xZn_{1-x}Al_2O_4$ spinels decrease by heat treatment temperature especially around the 450 nm of visible wavelengths which leads to the increase of reflectance spectra. Thus, the lightness attribute of samples increases and results in pigments with lighter blue hues [3].

Ferrite magnetic materials have been intensively studied because of the fundamental understanding as well as their applicability in a variety of areas such as high-density information storage, magnetic printing inks, ferrofluid technology, magnetic drug delivery, magnetic refrigeration, medical diagnostics, catalysts, magnetic resonance imaging enhancement and gas sensors [5-10]. Among spinel ferrites, cobalt ferrite has attracted considerable attention in recent years due to the unique physical properties such as high Curie temperature, large magneto-crystalline anisotropy, high coercivity, moderate saturation magnetization, large magneto-strictive coefficient, excellent chemical stability and mechanical hardness [11, 12]. Additionally, this material exhibits a significant higher magneto-striction than metallic Fe or Ni.

The physical and chemical properties of spinel nanoparticles are greatly affected by the synthesis route. The magnetic properties of the ferrites varied with size. Based on their results, they proposed that the critical sizes of the $CoFe_2O_4$ particles for the superparamagnetic relaxation at room temperature range from 4 to 9 nm [13].

In addition, magnetic nanocomposites consisting of spinel ferrite nanoparticles in a non magnetic SiO_2 matrix exhibit interesting properties arising in size effects and magnetic interactions [14-18] which depend strongly on particle shape and size, particle-matrix interactions and degree of dispersion throughout the matrix. To reduce the unwanted crystallite coarsening and particles aggregation, attempts have been made to synthesize nanocomposites by embedding ferrite nanoparticles in a suitable matrix [19]. Different matrixes such as resins [20], polymer films [21] and silica glasses [22, 23] have been studied. Studies on magnetic nanocomposites of ferrite nanoparticles dispersed in the silica matrix [24, 25] have revealed a behavior different from that of bulk systems.

To the best of our knowledge, there is no report on the comparison of the effect of heat treatment temperature on the colorimetric properties of ferrite nanoparticles and ferrite/silica nanocomposites. In this paper we describe for the first time the effect of heat treatment temperature on colorimetric properties of $CoFe_2O_4$ nanoparticles and $CoFe_2O_4/SiO_2$ nanocomposites.

2. Experimental

2.1. Samples preparation

All the chemicals used in this study were of analytical grade and used without any further purification. Nanocrystalline spinel Co-ferrites were synthesized by a polymeric precursor method [26]. Nanocomposites of cobalt ferrite dispersed in a silica matrix were prepared by sol-gel process using tetrakis(2-hydroxyethyl) orthosilicate (THEOS) as a water-soluble silica precursor of silica and metallic nitrates as precursors of the ferrite [27]. All nanopowders were characterized by XRD, FT-IR, SEM, TEM, STA (TG-DTG-DTA) and VSM techniques [26, 27]. The achieved Crystallite size (nm) of $CoFe_2O_4$ nanoparticles and $CoFe_2O_4/SiO_2$ nanocomposites treated at different temperatures are shown in Tables 1 and 2, respectively.

2.2. Calculating the colorimetric attributes

In order to find the colorimetric properties of nanoparticles and nanocomposites, the reflectance spectra of samples were measured by using the Spectrophotometer Color-Eye 7000A from Gretag Macbeth over the visible wavelengths from 400-700 nm by 10 nm intervals while the measurement geometry was d/8^o and the specular reflectance was included. According to the measured reflectance spectra, the CIEXYZ tristimulus values of samples were calculated under D65 standard illuminant and CIE1964 standard observers. Then, the CIELAB and the CIELCH colorimetric attributes of samples were computed based on Equations 1 to 5:

$$L^* = 116\,(Y/Yn)^{1/3} - 16 \quad (1)$$

$$a^* = 500\,[(X/Xn)^{1/3} - (Y/Yn)^{1/3}] \quad (2)$$

$$b^* = 200\,[(Y/Yn)^{1/3} - f\,(Z/Zn)^{1/3}] \quad (3)$$

$$C^* = (a^{*2} + b^{*2})^{0.5} \quad (4)$$

$$\text{Hue angle} = \tan^{-1}(b^*/a^*) \quad (5)$$

where, X, Y and Z are the CIEXYZ tristimulus values of the sample and Xn, Yn and Zn are those of the reference white. It is noticeable that the mentioned equations are applied for samples which their X/Xn, Y/Yn, and Z/Zn are greater than 0.01[28-31].

The L*, a* and b* respectively represent the lightness, redness-greenness and yellowness-blueness attributes of objects. Besides, the chroma value (C*) indicates the hue saturation while hue attribute of objects introduced by hue angle [28-31]. The computed colorimetric specifications of nanoparticles and nanocomposites are shown in Tables 1 and 2, respectively.

It is so important for some industries to match the color of their products. In this way, the colorimetric variations between the standard specimen and the produced samples are calculated by applying a color difference formula. Equation (6) indicates the CIE1976 color difference formula (ΔE_{ab}) while subscripts (s) and (B) in Equations 7 to 9 refer to the standard specimen and the produced batch, respectively [2].

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (6)$$

$$\Delta L^* = L^*_B - L^*_S \quad (7)$$

$$\Delta a^* = a^*_B - a^*_S \quad (8)$$

$$\Delta b^* = b^*_B - b^*_S \quad (9)$$

In order to investigate the effect of treatment temperature on colorimetric attributes of $CoFe_2O_4$ nanoparticles and $CoFe_2O_4/SiO_2$ nanocomposites, the color difference values between samples treated at different temperatures were calculated by employing equation (6). The nanoparticles and nanocomposites treated in 400 *ºC* were considered as the standard samples (S) and those specimens which treated in 500 *ºC*, 600 *ºC* and 700 *ºC* were defined as the batches (B). Tables 1 and 2 show the computed color difference values between samples treated at different temperatures.

3. Results and discussion

3.1. $CoFe_2O_4$ nanoparticles

Table 1 shows that the crystallite size of $CoFe_2O_4$ nanoparticles increases from 16 nm to 114 nm while the treatment temperature increases from 400 *ºC* to 700 *ºC*. Clearly, the variation in crystallite size of nanoparticles effects on light scattering properties which determine the colorimetric attributes of samples.

Figures 1 and 2 respectively show the a*b* and C*L* scatter plots of $CoFe_2O_4$ nanoparticles over the CIELAB and CIELCH color spaces while samples were treated at different temperatures from 400 *ºC* to 700 *ºC*.

According to Figure 1 and Table 1, all the treated nanoparticles are located in the first hue area. Except nanoparticles treated at 700 *ºC*, other samples represent approximately the same hue angles. On the other hand, as Figure 2 and Table 1 show, samples lightness and chroma decrease by increasing the treatment temperature. It means that samples treated at higher temperatures will be darker and more neutral. Besides, as Table 1 shows, decreasing of both a* and b* values results in decreasing of chroma values. It means that both the redness and yellowness tint effect of nanoparticles decrease by increasing the treatment temperature. Thus, the saturation attributes of nanoparticles decrease and make samples to be more neutral. In order to represent the colorimetric variations more clearly, the color differences between nanoparticles treated in 400°*C* and those treated with different temperatures are compared. According to Table 1, the color difference values also increase by increasing the treatment temperature from 500 ºC to 700 ºC.

Table 1: The colorimetric attributes as well as the crystallite size of $CoFe_2O_4$ nanoparticles treated at different temperatures. The last column shows the color difference values between nanoparticles treated at 400 ºC and those treated at different temperatures.

Temperature (ºC)	L*	a*	b*	C*	Hue angle	Crystallite size (nm)	ΔE_{ab}
400	23.02	2.76	4.46	5.24	58.24	16	0
500	18.04	2.62	4.03	4.79	56.91	30	5.00
600	14.99	2.02	2.62	3.30	52.37	61	8.27
700	13.81	1.10	0.89	1.41	38.97	114	10.02

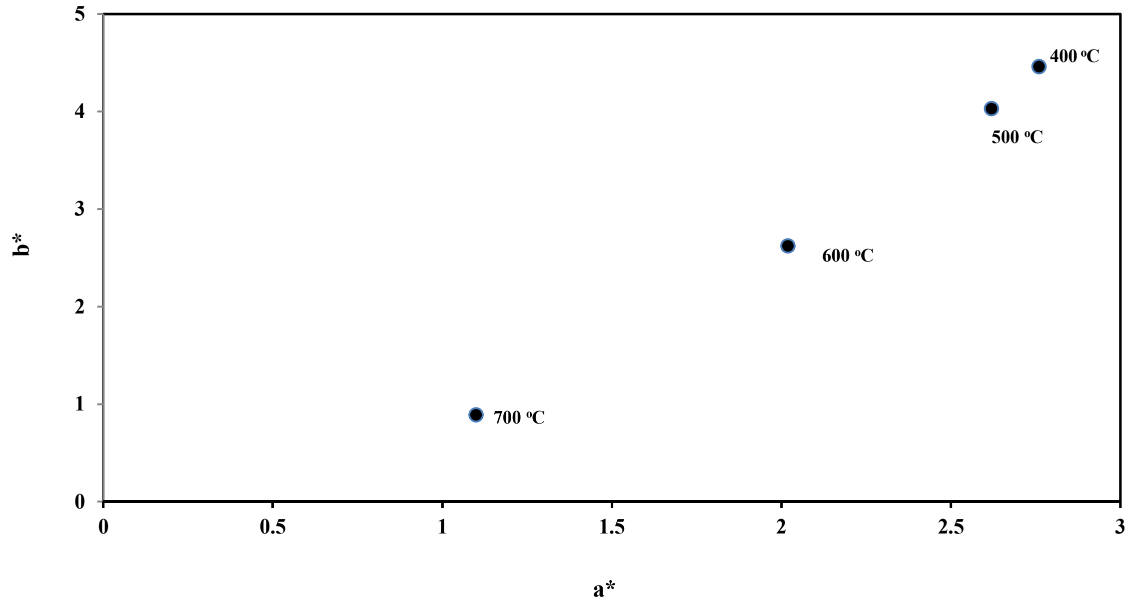

Figure 1: The a*b* scatter plot of $CoFe_2O_4$ nanoparticles.

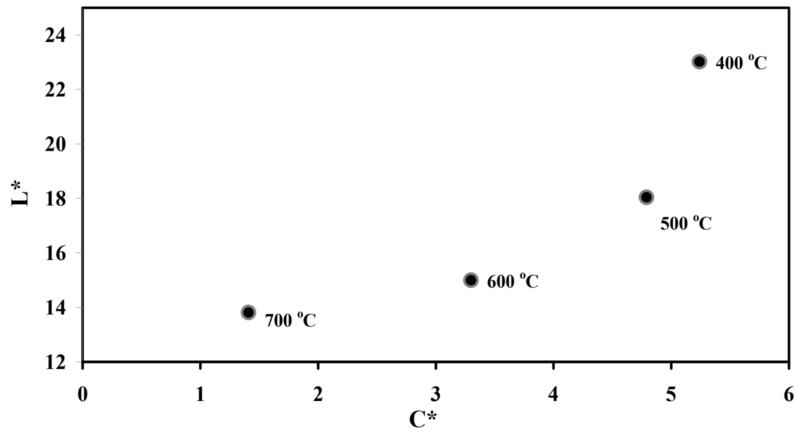

Figure 2: The C*L* scatter plot of $CoFe_2O_4$ nanoparticles.

Table 2: The colorimetric attributes as well as the crystallite size of $CoFe_2O_4/SiO_2$ nanocomposites treated at different temperatures. The last column shows the color difference values between nanocomposites treated at 400 ºC and those treated at different temperatures.

Temperature (ºC)	L*	a*	b*	C*	Hue angle	Crystallite size (nm)	ΔE_{ab}
400	22.17	3.5	7.85	8.59	65.97	6	0
500	22.68	3.24	7.53	8.20	66.72	8	0.66
600	23.13	2.62	6.39	6.91	67.71	9	1.96
700	23.92	2.01	4.44	4.87	65.64	30	4.11

3.2. $CoFe_2O_4/SiO_2$ nanocomposites

According to Table 2, the crystallite size of nanocomposites increases up to 5 times due to the increasing the treatment temperature from 400 ºC to 700 ºC. To determine the effect of crystallite size on the light scattering property of nanocomposites, the colorimetric attributes of $CoFe_2O_4/SiO_2$ nanocomposites are investigated. In this way, the a*b* and C*L* scatter plots of nanocomposites over the CIELAB and CIELCH color spaces are shown in Figures 3 and 4, respectively.

According to Figure 3 and Table 2, the hue angles of nanocomposites do not change significantly by increasing the treatment temperature. In other words, the temperature variation does not influence the hue property of $CoFe_2O_4/SiO_2$ nanocomposites.

As Table 2 and Figure 4 show, the chroma values of samples decrease by increasing the treatment temperature from 400 ºC to 700 ºC, while their lightness increase. In other words, samples become more neutral and lighter while the treatment temperature increases. Regarding the a* and b* values shown in Table 2, it is found that the decrease of chroma values is related to the decrease of both the redness and yellowness tints of nanocomposites. In order to determine the effect of treatment temperature on colorimetric attributes of nanocomposites, the color difference values between samples treated on 400 ºC and those treated at different temperatures are calculated and shown in Table 2. According to Table 2, the color difference values increase by increasing the treatment temperature.

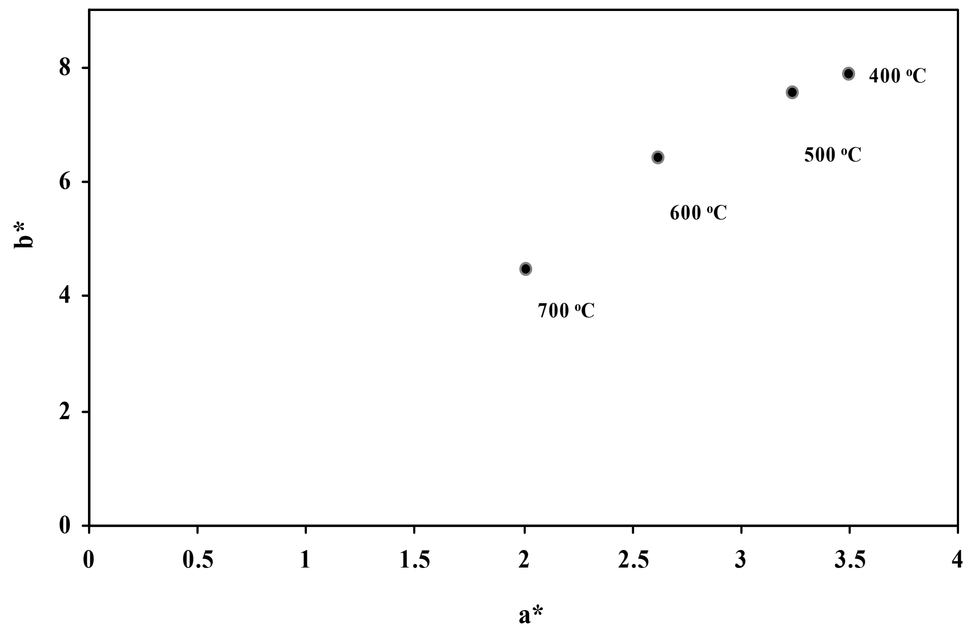

Figure 3: The a*b* scatter plot of $CoFe_2O_4/SiO_2$ nanocomposites.

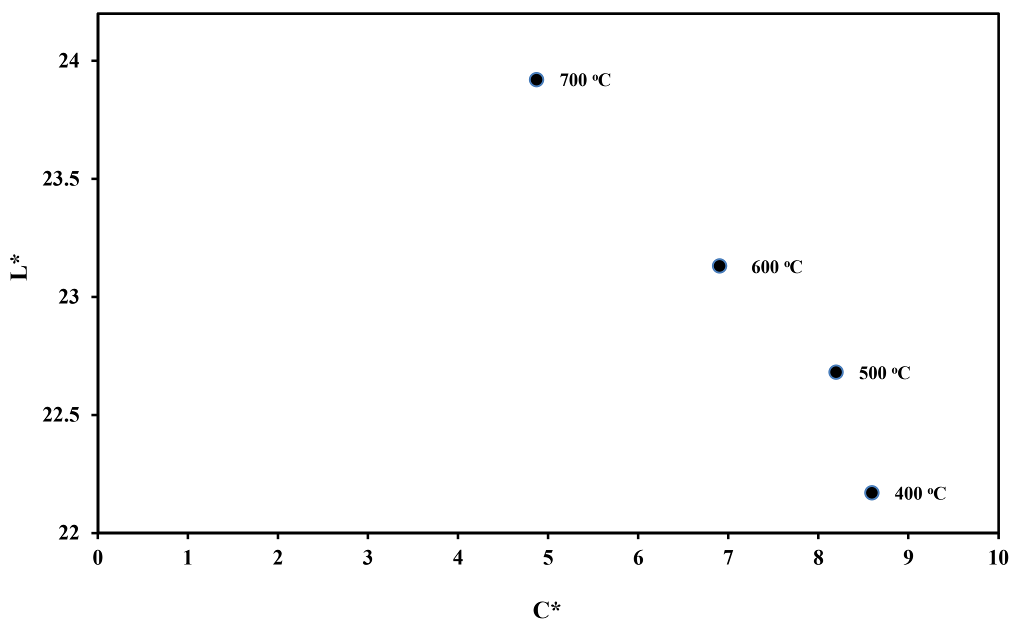

Figure 4: The C*L* scatter plot of $CoFe_2O_4/SiO_2$ nanocomposites.

Table 3: The colorimetric attributes as well as the color difference values of $CoFe_2O_4$ nanoparticles and $CoFe_2O_4/SiO_2$ nanocomposites treated at different temperatures.

Temperature (ºC)	Nanoparticles			Nanocomposites			ΔE_{ab}
	L*	C*	Crystallite size (nm)	L*	C*	Crystallite size (nm)	
400	23.02	5.24	16	22.17	8.59	6	3.57
500	18.04	4.79	30	22.68	8.20	8	5.84
600	14.99	3.30	61	23.13	6.91	9	8.99
700	13.81	1.41	114	23.92	4.87	30	10.75

3.3. Comparing the nanoparticles and nanocomposite

In order to more convenient compare the optical properties of $CoFe_2O_4$ nanoparticles and $CoFe_2O_4/SiO_2$ nanocomposites, the corresponding L* and C* values as well as crystallite size are listed again in Table 3

According to Table 3, the $CoFe_2O_4/SiO_2$ nanocomposites benefit from smaller crystallite size in comparison to $CoFe_2O_4$ nanoparticles. Besides, regarding to the L* values, the nanoparticles are darker than nanocomposites treated at the same temperature, except for the treatment temperature of 400 *ºC*.

It seems that the dispersion of nanoparticles in SiO_2 matrix prevents the nanoparticles agglomeration and causes the nanocomposites to be smaller and lighter than nanoparticles. Besides, regarding to a* and b* values, the nanocomposites benefit more from reddish and yellowish tints than nanoparticles. By considering the chroma values of materials shown in Table 3, it is found that nanoparticles are more neutral than nanocomposites treated at the same temperatures.

On the other hand, regarding to the variation of lightness and tinting factors, it is expected that the color difference values between nanoparticles and nanocomposites increase by increasing the treatment temperature. In this way, the color differences of $CoFe_2O_4$ nanoparticles and $CoFe_2O_4/SiO_2$ nanocomposites treated at the same temperatures are calculated based on equation (6) and shown in Table 3.

Based on the color difference values represented in Table 3, the colorimetric variations between nanoparticles and nanocomposites increase by increasing the treatment temperatures from 400 *ºC* to 700 *ºC*.

4. Conclusions

The optical properties of $CoFe_2O_4$ nanoparticles and $CoFe_2O_4/SiO_2$ nanocomposites treated at different temperatures were investigated. Results showed that the chroma of both nanoparticles and nanocomposites decrease by increasing the treatment temperature while their lightness attributes represent reverse behavior. In fact, the nanoparticles became darker by increasing the treatment temperature while the nanocomposites' lightness increased. Besides, nanoparticles were more neutral and darker than nanocomposites treated at the same temperatures. The color difference values between nanoparticles and nanocomposites also increased by increasing the treatment temperature.

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