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Synthesis and Characterization of $CoAl_2O_4$ Nano Pigments by Polyol Method

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ABSTRACT

*Blue nano pigments of $CoAl_2O_4$ were successfully prepared by polyol method. Two different groups of materials containing chloride and acetate compounds were used to synthesis the nano pigments. The nano pigments were calcinated at 1100 °C. The $CoAl_2O_4$ nano pigments were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), dynamic light scattering (DLS), UV–Vis spectroscopy and CIE-L*a*b* colorimetric measurement. Dynamic light scattering analysis confirmed the formation of nanoparticles in the suspensions. XRD data of $CoAl_2O_4$ powders shows the acetate compounds resulted in a mono-phase $CoAl_2O_4$ spinel structure, while the chloride compounds resulted in two phases of $CoAl_2O_4$ and Al_2O_3 crystal structures. The SEM images showed that the average size of nano $CoAl_2O_4$ pigments is about 50 nm for all nano pigments while they have some agglomerations. The formation of blue pigments in all samples was confirmed by means of colorimetric parameters and DRS spectra. The purity and intensity of color for the samples were different. Prog. Color Colorants Coat. 10 (2017), 231-238© Institute for Color Science and Technology.*

1. Introduction

Nanopigments are chemically insoluble and physically inert substances with a particle size less than 100 nm [1-5]. The nano pigments can be organic or inorganic which should be dispersed into a media by some binders. Most of blue inorganic pigments are based on cobalt ions; cobalt aluminate ($CoAl_2O_4$) is one of the usual compounds which used as inorganic pigment [6, 7]. This pigment has very good optical characteristics and owns high resistance to the light, weather, acids and atmospheric agents. Therefore, it has been used widely for coloration of plastics, paints, fibers, papers, rubbers, glasses, cement, and ceramic bodies [6-13]. Cobalt aluminate is crystallized in a normal spinel structure of the general formula AB_2O_4 with a cubic system and space group $Fd\bar{3}m$. The unit cell of a normal spinel structure contains 32 O^{2-} anions, 8 divalent cations A^{2+} in 8 tetrahedral and 16 trivalent cations B^{3+} in 16 octahedral [6, 14, 15].

Pigments of $CoAl_2O_4$ have been typically synthesized in solid state reaction at high temperature. The chemical composition and particle size were nonuniform with a high level of impurities [9, 16]. Some chemical techniques have been applied to prepare $CoAl_2O_4$ including sol–gel [1, 17, 18], hydrothermal [19, 20], co-precipitation [9, 11, 15] and polymeric precursor treatment [21].They have led to synthesis of $CoAl_2O_4$ spinel by a fine particle size (nano particle) and uniform distribution. However, materials fabricated using these methods are usually expensive and their efficiency is low.

A suspension containing crystalline $CoAl_2O_4$ nanopigments was synthesized by polyol method [22]. Polyol is a low temperature fabrication method in which

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the formation of aggregates during the reaction is relatively less. Final product could be a stable suspension with a particle size smaller than 200 nm which can be used in ceramic printing industry. In this method, a liquid with a high boiling point e.g., ethylene glycol (EG), diethylene glycol (DEG) [23], triethylene glycol (TREG) or tetra ethylene glycol (TEG), is used as a solvent [22, 24]. Also, some additives are used as protecting agents or stabilizers [25], particle growth inhibitor or reducing agents of the metallic ions [26, 27].

In this paper, three samples of $CoAl_2O_4$ nanopigments were synthesized by polyol method in a suspension. Two suspensions were stable while one of them precipitated after some time. The optical and structural properties of samples were investigated and compared to each other. They are going to be used as ink for printing on the ceramic.

2. Experimental

2.1 Synthesis of $CoAl_2O_4$ nano pigments

The precursors were aluminum hydroxide acetate ($AlOH(CH_3COO)_2$, purity; 96%, Aldrich), cobalt acetate tetra hydrate ($Co(CH_3COO)_2.4H_2O$, purity; 99%, Merck), hydrochloric acid (HCl, purity; 99%,Merck), ethanol (purity; 96% , Merck), DEG (purity; 99% , Merck), cobalt chloride tetra hydrate ($CoCl_2.4H_2O$, purity; 99%, Merck), aluminum chloride ($AlCl_3$, purity; 99%, Merck) and ammonium hydroxide solution (25%). Three samples of $CoAl_2O_4$ nano pigments were synthesized by polyol method and labeled C_1, C_2 andC_3. The precursors for synthesizing each sample are reported in Table 1. For synthesizing C_1, the precursors were placed in a flask fitted with a reflux condenser. 30 g diethylene glycol was added and the solution was stirred strongly for 30 min. The mixture was heated at 180 °C for 12 hours. The suspension was cooled to room temperature and diluted with 30g ethanol. The preparation results in a reddish blue suspension. For C_2 and C_3, the process was exactly the same as C1 but they were heated for 3 hours. The outcome of C2 was a violet suspension and it was a dark blue for C3. Nanopigments were separated by centrifugation at 3800 rpm for the characterizations. Then they were dried at 110 °C and annealed at 1100 °C for 2 hours.

2.2. Characterizations

The optical properties of the suspensions and the powders were measured by employing Avantes spectrophotometer model avaspec-2048 equipped with Ava light-DH-S-BAL as a source. The absorption spectra of suspensions were measured using transmittance of a cell containing 4 mL of suspension; while diffuse reflectance spectra were measured using a flat surface of powder. The particle size distribution and zeta potential of the particles in suspensions were

Table 1: Precursors for synthesizing of the samples were listed below.

Compound	C_1	C_2	C_3
$Co(CH_3CO_2)_2.4H_2O$	0.298	0.298	-
$AlOH(CH_3CO_2)_2$	0.388	0.388	-
H_2O	-	1	1
$(HOCH_2CH_2)_2O$	30	30	30
C_2H_5OH	30	30	30
NH_4OH	-	0.5	0.5
$CoCl_2.4H_2O$	-	-	0.299
$AlCl_3$	-	-	0.336
HCl	1.415	-	-

determined based on dynamic light scattering method using Nano-ZS Malvern Instruments. It uses a cell containing 4ml of each suspension for measurement. The morphology of the powders was determined using VEGA3 TESCAN as a scanning electron microscope (SEM). The samples were coated with a thin layer of Au to prevent charging process. Size measurement of the particles was carried out by "Nano Measurement" software using SEM images. The X-ray diffraction (XRD) patterns of the powders were recorded using Philips X'Pert Pro machine using $Cu_{K\alpha}$ radiation: λ=1.5406 Å as a source. In addition, color parameters L*, a*, b*, c* and h* of nano-pigments were measured on the powder samples following the CIE (Commission Internationale de l'Eclairage) colorimetric standard using X-Rite SP-64 spectrophotometer.

3. Results and Discussion

The polyol method was used to prepare the $CoAl_2O_4$ nano pigments by two groups of materials including acetates (C_1 and C_2) and chlorides (C_3). Photographs of C_1, C_2 and C_3 nano pigments, synthesized by polyol route are shown in Figure 1-a, 1-b and 1-c after annealing at 1100°C. Blue color was obtained for all the samples which can be an evidence for the formation of typical spinel structure.

The SEM images of pigments are shown in Figure 2. Figures 2-a, 2-b and 2-c show the SEM images of C_1, C_2 and C_3, respectively. Figure 2-a shows that nanoparticles are mostly spherical. The histogram showing the number of particles versus size for C_1 is demonstrated in figure 2-d. It can be observed that it is similar to a typical Gaussian curve with an average size of 50 nm. There are some agglomerated particles in the image but the number of agglomerations is less than that of the two other samples. Figure 2-b shows the particles of sample C_2 in the same shape. The histogram of the number of particles versus size for image 2-b is demonstrated in Figure 2-e. It can be observed that it is similar to a typical Gaussian curve and the average particle size is about 55 nm. Some agglomerated particles bigger than 300 nm are also observed. Figure 2-c shows SEM image of sample C_3 which was synthesized by chloride group materials and resulted in blue nano pigments of $CoAl_2O_4$. The histogram of the number of particles versus size for image 2-c is demonstrated in Figure 2-f. It shows that the average size of the particles is about 50 nm. The number of agglomerated particles in sample C_3 is more than sample C_1 and C_2. The agglomerated particles may be formed in drying process. The size of the agglomerated particles in sample C_3 is about 500 nm. It can be concluded that the average particle size of all samples is about 50 nm.

Figure 3 shows XRD patterns of nano pigment samples C_1, C_2 and C_3 after annealing at 1100 °C. From figure 3-a and 3-b, it can be observed that all peaks of C_1 and C_2 are indexed to spinel structure of $CoAl_2O_4$ and they were crystallized in a single phase structure. A similar structure of $CoAl_2O_4$ was observed for C_1 and C_2 and it shows that 1100 °C is a good temperature for synthesis of $CoAl_2O_4$ in a spinel structure by using cobalt acetate in polyol method.

Figure 3-c shows that C_3 is composed of two crystal structure containing $CoAl_2O_4$ and Al_2O_3. It is well known that Al_2O_3 crystal formation can occur at temperatures higher than 900 °C and it is completed at 1100 °C [6]. Formation of Al_2O_3 may be due to $AlCl_3$ used as precursor. Since the samples C_1 and C_2, synthesized using acetate precursors, were crystallized in a single phase of $CoAl_2O_4$, the formation of Al_2O_3 can be attributed to fast hydrolysis of $AlCl_3$ in ammonia-water solution and formation of $Al(OH)_n^{+3-n}$ without any bonding to cobalt ions during reflux process.

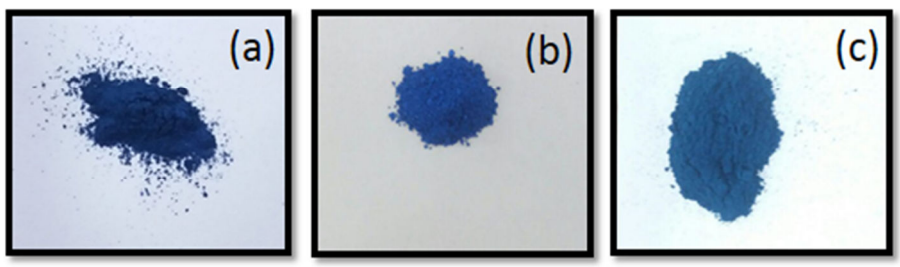

Figure 1: Photographs of nano pigment samples C_1, C_2 and C_3 annealed at 1100 °C. (a) C_1 , (b) C_2 and (c) C_3.

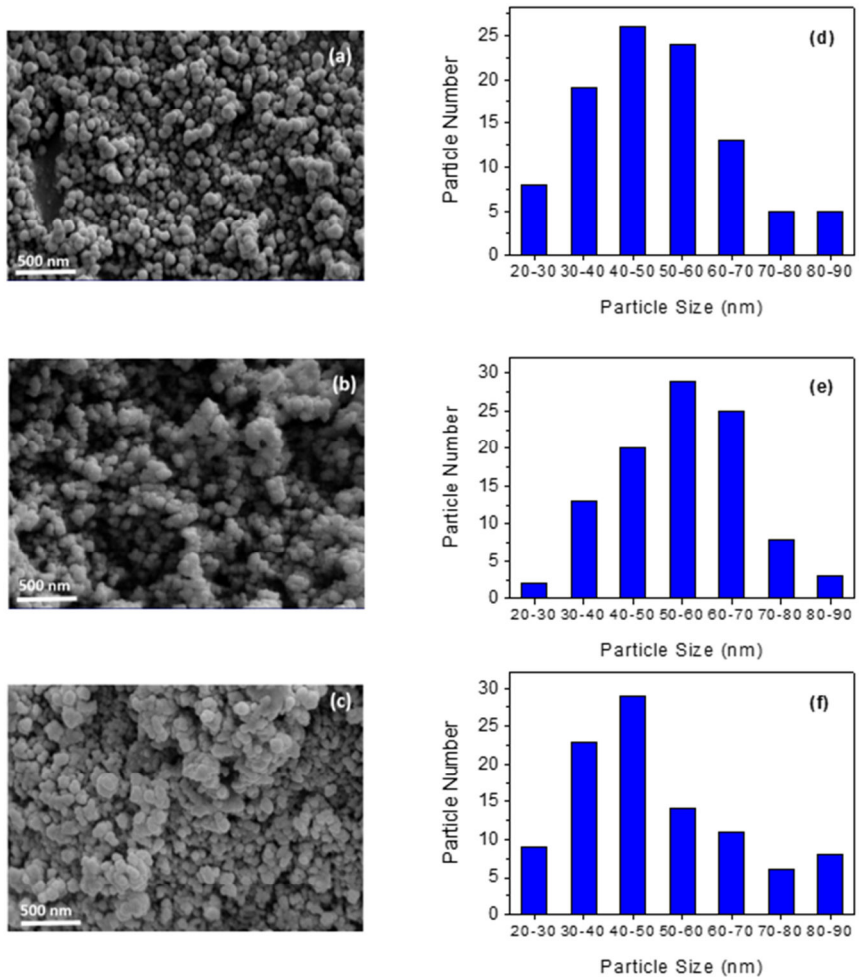

Figure 2: SEM images of nano pigment samples C_1, C_2 and C_3 after annealing at 1100 °C. (a) and (d) C_1, (b) and (e) C_2, (c) and (f) C_3.

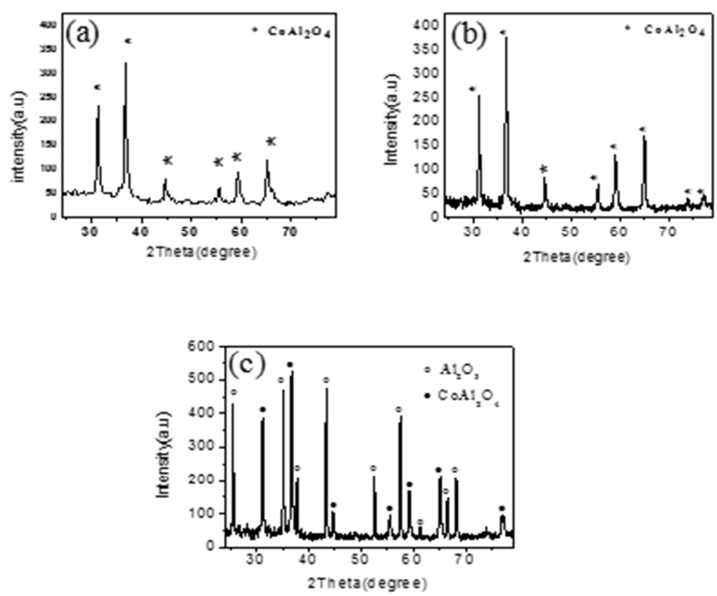

Figure 3: XRD patterns of nano pigment samples C_1 (a), C_2 (b) and C_3 (c) annealed at 1100 °C.

Table 2 shows the colorimetric data of the nanopigments after annealing at 1100 °C. The yield of blue color is mainly controlled by the parameter b*; a negative value for b* indicates blue color. On the other hand, L* component indicates the brightness of pigments. The value of b* for sample C_1, C_2 and C_3 is -18.96, -40.02 and -24.65, respectively. Therefore sample C_2 shows higher intensity of blue color comparing to C_1 and C_3. Also the brightness (L*) of sample C_2 is higher than that of C_1 and C_3. The magnitude value of a* for C_2 (~ -3.86) is less than that of samples C_1 and C_3, which indicates the intensity of green component of the color for C_1 and C_3 is more than that of C_2. The c* and h parameters were also analyzed. H parameter shows the purity of samples. It can be observed that all samples have a high purity degree of blue color, while C_2 has more purity (~271.3˚) than other samples. The value of c* also shows higher intensity for sample C_2. So sample C_2 is bluer than C_1 and C_3.

It has been reported that for spinel structure of AB_2O_4, there are three structures containing normal, inverse and a mixture of both of them. In normal spinel, A^{2+} ions place in tetrahedral sites and B^{3+} ions occupy octahedral sites of the lattice. In the inverse structure, $B^{3+}$and A^{2+} ions are placed in tetrahedral and octahedral sites, respectively. For the mixture of normal and inverse structure, some of A^{2+} ions replace in octahedral sites and some of B^{3+} ions replace in tetrahedral sites of spinel lattice [28, 29]. The color of $CoAl_2O_4$ can be changed by placing Co^{2+}, Co^{3+} and Al^{3+} ions in tetrahedral and octahedral sites of the

Table 2: Color parameters of the powders synthesized and annealed at 1100 °C.

Code	L*	a*	b*	c*	h
C_1	26.35	-6.77	-18.96	20.13	250.35
C_2	40.35	-3.86	-40.02	40.20	271.3
C_3	27.39	-5.02	-24.65	25.16	258.49

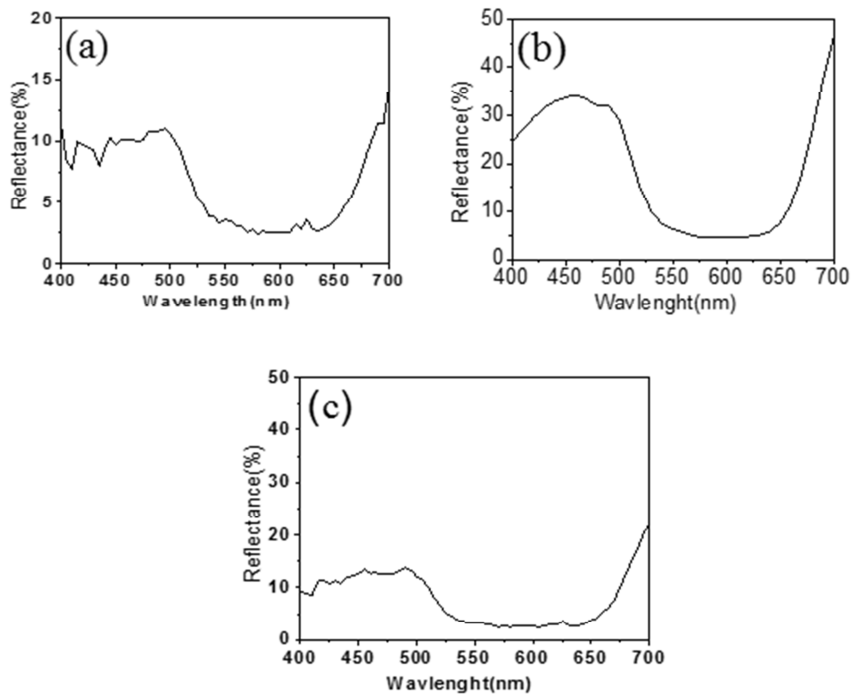

Figure 4: Diffuse reflectance spectra of nano pigments (a) C_1, (b) C_2 and (c) C_3.

lattice and formation of normal, inverse or mixture structure. Normal $CoAl^2O^4$ spinel structure is blue; for the mixture and inverse phases the color changes from green to black [6, 29]. On the other hand, the amount of replacing Co^{2+}, Al^{3+} and Co^{3+} in tetrahedral and octahedral sites can change the color parameters of $CoAl_2O_4$. The color differences of C_1 sample relative to C_2 may be due to their structure and replacement of Al^{3+} and Co^{2+} in the tetrahedral and octahedral sites of lattice. It seems that substitution of Co^{3+} or Al^{3+} instead of Co^{2+} ions in tetrahedral sites is the reason for decreasing of a* and increasing of b* in C_1 and C_3 samples relative to C_2. On the other hand, XRD pattern of C_1 and C_2 show the spinel structure of $CoAl_2O_4$; however the intensity of peaks for C_2 sample is more than that of C_1. The extra phase of Al_2O_3 of C_3 sample also can be the reason for low blue color.

Diffuse reflectance spectra of nano pigments are shown in Figure 4. The spectra show a peak at 400-500 nm and another one at 700 nm for all samples. It is well known that the peaks in the region of visible light at 400-500nm belong to the blue and indigo blue color. By comparing the intensity of peaks at 400-500 nm for all samples, the bluer color of sample C_2 relative to C_1 and C_3 can be understood. The peak at 700 nm belongs to red color. It shows that all samples have a small component of red color and it is confirmed by a^* parameters in Table 2.

The particle size distribution for the suspension of samples was measured by dynamic light scattering method and reported in Figure 5. Figure 5-a, 5-b and 5-c shows particle size distribution for C_1, C_2 and C_3 samples, respectively. The range of particle size for C_1 and C_3 suspension is 11-25 nm and 11-45 nm, respectively, while it is 1000-6000 nm for C_2. Figure 5-b does not show a typical Gaussian curve. It is mainly because C_2 suspension has some flocculated particles and it seems to be low stable. The average size for the suspension of samples C_1 and C_3 is approximately 22.7 nm and 19.4 nm, respectively, while it is 3019 nm for C_2. Zeta potential of the suspended particles in C_1 and C_3 samples is measured; 33mV and +19.6 mV, respectively, while the suspension of C_2 was not stable for zeta potential measurement and it made some precipitation after 20 days. It seems that the bigger particles in C_2 sample were composed of some flocculated particles. This phenomenon can be understood from the precursors. The suspended particles in C_1 were charged negatively (ζ= -33mV) because of dissociation and hydrolysis of acetate ions and production of a high amount of OH^- ions in the solution. It is expected that addition of ammonia accelerates the hydrolysis reaction and it causes particle flocculation in the solution. Also it can be observed that the average particle size of suspension and powder of the samples are not exactly the same. The reason may be due to the growth and agglomeration of particles after annealing at 1100 °C.

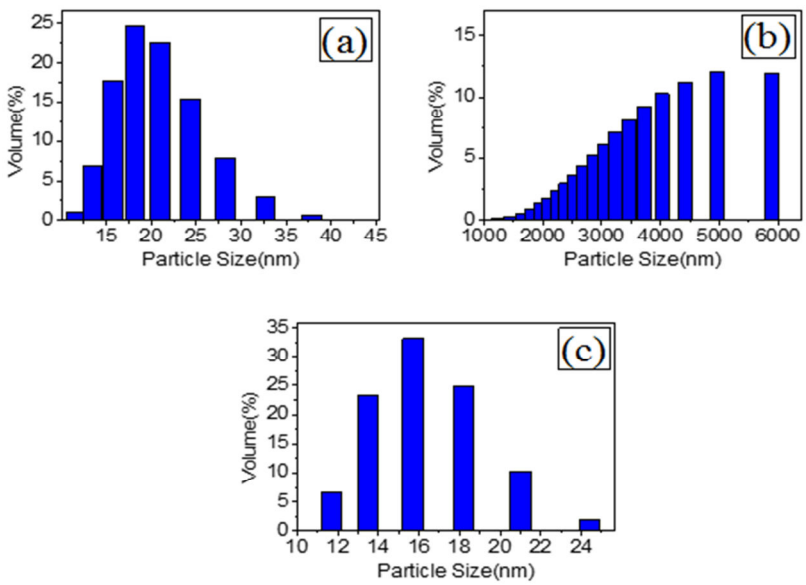

Figure 5: Particle size distribution for C_1 (a), C_2 (b) and C_3 (c) suspensions after refluxing.

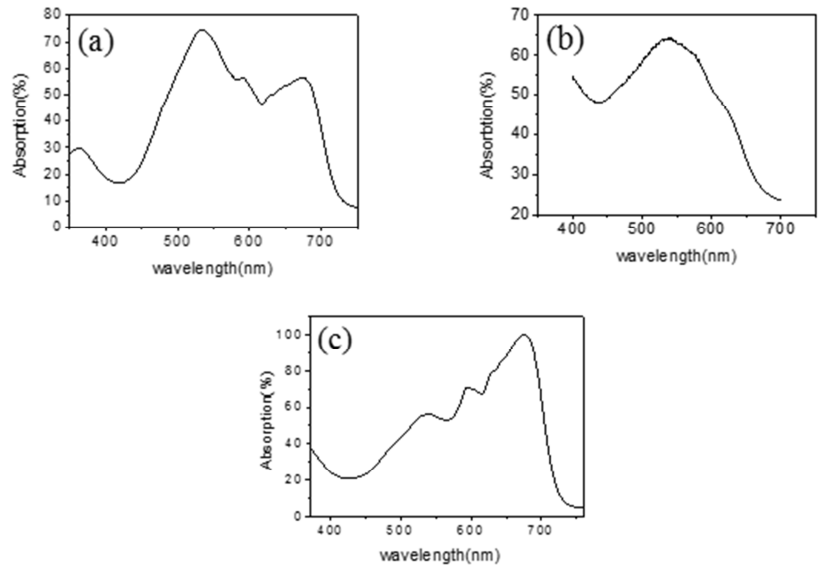

Figure 6: UV/Visible absorption spectra of suspensions after refluxing; (a) C_1, (b) C_2 and (c) C_3.

Figure 6-a, 6-b and 6-c demonstrates the UV/Visible absorption spectra of C_1, C_2 and C_3 suspension samples, respectively. The decrease of absorption, especially at 420 nm in figure 6-a, shows the blue color for C_1 suspension. The absorption spectrum of C_2 suspension also shows a minimum near the blue region at 440 nm. Although the absorption decreases to a minimum at 440 nm, the absorption at minimum is not as low as that of C_1 and C_3. Also the absorption decreases at 700 nm for C_2 suspension. The absorption of C_2 suspension at 440-700 nm shows that the color is almost purple. The decrease of absorption peak at 420 nm in figure 6-c shows the blue color of C_3 suspension.

The absorption bands between 400–500 nm, corresponding to C_2 sample, were due to the Co^{3+} component of Co_3O_4 and it seems that a thin layer of Co_3O_4 was formed on the surface of particles in the suspension [30]. Since there is not any peak in 400–500 nm region in diffuse reflectance spectra of this sample and also XRD does not show any structure related to Co_3O_4, it can be concluded that a phase transition to $CoAl_2O_4$ has been occurred after heat treatment for the obtained pigments. The energy level for Co^{2+} (3d7) in both octahedral and tetrahedral ligands has some spin-allowed transitions at around 546, 590, 630 and 680 nm. These bands appeared in the spectra and were attributed to a Jahn–Teller distortion of the tetrahedral structure which is responsible for the blue coloration [31]. The intensity of these peaks is different and it may be attributed to surface states of the ions.

4. Conclusions

The present study reported synthesis and characterization of three nano blue pigments of $CoAl_2O_4$ crystallized in spinel structure. The synthesis of $CoAl_2O_4$ samples were successfully carried out using polyol method and two groups of material containing chloride and acetate compounds. The results of DLS experiment approved the formation of $CoAl_2O_4$ nanoparticles in the suspensions with different sizes and zeta potentials. Zeta potential of the nano pigments synthesized by acetate compound and acid (C_1 sample) was -33 mV while for those synthesized by chloride compound and base (C_3 sample) was + 19.6 mV. The suspension synthesized by acetate compound and base (C_2 sample) was unstable. The average size for the particles of suspensions C_1 and C_3 was approximately 22.7 nm and 19.4 nm, respectively, while it was 3019 nm for C_2. According to XRD and SEM results, crystalline nano pigments have been obtained. The SEM results showed the average size of 50nm for all samples. The measurement of color parameters showed different types of blue color for the samples. Results of the present study demonstrated that polyol route is an effective method to synthesize blue $CoAl_2O_4$ nano pigments and the suspension can be used as ink for printing process.

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