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Chemical Synthesis of Nano-Crystalline Nickel-Zinc Ferrite as a Magnetic Pigment

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ABSTRACT

he nano-crystalline nickel-zinc ferrite was prepared via chemical synthesis. Zinc nitrate, nickel nitrate, iron nitrate hydrate, citric acid and ethylene glycol were used as precursor materials. Crystallization behavior of the precursor was studied by X-ray diffraction (XRD). Nanoparticle phases can change amorphous to spinel ferrite depending on the calcination temperature and crystallite size calculated by Scherrer's formula about 26-105 nm with the calcinations temperature. Morphological and structural properties were investigated by scanning electron microscopy (SEM). The powder density was measured using a helium pycnometer. Magnetization measurements were carried out on an alternative gradient force magnetometer (AGFM), which revealed saturation magnetization of the samples were strongly dependent on the calcination temperature and particle size of the sample and the saturation magnetization values of the samples increased as a function of the calcination temperature. Colorimetric analysis was measured by using UV-visible spectroscopy in the range of 300-700 nm. These result indicated a correlation between pigment color and calcinations temperature. The color of the pigment ranges from reddish brown to deep brown depending on the calcination temperature. Finally our results showed that the chemical synthesis method leads to obtain nano crystalline nickel zinc ferrite with good controllable stoichiometry at low temperature. Prog. Color Colorants Coat. 3(2010), 9-17. © Institute for Color Science and Technology.

1. Introduction

Magnetic nano powder of spinel ferrite (MFe₂O₄, M= Mg, Fe, Mn, Co, Ni, Zn, Cu, Cd) is a technologically important material which was first synthesized 50 years ago. Special physico-chemical properties of these materials result different application such as radio frequency coils, transformer, magnetocaloric refrigeration, contrast enhancement in magnetic

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resonance imaging (MRI), magnetically guided drug delivery, ferro fluid, microwave adsorbing material, sensor, as radar absorbing materials (RAM) in military to increase the invisibility to radar and heat-resistant pigments [1,8]. In this group high electrical resistivity and excellent magnetic properties make this ferrite a good candidate as a core material for power transformers in telecommunication and electronic applications in megahertz frequency regions [9]. Magnetic inorganic pigments have been used in high-tech applications because of some of their unique properties [10, 11]. In the past, nickel zinc ferrites are prepared by conventional methods, which has disadvantages such as high period heating which may result in Zn volatilization and change the stoichiometry [12]. In recent years, chemical methods such as co-precipitation [13], sol-gel [14] and hydrothermal [15] are used to synthesis these materials.

This paper is concerned with the synthesis of spinel based brown pigments (InOrg Brown 1388), which has been widely studied during last decades to improve color hue. In this study nano-crystalline magnetic pigment was synthesized via polymeric precursor method with a good stoichiometric control.

2. Experimental

Nano crystalline nickel zinc ferrite was synthesized by a polymeric precursor method. This method was first introduced by Pechini [16] uses citric acid as chelating agent and ethylene glycol as reaction medium in the formation of precursor [17]. It is based on polymerization of metallic citrate by using ethylene glycol. A hydrocarboxylic acid, such as citric acid, is used in an aqueous solution in order to chelate cations. The addition of a glycol, such as ethylene glycol, leads to the formation of an organic ester. Polymerization, promoted by heating, results in a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix.

Citric acid (CA), ethylene glycol (EG) and metallic nitrate such as $Ni(NO_3)_3.6H_2O$, $ZnNO_3.6H_2O$ and Fe₂ $(NO_3)_3.9H_2O$ was employed as precursor materials. Initially citric acid (CA) was added to 500 ml balloon of deionized water with constant stirring. Then ethylene glycol (EG) was added to the solution, at a mass proportion of 60% CA to 40% EG to prepare first solution. Secondary solution was prepared by mixing metallic nitrate in deionized water. The molar ratio of total metal ions to citric acid was kept constant at 1:3 for all reactions. Finally, secondary solution was added to

the first one and stirred by reflux. This solution was heated at 80 °C for 2 hours to achieve complete chelation. Then temperature was increased to 90-110°C to promote polyesterification reaction. This heating process accelerated esterification between CA and EG and eliminated the remaining water, a clear, transparent, solid and amorphous dark resin was produced. The resin was heated at 300 °C for 1 hour to decompose organic compounds. The powder precursor was milled in a planetary mono mill (model Pulversette 6) with zirconium mortar and passing through a 170-mesh sieve. The powder precursor was put inside of an alumina crucible and calcined by heating to 400, 600, 800 and 1000° C at a heating rate of 10° C/min under the ambient atmosphere and maintained for 1 hour at the target temperature.

Crystallization behavior and thermal decomposition characteristics of the precursor were studied by X-ray diffraction (XRD) technique using a Siemens diffractometer (model D-5000) with Cu Ka radiation (λ =1.5406Å).

Morphological and structural properties were investigated by scanning electron microscopic (SEM) Philips (model XL 40).The powder true density was measured using a helium pycnometer (Pycnometer Micromeritics, model Accupyc 1330).

Magnetization measurements were carried out on an alternative gradient force magnetometer (AGFM) model 155 at room temperature in 10 kOe field strength.

Fourier transforms infrared spectroscopy (FT-IR) spectra of samples were made with PerkinElmer spectrum FTIR spectrophotometer (model spectrum one) in the range of 4000-400 cm⁻¹.

3. Results and discussion

XRD patterns of powder precursor and samples after being heat treated at 400, 600, 800 and 1000°C for 1 hour is shown in Figure 1. As seen in the Figure 1 no peak is detected for the powder precursor which means it is an increasing amorphous powder and calcination temperature to 400 °C results in appearance of ferrite phase nuclei. However, the major phase in all preparations was the spinel phase (Nickel zinc ferrite) with space fd³m group and increasing the temperature not only leads to higher crystallinity (intensity) but also increased the particle size. Conventional methods need to high temperatures and prolonged heating time [18, 19], but in this method, ferrite phase can produce very fast at low temperature. The mean crystallite sizes are



Figure 1: XRD pattern of samples after heat treatment at 400 - 1000 °C for 1 h.

calculated from (311) peak using Scherrer's formula $d=0.9 \text{ k}\lambda/\text{Bcos}\theta$, where d is the mean diameter in Å, K is the constant (shape factor), B is the half maximum line width, and λ is the X-ray wavelength [20] about 26-105 nm.

FTIR spectra are of polymeric precursor, powder precursor were shown in Figures 2(a) and 2(b).

As seen in Figures 2(a) and 2(b), in the spectrum of the polymeric resin precursor broad absorption bands around 3400 cm⁻¹ and 1732cm⁻¹ are attributed to the stretching vibration of the hydrogen-bonded O-H groups and uncoordinated carbonyl group, respectively. Those at 2930-2990cm⁻¹ are the aliphatic C-H stretch. An absorption band at 1074cm⁻¹ is the C-O stretch related to the formation of ester from -CH₂-OH group in ethylene glycol and the carboxyl group of the citric acid [21, 22].

The bands at ~ 1380cm⁻¹ and ~ 1600cm⁻¹ are the asymmetric and symmetric C=O stretching modes, respectively, which confirm coordination of the carboxylate groups by metal ions to form a chelated complex and successive esterification reaction between CA (free and complexed) and EG [23].

In the FT-IR spectra of the powder precursor (Figure 2(b)) the absence of some organic bands could be ascribed to the decomposition of most organic ligands in the gel after primary calcination [22].

The FT-IR spectra of calcined powder are reported in Figure 3 As seen in these spectra all the previosely mentioned absorption bands have disappeared and only strong absorption bands around 500 cm⁻¹ and 600 cm⁻¹ due to the metal-oxygen bonds are observed [24].



Figure 2: FT-IR-spectra of a polymeric resin precursor (a) and powder precursor (b).



Figure 3: FT-IR spectrum of sample calcined at 400 °C.

The SEM micrograph of calcined sample at lowest and highest temperatures are shown in Figure 4(a) and (b). According to Figure 4(a), the average grain size achieved about 25 nm and increasing the temperature cause an increase in crystallite size which confirm the X- ray diffraction pattern.

The density of the powder measured via helium pycnometer technique was about 5.73 g/cm^3 . This is in agreement with the literature [8] and confirms formation of the spinel phase.



Figure 4: SEM of the nickel-zinc pigments after calcination at (a) 400°C, (b) 1000 °C.

Colorimetric parameters (L*, a* and b*) and diffuse reflectance of nickel zinc ferrite pigments were measured with spectrophotometer from 300 to 700 nm, using the D65 illuminant. In this system, L* is the lightness axis (where black is equal to 0 and white to 100), b* represents the color varying from blue (negative axis) to yellow (positive axis), a* represents the color varying from green (negative axis) to red (positive axis). The results show in Table 1 and Figure 5.

Table 1 shows the data of the colorimetric coordinates of nickel zinc ferrite pigments are in agreement with Figure 4.

The results show that, the L*, a* and b* parameters decreased when the calcination temperatures increased. Therefore, the results of colorimetric measurements indicate color variation from reddish-brown to darkbrown consequence increasing as а the temperature. The diffuse reflectance curves of the synthesized spinel pigments are shown in Figure 6. These data also confirm the reduction of brightness of the pigments with increasing calcination temperature. Decrease in the L* parameter that takes place may be mainly associated to the sintering of the powder and increasing particle diameter from 26 to 105 nm, which leads to the decrease of the overall reflecting surface of the powder, which caused the decrease of the overall reflecting surface of the powder [25].

It is quite evident that the system undergoes a remarkable modification this is probably related to the elimination of defects, as oxygen vacancies, when temperature is raised [26], lead to less distorted cationic sites, with better defined colors because defects lead to distorted tetrahedral and octahedral sites, changing the ligand-field around the chromophore, changing the observed color [27].

Table 1: Colorimetric coordinates (L*, a*, b*) of nickel-zinc pigments prepared via the polymericprecursor method as a function of the heattreatment temperatures.

Heat treatment (°C)	Illume	L*	a*	b*
400	D65	45.48	10.76	10.17
600	D65	44.41	9.75	9.21
800	D65	42.07	4.06	3.14
1000	D65	42.52	5.62	3.87



Figure 5: Spectral reflectance curve of samples were calcined at different temperatures.



Figure 6: Colorimetric coordinates, as a function of heat treatment.



Figure 7: Hysteresis loops of the nickel-zinc pigments calcined 400 and 1000 °C.

Figure 7 shows the magnetic hysteresis loop of the samples calcined at different temperatures (400 °C, 1000°C) In Figure 7, both curves show not only a ferromagnetic behavior but also the saturation magnetization values which were very affected by increasing the temperature as a consequence of gradual increase in crystallinity and particle size [28], a similar behavior has been reported for other magnetic materials [23]. Consequently, the maximum values can be obtained for the sample which calcined at high temperature. The saturation magnetization of the powder calcined at 400 °C and 1000°C under ambient atmosphere is 34 emu/g and 90 emu/g, respectively.

4. Conclusions

The chemical synthesis method was employed to prepare magnetic pigment at low temperature improved magnetic properties through a good stoichiometric control. FT-IR spectra indicate that successive esterification reaction and formation of metal-oxygen bands attributed to the spinel phase. XRD patterns reveal that the precursor method can produce nickel zinc ferrite at relatively low temperatures with high magnetization. SEM images show that the sample synthesized at 400 °C has nearly homogeneous grain distribution with an average size about 20-30 nm. Determined average crystallite size using Scherrer's equation confirms crystal growth with enhancement of calcination temperature. Increase of calcination temperature causes more saturation of magnetization. Colorimetric results indicate that there exists a correlation between pigment color and calcinations temperature. The color of the pigment changes from reddish-brown to dark-brown depending on the calcination temperature.

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