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Incorporation of Metal Oxides on Mica Flakes as Green Pearlescent Pigments: Preparation and Analysis

***M. Cheraghipoor** [1], **M. Zakeri** [2*]*

[1] Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, Zahedan, Iran
[2] Department of Chemical Engineering, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan, Iran

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ABSTRACT

Pearlescent pigments represent a variety of pigments that can generate pleasant optical appearances in the system because of their ability of easy parallel orientation of a large number of platelet-like particles. In the present work, the green pearlescent pigments based on mica (biotite) and mica-titania flakes covered with a thin film of nickel oxide have been prepared by novel methods via the homogeneous precipitation of nickel acetate with sodium/potassium hydroxide, and in the presence of mica (biotite), titania, ammonium molybdate or mica-titania flakes. The synthesized pigments were characterized by means of X-ray diffractometery (XRD), Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and X-Ray fluorescence (XRF) analyses. By comparing the XRD pattern of synthesized pigments with the mica based pattern, it is clear that the structure of the support does not change due to the layering on these bases. The XRF analysis shows that the nickel compound is layered well on the mica at 8.823 %. The quantity and quality of the pigments produced by methods 1 and 2 were approximately the same. Consequently, to make commercial savings, method 1 was recommended for the preparation of the metallic pearl pigments and mica was known as the best support for the production of the pearlescent pigments by the introduced method. Furthermore, the TGA/DSC curve showed that the introduced pigments were stable up to 200 °C. The results showed good chemical resistance and pearl luster effects for the produced pigments.

1. Introduction

Pearlescent pigments represent a variety of pigments that can show pearl shine when covered with a thin film of metallic oxides due to angle-dependent optical effects with different refractive indices [1, 2]. Hence, these pigments can be a good choice to create the unique color effects for industrial and pharmaceutical applications [3, 4]. Pearlescent pigments are stable materials in acidic or basic conditions and can tolerate temperatures up to 800 °C [4]. They are resistant to weathering, sunlight and heat and are widely used as coloring agents in high

[*]Corresponding author: m_zakeri@eng.usb.ac.ir

temperature-resistance painted porcelain enamel [5]. In addition, they have particular properties such as: the electrical conductivity, sensitivity to the laser reflection and magnetic properties [6]. Unlike other pigments, in which the absorption and scattering of visible light are functional principles [7], the pearlescent pigments are usually inclusive of single crystals and/or multilayer structures in such a way that each layer can have different refractive indexes [1]. If these flakes are dispersed in a translucent environment with a minor refractive index, an optical effect that is similar to that of natural pearls and shells is confirmed, when the irradiation toward the flakes is under atmospheric conditions, the flakes surface will reflect part of the light and transmit the rest [8]. According to the rules of the main thin layers of optical solids, the wavelength of the light, which is amplified by interference, depends on the thickness and the refractive index of the layers [9]. The pearlescent pigment based on mica or mica-titania is a type of pigments that is synthesized via TiO_2 or other metal oxide coatings on thin layers of mica and is popular because of its excellent chemical stability [10]. Mica has several types including sericite, biotite, lepidolite, muscovite, phlogopite, and vermiculite that are different in the chemical composition [11]. From among different kinds of mica, muscovite is usually used as a base for the preparation of colored pigments. Mica-titania pigments can be synthesized by several techniques. The most widely used technique is the heterogeneous nucleation in solutions. This technique consists of the homogeneous hydrolysis and titration methods alternatively. Moreover, the mentioned method can improve the adhesion of the metal oxide to the support surface [12-15].

V. Štengl et al. [9], investigated the synthesis of the colored pigments based on mica coated with metal oxides by the homogeneous hydrolysis method. They demonstrated that mica granularity and the thickness of the oxide layers have important effects on the properties of the final pigments. Q. Gao et al. [10], used the method of the hydrolysis of a $TiCl_4$ ethanolic solution in water for the preparation of TiO_2-coated mica-titania pigments. The characterization of the pigments showed that the obtained pigments had a high photostability under ultraviolet light. M. Hosseini-Zori [3], prepared red and gold muscovite pigments using iron and zirconium oxides nanoparticles. The results of that investigation demonstrated that the red factor was affected by the iron content. Xiaojuan et al. [16], studied the effects of several important parameters such as the value of pH, on the final properties of mica/Fe_3O_4 pearlescent pigments prepared by co-precipitation. The results indicated that in the pH value equal to that of the co-precipitation of Fe^{+3} and Fe^{+2}, the pearly shining of pigments is considerable. Hosseini-Zori [17], synthesized dark gold to bronze mica clay pigments. In that research mica flakes (phlogopite and muscovite) were covered with iron-zirconium oxide nanoparticles by homogeneous precipitation. The analysis of the results revealed that the hue and pearl effect of muscovite was better than those of phlogopite. In this work, our aim is to establish an efficient protocol for the preparation of green pearlescent pigments based on mica (biotite), mica-alumina and mica-titania flakes covered with a thin film of nickel oxide using the homogeneous precipitation of nickel acetate with sodium hydroxide. Simplicity, the reduction of the energy consumption as a result of using ambient temperature and the production of pigments with acceptable pearl luster effects are the most important advantages of this method.

2. Experimental procedure

2.1. Material and instrumentation

All reagents (Nickel acetate, Ammonium molybdate, Sodium hydroxide, Potassium hydroxide) were purchased from Merck and used without further purification. The selected mica for this work (biotite) has been purchased from West Micronized Company (Hamedan, Iran), characterized by X-ray diffractometery and used without further purification. The experiments were performed at temperatures of 25, 60 and 400 °C. The powder X-Ray diffraction patterns were measured with the D8, Advance, Bruker, axs, diffractometer using the CuKα irradiation (λ= 0.15418 nm) with the following measurement conditions: XRD patterns from 20° to 60° 2θ were recorded at room temperature , a tube voltage of 40 kV, a tube current of 40 mA, a step scan mode with the step size of 0.02° 2θ and a counting time of 1 s per step. X-Ray fluorescence (XRF) analyses were taken by a Philips (PW2404 model) spectrometer. Thermal analysis (DSC/TGA) data were recorded on a STA-1500t (Rheometric scientific) instrument. The analysis was carried out in air atmosphere in a temperature up to 600 °C with a heating rate of 10 °C/min.

2.2. Preparation of pearlescent pigments

Method 1: Mica, mica-titania, titania, or ammonium molybdate (1 g) dissolved in 6 ml of a NaOH solution (1 M) and stirred in order to become a suspension. Nickel acetate (3 ml, 1M) was added to the suspension, which was stirred at room temperature for 10 min. The resulting colored suspension was filtered and washed with cold water and dried in air to afford the pigment powder with a pearlescent luster.

Method 2: Mica (1 g) was dissolved in 6 ml of a KOH solution (1 M) and stirred in order to become a suspension. Then the mixture was stirred along with heating at 60 °C for 1 h. Afterwards, nickel acetate (3 ml, 1 M) was added to the resulting mixture and stirred along with heating at 60 °C for another 1 h. After completion of the reaction, the mixture was cooled to room temperature, filtered and washed with cold water twice to obtain the pigment powder after air drying.

Method 3: Mica (1 g) and NaOH (0.36 g) were physically combined and heated in an electric furnace until the mixture melted. Afterwards, 0.48 g of the transition metal salt was added and the mixture was heated at 400 °C for 10 min. The resulting mixture was cooled to room temperature and dissolved in 100 ml of water and filtered. The color pigment was washed with cold water and dried in air to afford the pigment powder.

2.3. Extrusion of pearl pigments

Polypropylene (3 g) was heated in an oven up to 180 °C (12 h) and then 10 % (w/w) of the nickel pearlescent pigment (from method 1) was added and mixed physically. The mixture was extruded as a shiny brown wire in the extrusion apparatus.

3. Results and discussion

The selected mica for this work is biotite which has been characterized by the X-ray diffraction analysis. The formula for biotite is $K(Mg/Fe)_3(A1Si_3O_{10})$ $(OH)_2$, and this is confirmed by XRF.

The interference of colors was obtained by coating minuscule mica plates with metal oxides [18]. Based on the angular dependence of the interference color one of the pearlescent pigments shows a few degrees of color shift. The effect of the pigments on mica is typically produced by the deposition of the metal oxide layers on the mica surface in an aqueous suspension followed by a calcination process. The interference color of these pigments is dependent on the thickness of the metal oxide layer. Therefore, the thickness control is one of the most important factors for the reproducible manufacturing of the metal oxide-mica pigments. When these pearl pigments are orientated parallel to the surface of the substrate within a transparent medium, the incident light to each pigment plate is regularly reflected and the optimum pearl luster effect is achieved (Figure 1) [19].

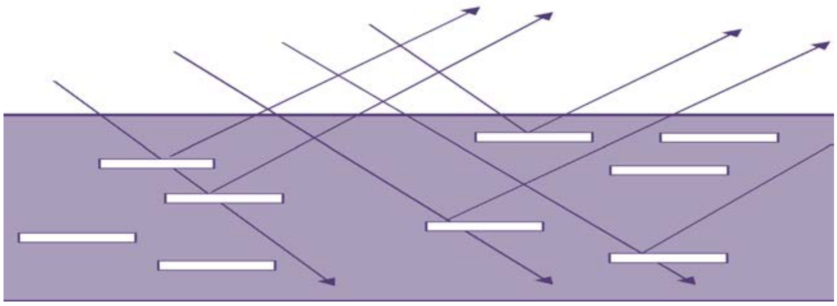


Figure 1. Regular multiple reflections.

The synthesized pigments were prepared via three distinct methods and in good yields. The related results are summarized in Table 1. From Table 1, it is clear that the quantity and quality of pigments produced by Methods 1 and 2 were approximately the same. Hence to make commercial savings, Method 1 was recommended for the preparation of metallic pearl pigments, and also, mica was known as the best support for the preparation of pearlescent pigments by these methods. The produced pearlescent pigment had a black color according to Method 3, because hydrated molecules omit water from their structures and convert to black oxides.

Table 1

Yields of different methods for the pearlescent pigments preparation.

Pearl pigment	Support	Method	Alkaline solution	Temperature (°C)	Color	Yield %
Ni (II)	Mica	1	NaOH	25	Shiny green	94
Ni (II)	TiO_2	1	NaOH	25	Opaque green	83
Ni (II)	Mica/TiO_2	1	NaOH	25	Opaque green	87
Ni (II)	$(NH_4)_2MoO_4$	1	NaOH	25	Opaque green	80
Ni (II)	Mica	2	KOH	60	Shiny green	93
Ni (II)	Mica	3	NaOH	400	Black	75

Figure 2 is the representative micrograph of the same sample showing the high reflectivity of pearl pigments. As shown in Figure 2, the support mica flakes were coated with thin and shiny colored layers of transition metal oxides or hydroxides. As seen in Figure 2F, the black minuscule of pigments was produced because of the elimination of water from hydrated molecules and the conversion of those molecules to oxides [20]. The extrusion of polypropylene with nickel/mica pearlescent pigments produced shiny green polymer wires (Figure 3).

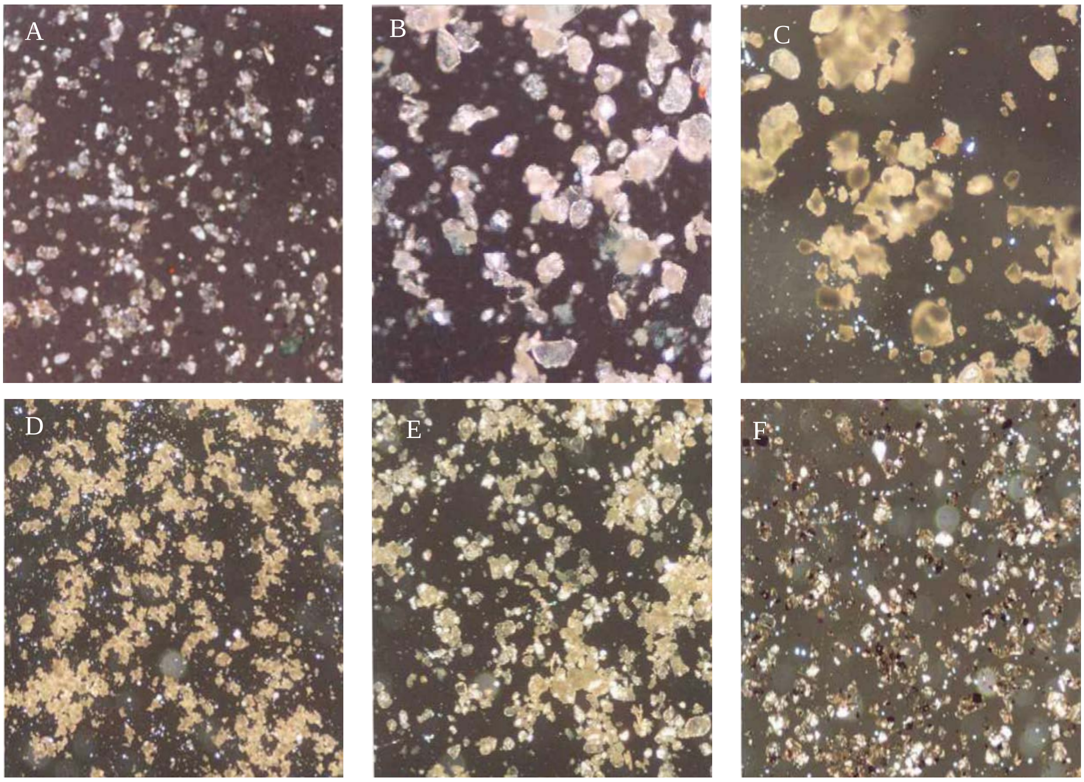


Figure 2. Representative micrograph of selected pearl pigments (A) Ni/mica pearl pigments prepared by method 1 (magnification*100), (B) Ni/mica pearl pigments prepared by method 1 (magnification*40), (C) Ni/mica-TiO_2 pearl pigments prepared by method 1 (magnification*40), (D) Ni/ TiO_2 pearl pigments prepared by method 1 (magnification*100), (E) Ni/mica pearl pigments prepared by method 2 (magnification*40) and (F) Ni/mica pearl pigments prepared by method 3 (magnification*40).

Figure 3. Extrusion of polypropylene with nickel pigments.

3.1. XRD analysis of nickel pearlescent pigments

The XRD patterns of the particles used as substrates in this study are presented in Figure 4. After comparing the selected mica XRD pattern with the types of mica XRD, it was revealed that the selected mica has had the biotite structure. The color of the selected mica is light, which is not high in iron (II) and (III) ions. Biotite crystals are seen as pseudo hexagonal plates. An interesting feature of the biotite is its high coefficient of failure compared to those of other types of Mica.

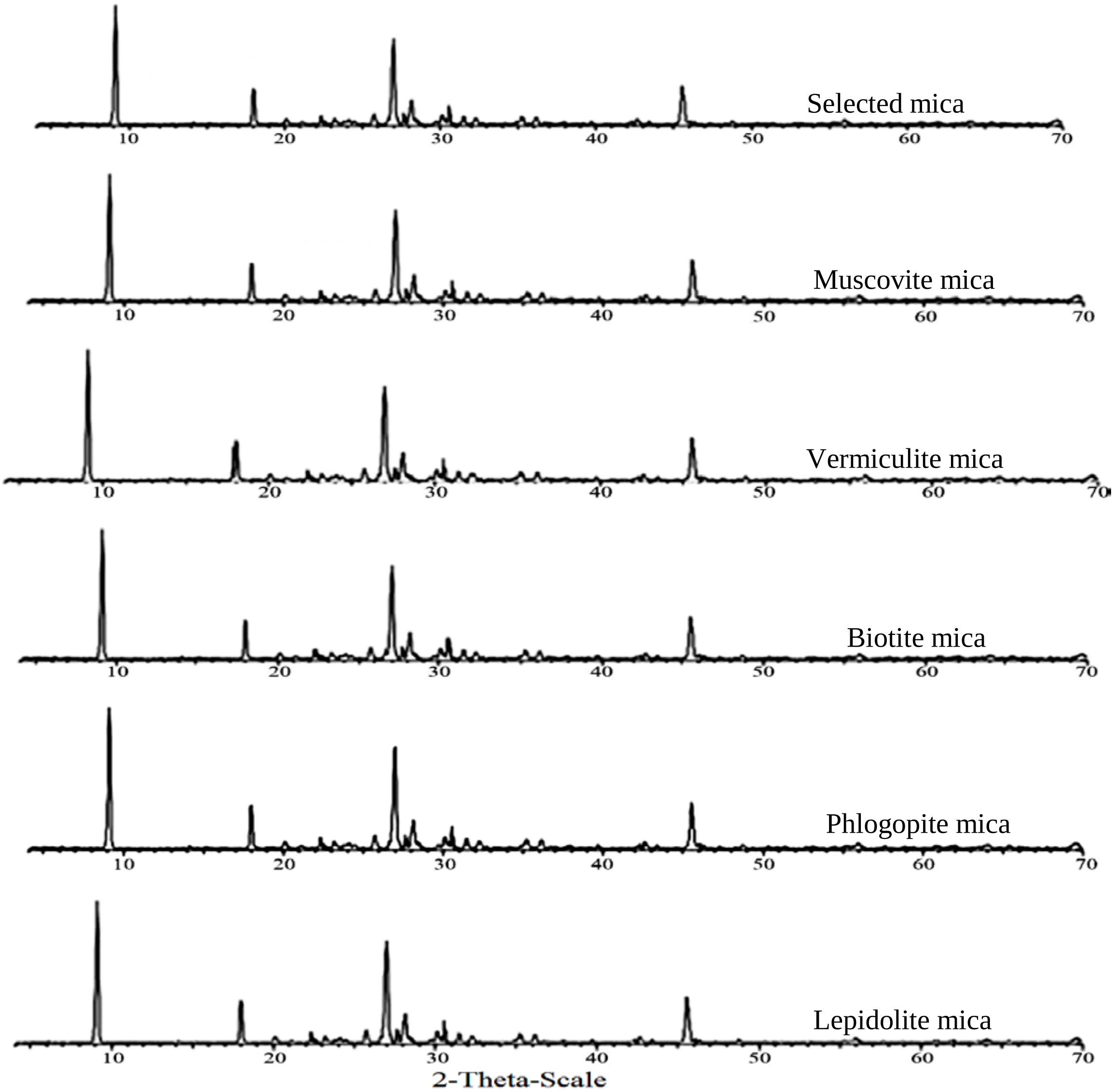
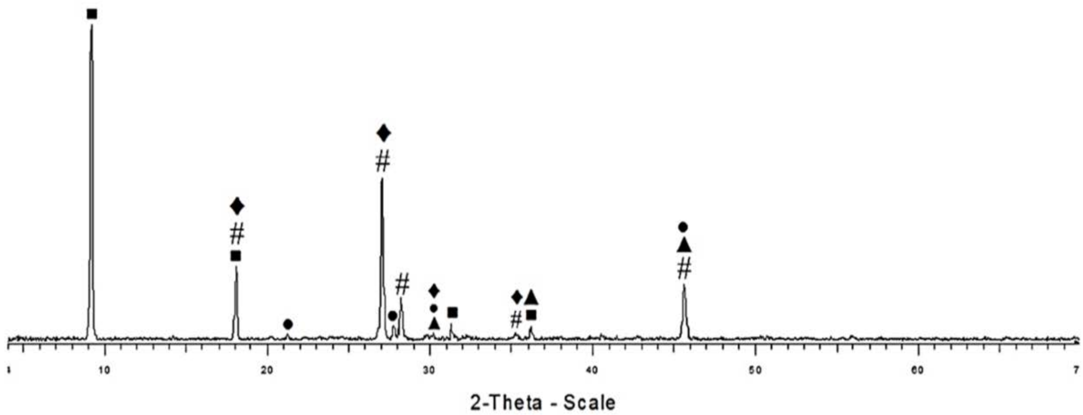


Figure 4. Comparison of the selected mica XRD pattern with the types of mica XRD.

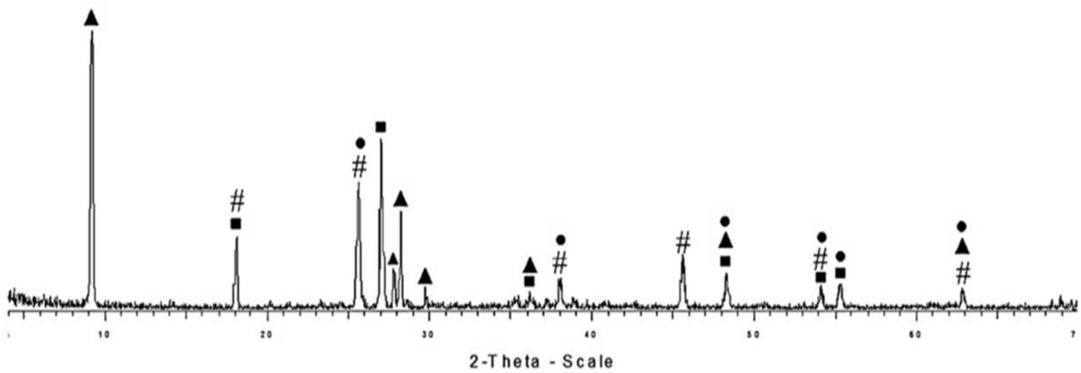
The XRD patterns for nickel pearlescent pigment are shown in Figures 5 and 6. The pearl pigments were clearly crystalline and the XRD patterns of the Ni/mica and the Ni/mica/TiO_2 pigments showed that the green pearlescent pigments contained metal oxides, that were deposited on the surface of mica and titania. As it was shown in Figure 5, the actual phases of Ni/mica pigments were Na_5NiO_4 (Orthorhombic), $NiClO_43H_2O$, $NiCl_2$ (Rhombohedral), $NaClO_2$ and $NaClO_3$ (Cubic). The XRD measurement of the Ni/mica pigment powder exhibited diffraction pattern characteristics of the Na_5NiO_4 orthorhombic structure with pronounced 9, 18, 31.5 and 36 peaks (Figure 5). The position of the peaks obtained at (18, 27, 28.5, 35.5 and 45.5), (30, 36 and 45.5), (21.5, 27.5, 30 and 45.5) and (18, 27, 30 and 35.5) was considered to contribute to the phase of

$NiClO_43H_2O$, $NiCl_2$ (Rhombohedral), $NaClO_2$ and $NaClO_3$ (Cubic) respectively (Figure 5). The XRD pattern of Ni/mica/TiO_2 pigments is shown in Figure 6. In Figure 6, the position of the peaks obtained at (18, 27, 36, 48.5, 54 and, 55.5), (18, 25.5, 38, 45.5, 54 and 63), (9, 27.5, 28.5, 30, 36, 48.5 and 63) and (25.5, 38, 48.5, 54, 55.5 and 63) are considered to contribute to the phase of FeMgTiO, $Fe_2NiTi_3O_{10}$ (Orthorhombic), $K(MgAl)_2Si_3AlO_{10}(OH)_2$ and $Al_4Ti_2SiO_{12}$ (Tetragonal) respectively. This evidence indicates that the specified layer of $NiCl_2$ has been coated on the mica surface.



■	Na_5NiO_4 (Orthorhombic)	2θ: 9, 18, 31.5, 36
#	$NiClO_43H_2O$	2θ: 18, 27, 28.5, 35.5, 45.5
▲	$NiCl_2$ (Rhombohedral)	2θ: 30, 36, 45.5
●	$NaClO_2$	2θ: 21.5, 27.5, 30, 45.5
♦	$NaClO_3$ (Cubic)	2θ: 18, 27, 30, 35.5

Figure 5. XRD patterns of Ni/mica pigments.



■	FeMgTiO	2θ: 18, 27, 36, 48.5, 54, 55.5
#	$Fe_2NiTi_3O_{10}$ (Orthorhombic)	2θ: 18, 25.5, 38, 45.5, 54 and 63
▲	$K(MgAl)_2Si_3AlO_{10}(OH)_2$	2θ: 9, 27.5, 28.5, 30, 36, 48.5, 63
●	$Al_4Ti_2SiO_{12}$ (Tetragonal)	2θ: 25.5, 38, 48.5, 54, 55.5, 63

Figure 6. XRD patterns of Ni/mica/TiO_2 pigments.

3.2. XRF analysis of the nickel pearlescent pigments

The chemical composition of biotite was $K(Mg/Fe)_3(AlSi_3O_{10})$ $(OH)_2$ which was confirmed by XRF. The data of the XRF analysis of Ni/mica pearl pigments is presented in Table 2.

Table 2
XRF analysis data for Ni/mica pearl pigments.

Pearl Pigment	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**
Ni-Mica	0.894	0.277	20.025	32.474	0.042	0.953
Pearl Pigment	Cl	K_2O	CaO	TiO_2	Fe_2O_3	NiO
Ni-Mica	2.251	11.766	3.029	-	1.892	8.823

The XRF data showed that mica contained the elements of K, Cl, Ca, Mg, Al, Si, Fe. The XRF analysis also shows that the nickel compound is layered well on the mica at 8.823 %. The pearl pigments contained 0.894 (%) of Na_2O, 0.277 (%) of MgO, 20.025 (%) of Al_2O_3, 32.474 (%) of SiO_2, 0.042 (%) of P_2O_5, 0.953 (%) of SO_3, 11.766 (%) of K_2O, 1.892 (%) of Fe_2O_3, and 8.823 (%) of NiO after washing and drying operations.

3.3. TGA and DSC analyses for Ni/mica pigments

Differential scanning calorimetry (DSC) and thermo-gravimetry (TG) measurements have been employed in this study in order to verify the bonds and composition of prepared compounds. Thermal decomposition curves of the pearlescent pigments are illustrated in Figure 7. The two prominent changes in the TGA curves, corresponding to the two peaks on the DTG curves, indicated that the thermal decomposition of the nickel pigments consisted of a two-step process. This analysis shows two weight losses even up to 49 % in higher tempratures as a result of the evaporated gas and moisture, such as HCl and H_2O. It can be concluded that weight losses have been taken place in 2 steps. It is assumed that the endothermic weight losses below 220 °C (170-220) is due to the removal of adsorbed water, while the second peak at 220–500 °C can be assigned to the dehydration of the pigments. In the DSC analysis, the peak at 90 °C is related to 16 percent of endothermic weight losses because of the humidity reduction. In addition, the peak at 302 °C corresponds to 33 % of endothermic weight losses because of the dehydration of the pigments. The TGA/DSC curves prove that the pigments could be stable at up to 200 °C.

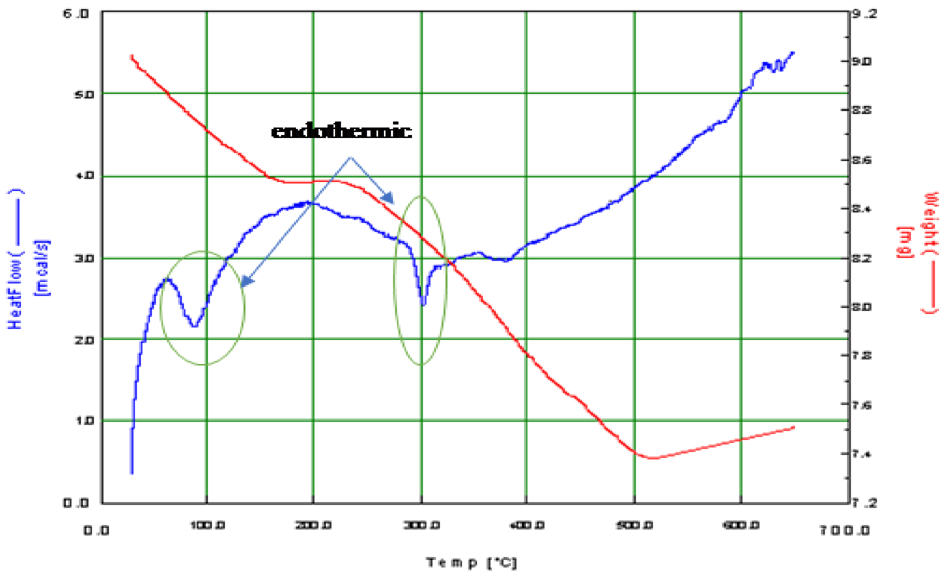


Figure 7. TGA/DSC analysis for Ni/mica pigments.

4. Conclusions

Several metallic pearl pigments were prepared by novel methods and characterized by TGA/DSC, XRF and XRD techniques. These pigments have a good chemical resistance and pearl luster effects. By coating minuscule mica, titania or mica/titania flakes, the different colors were obtained. According to the XRD analysis, the selected mica was biotite. The formula of biotite was $K(Mg/Fe)_3(A1Si_3O_{10})(OH)_2$ which was confirmed by XRF. An interesting feature of biotite is its high refractive index compared to those of other types of mica. XRD patterns of the Ni/mica pigments and the Ni/mica-TiO_2 pigments showed that the green pearlescent pigments contained nickel oxide and nickel titanium oxide that covered the mica surface. By comparing the XRD pattern of synthesized pigments with the mica base pattern, it is clear that the structure of the support does not change due to the layering on these bases. The chemical composition of the colored layers on the base is fully characterized by XRD. The XRF data proved that the mica contained K, Cl, Ca, Mg, Al, Si, Fe compounds. The XRF analysis also shows that the nickel compound is layered well on the mica at 8.823 %. The quantity and quality of the produced pigments by methods 1 and 2 were approximately the same. Consequently, to make commercial savings, method 1 was recommended for the preparation of the metallic pearl pigments and mica was known as the best support for the production of the pearlescent pigments by the introduced method. The melting method produced a black pigment because of omitting water from molecular structures of nickel pigments which converted it to the black oxides. The TGA/DSC curve displayed that the pigments were stable at up to 200 °C. Based on the results the quality of the synthesized pigments in this study is suitable enough, so that the extruding of polypropylene with these pigments creates a colored metallic tube. These pigments are easily spread in a variety of molten polymers and produce a uniform and brilliant color.

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