Synthesis and Characterization of Red Pearlescent Pigments Based on Muscovite and Zirconia-Nanoencapsulated Hematite

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1. Introduction
Mica is a general name for a group of complex hydrous potassium–aluminum silicate minerals that differ in chemical composition; examples are biotite, lepidolite, muscovite and vermiculite.

Mica has a low expansion coefficient, high dielectric strength, good electrical resistance, a uniform dielectric constant and high capacitance stability, which was known as one of the best electrical and thermal insulators. The iron content determines its color. Muscovite is generally grey, green, or brown; biotite is brown or black, lepidolite is pink or green, muscovite is light brown to yellow and vermiculite is brown. Among mica varieties, muscovite has the greatest commercial value and is the mica that is ground and pulverized into pigment grade.

One of the most important applications of mica is pearlescent (luster, nacreous) pigments [1–3], which consist of transparent mica flakes coated on all sides with a thin layer of metal oxide, mostly titanium dioxide. The presence of a highly refractive and reflective surface layer covering the less refractive support material results in a significant pearlescent effect and provides colors resulting from light interference.

A pearlescent pigment is a kind of pigment showing a pearlescent-shine due to angle-dependent optical effects deriving from alternating transparent layers with different refractive indices [4]. The most widely used pigments of this type consist of mica platelets coated with titanium dioxide (and sometimes other transition metal oxides) and their unique pearlescent effect occurs because the
transparent mica particles allow a portion of the incident light to be transmitted. When this transmitted light meets boundary surfaces with different refractive indices, a portion of the light is reflected. The total reflected light is made up of portions that have travelled on different paths producing optical interference [5, 6]. This lustre effect is also influenced by the mica particle size, so that the coarser is the platelet (e.g., >50 mm) the stronger is its shine; the opposite causes a satin appearance [4, 5].

Iron oxide-coated mica pigments are thermally stable. Furthermore, they are non-combustible and not self-igniting, do not conduct electricity and are innocuous to human health. For these reasons, mica-based pearlescent pigments can be used in nearly all thermoplastics, cosmetics, food packaging, children toys, paints, and automobiles coating. These pigments can be also utilized for security purposes, since their angle-dependent optical effects cannot be easily counterfeited with copier machines or photographic techniques, so fostering their use on banknotes in many countries [7].

The peculiar characteristics of mica coated pigments, such as the illusion of optical depth or the eye catching effect, are highly interesting also in ceramic decoration, as they cannot be reproduced otherwise with current ceramic pigments. In particular, the possibility to get a luster effect, replacing precious metals, has been recently appraised in ceramic productions fired at low temperature [8]. On the other hand, among synthetic ceramic pigments with lustre effect, there is a restricted choice for colored shade, in fact just gold and silver shade could be possible to apply current pearlescent pigments into glassy coatings preserving their optical appearance or third fire decoration and other low temperature ceramics. Nowadays, the ceramic industry is continuously looking for new materials that are able to impart some innovative aesthetic effects in decorated wares, especially wall and floor tiles or tableware [4, 9].

Hematite pigments have a long history as red/orange pigment and can use for ceramic application by encapsulation. Hematite as a natural and non toxic red ceramic pigment has been known since prehistoric times, it is also plenty and cheap, therefore hematite is the best choice for coating mica in order to obtain red lustre effect [10-12]. But no data are available in the literature. Previous studies concern just the utilization of mica [4].

Intensively colored pigments based on mica particles coated with color oxides of metals other than Ti have been much less studied. Junru [13] prepared cobalt blue mica coated titania pearlescent pigment from solution Co(NO₃)₂.6H₂O, Al(NO₃)₃,9H₂O, Na₂SO₄ and urea. However, intensively colored mica pigments and pigments with particle size above 100 mm (for special decorative applications) cannot be prepared using the method described [14]. S’ tengl [14] prepared colored mica pigments based on mica flakes covered with surface oxide-hydroxide layer of different metals, such as Ti, Cr, Fe, Al, Co, Ni, Zn and Cu by homogeneous precipitation of metal sulphates, but did not describe details and effect of layer morphology on the obtained pearlescent shade by the GonioSpectrophotometer.

The pigments based on mica coated have been tested for their use in various applications successfully, such as organic coatings, plastics, glasses, ceramics and paper. α-Fe₂O₃ exhibited similar properties to the MIOX pigments based on mineral specularite (lamellar form of α-Fe₂O₃) used for barrier type corrosion protection of metal surfaces [14].

In this paper, preparation of intensively red colored hematite on muscovite particles is described based on the nano hematite in situ formed in aqueous media in the presence of muscovite particles and zirconium chloride. The technological characterization, microstructure and thermal stability of pearlescent pigments have been assessed by FT-IR analysis, evaluating colorimetric parameters, phase composition and surface microstructure.

2. Experimental

2.1. Synthesis of red colored mica pigment

The preparation of surface-treated muscovite was performed using controlled homogeneous hydrolysis, in which a mixture of iron oxides-hydroxides nano encapsulated in zirconium oxide is coprecipitated onto the lamellar particle surface [9-11]. Table 1 shows chemical composition of applied Muscovite.

12.5 g of muscovite was suspended in 500 cc of deionized water, iron sulfate; zirconium chloride and urea were added to the mixture which was heated to 80°C. The change in pH was continuously monitored. The synthesis was completed after reaching pH=7. The final composition would be X(ZrO₂-0.5 Fe₂O₃) muscovite; therefore, the amount of the raw materials was calculated according to the above formula. The effect of X value in the range of 0.5 and 1.5 was also studied.

The reaction completion was shown by the release of ammonia developed in the reactor. The mixture was then
kept in the reactor under continuous stirring at room temperature. The product was obtained by decantation, washing, filtration and drying at 110 °C. The dry pigment was annealed at 800 °C for 2 h.

### Table 1: Chemical analysis of the muscovite by X-ray fluorescence.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>% in muscovite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>46.835</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>36.496</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.271</td>
</tr>
<tr>
<td>MgO</td>
<td>0.698</td>
</tr>
<tr>
<td>K₂O</td>
<td>11.36</td>
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<tr>
<td>Na₂O</td>
<td>0.664</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.917</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>0.237</td>
</tr>
<tr>
<td>Rb</td>
<td>0.043</td>
</tr>
<tr>
<td>Sr</td>
<td>-</td>
</tr>
<tr>
<td>LOI</td>
<td>4.45</td>
</tr>
</tbody>
</table>

### 2.2. Characterization methods

The spectral reflectance of the pressed powder of the colored mica was measured using a GretagMacbeth GonioSpectrophotometer Color-Eye741GL. L*a*b* color parameters have been measured following the CIE (Commission Internationale de l’Eclairage) colorimetric method. In this method, L* is the lightness axis (from black (0) to white (100)), a* is the green (−) to red (+) axis, and b* is the blue (−) to yellow (+) axis.

The microstructure studies were performed using a SEM Leo 1455 VP microscope equipped with SE (secondary electron) detector and backscattered. FT-IR analysis was carried out using a Thermo Nicolet. To characterize the crystalline phases in the raw and the annealed samples, X-ray diffraction patterns were collected using a conventional powder technique in a Siemens Diffractometer Siemens (D500 mod) employing Cu Ka Ni-filtered radiation.

### 3. Results and discussion

It is known [14] that upon heating to 80-100 °C in water, urea decomposes and produces ammonia and carbon dioxide. In the context of the mica pigment preparation method used here, due to the action of the urea decomposition products, the pH of the solution increases slowly and homogeneously throughout the whole solution and causes hydrolysis of the presenting metal ion. In comparison with heterogeneous precipitation, when the neutralizing agent, iron and zirconium ions solution are mixed, the hydrolysis process occurs at high speed, while the homogeneous hydrolysis is several orders slower. As such, the hydrolysis produced particles can better develop a crystal structure. The gradual increase of pH results in the nucleation and growth of nanosize particles of the solid hydrolysis products. Depending on the reaction conditions, these nanoparticles either agglomerate into spherical clusters or can be deposited onto the surface of a suitable substrate present in the reaction mixture [14-15].

### 3.1. FT-IR analyses

The Figure 1 shows IR spectra of the raw and the heat treated sample with X= 1.5.

![Figure 1: IR spectra of the (a) raw and (b) heat treated sample with X= 1.5.](image-url)
When the prepared particles are dried at 110°C without heat treatment, the strong band at about 1100 cm\(^{-1}\) is related to the residual organic urea. However, the intensity of these bands decreases with heat treatment temperature in the same annealed sample.

The broad absorption peak appearing near 3400 cm\(^{-1}\) relates to a stretching vibration of O-H group. At 1620 cm\(^{-1}\), a band assigned to water also appears. The OH band intensities show a significant decrease in the case of heat treatment at high temperature.

It is reported that the physisorbed water is easily removed from the surface but the decrease in the OH band intensities bonded to muscovite may be attributed to the OH groups produced by a dehydroxylation of its surface.

Si-O-Si bonds appeared in the range of 500-600 cm\(^{-1}\) as the result of muscovite structure. At a fixed X value, the sharp peak at 450 cm\(^{-1}\) appears after annealing is related to hematite crystallization. It is considered that after heat treatment, hydrolysis and condensation are relatively slow and the peaks at about 1000-1100 cm\(^{-1}\) are related to organic groups [16].

### 3.2. Thermal evolution of crystalline phases by XRD analysis

The XRD patterns of samples with X= 0.5 show that raw and annealed samples are approximately similar because the amount of metal oxides in samples with X= 0.5 are smaller than that of detected by XRD. In other words, the detection of inorganic phases by XRD depends on the instrument data sheet and the chemical composition. For example, Figure 2 shows XRD pattern of raw sample with X= 1.5 and Figure 3 is related to the same sample after annealing. For X= 1.5, the raw sample show muscovite peaks and some amorphous area.

![Figure 2: XRD pattern of sample raw sample with X= 1.5.](image)

![Figure 3: XRD pattern of annealed sample with X= 1.5 muscovite.](image)
Therefore, the raw reacted ions are not crystallite. The same sample annealed at 800°C contains crystalline phases (hematite, baddeleyite and tetragonal zirconia) whereas raw samples were amorphous.

3.3. Colorimetric analysis of samples by CIElab values

The color shade of the final pigment depends on the granularity and the amount of the hematite deposit [14]. The prepared pearlescent pigments with X= 0.5 show dark gold shade and the increasing of the X value results in red pearlescent shade.

Table 2 is color scheme for prepared red pearlescent pigments (in system CIE L*a*b) at different X values. Therefore, various shades from gold to red obtained depending on the mole ratio or weight percent of the nano encapsulated hematite.

3.4. Microstructure analysis of samples by SEM techniques

Figures 4 and 5 show SEM micrographs of the annealed samples with X= 0.5 and 1.5, respectively, obtained by secondary detectors at different magnifications. There were some very fine white dots smaller than 50 nm in Figure 4(b), the amount of which is very low, therefore they are not clustered on the surface of the mica and as can be seen at lower magnification, the other irregular grains are fine particles of mica ore.

The pearlescent pigment consists of well distinguishable spherical nanoparticles, covering the surface of the muscovite mica.

The diameter of the spherical nanoparticles is equal or less than about 50 nanometer in Figure 4, but it increases to 100 nm in the second sample in Figure 5. It seems that higher X value up to 1.5 may control the size of the nanoparticles and improves their distribution. The nanoparticles are homogeneous and there are no signs of peeling.

Table 2: Color scheme for prepared red and gold pearl pigments (in system CIE L*a*b) by Illum D65.

<table>
<thead>
<tr>
<th>X value</th>
<th>Angle</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>C*</th>
<th>h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>20°</td>
<td>48.38</td>
<td>11.95</td>
<td>11.28</td>
<td>16.43</td>
<td>43.37</td>
</tr>
<tr>
<td>1.5</td>
<td>45°</td>
<td>38.50</td>
<td>16.69</td>
<td>15.40</td>
<td>22.71</td>
<td>42.69</td>
</tr>
<tr>
<td>1.5</td>
<td>75°</td>
<td>38.92</td>
<td>20.69</td>
<td>19.27</td>
<td>28.27</td>
<td>42.97</td>
</tr>
<tr>
<td>1.5</td>
<td>110°</td>
<td>40.18</td>
<td>22.97</td>
<td>21.43</td>
<td>31.42</td>
<td>43.01</td>
</tr>
<tr>
<td>0.5</td>
<td>20°</td>
<td>99.107</td>
<td>3.964</td>
<td>17.155</td>
<td>17.607</td>
<td>76.99</td>
</tr>
<tr>
<td>0.5</td>
<td>45°</td>
<td>59.753</td>
<td>6.192</td>
<td>18.644</td>
<td>19.645</td>
<td>71.629</td>
</tr>
<tr>
<td>0.5</td>
<td>75°</td>
<td>48.494</td>
<td>8.069</td>
<td>20.537</td>
<td>22.065</td>
<td>68.55</td>
</tr>
<tr>
<td>0.5</td>
<td>110°</td>
<td>48.059</td>
<td>8.56</td>
<td>21.846</td>
<td>23.463</td>
<td>68.602</td>
</tr>
</tbody>
</table>

Figure 4: SEM micrographs of annealed sample with X= 0.5 by secondary detector at different magnifications.
The amount of nanoparticles precipitated outside the mica surface is not significant. No destruction or sintering of the mica particles was observed during the annealing process, except the color changes due to the crystallization of the nano hematite.

4. Conclusions
In order to prepare red and gold ecologically friendly pearlescent pigments by co-precipitation process, nano hematite encapsulated particles were formed in situ on muscovite flakes. FT-IR analysis, X-ray diffraction patterns, Gonio spectrophotometer and scanning electron microscopy results indicate that nano hematite particles have covered the muscovite in order to produce gold and red pearlescent pigment. The pearlescent pigment consists of well distinguishable spherical nanoparticles of hematite and zirconia in monolithic and tetragonal structures, covering the surface of the muscovite mica. Gold pearlescent pigment based on muscovite has been obtained by controlling the amount and the particle size of nano spherical hematite. Various shades from gold to red were obtained depending on the mole ratio or weight percent of the nano hematite.

5. References


