Synthesis of novel red phosphate pigments from manganese carbonate to imitate natrophilite

(Síntese de novos pigmentos de fosfato vermelho de carbonato de manganês como imitação da natrofilita)

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Abstract

A novel red pigment, sodium manganese phosphate (NaMnPO4), imitating natrophilite, was synthesized from manganese carbonate by heating under various conditions. The powders obtained were investigated by X-ray diffraction (XRD) analysis, infrared spectroscopy, ultraviolet-visible reflectance spectroscopy, and L*a*b* color space. Samples synthesized at 500-800 °C presented XRD patterns associated with NaMnPO4. By heating at a higher temperature, the samples exhibited lighter color. The sample synthesized at 700 °C indicated the highest a* value. Furthermore, the effects of varying relative amounts of constituents were also studied. The temperature and period of heating, volume of water, and phosphate content affected the color phase of the pigments.

Keywords: red pigment, natural ores, phosphate materials.

INTRODUCTION

The use of harmful metals is being restricted worldwide by various government regulations in an attempt to reduce and control the environment pollution. However, the lack of alternatives necessitates the use of materials containing harmful metals in many fields [1, 2]. For example, inorganic color pigments with metals such as mercury, cadmium, and lead exhibit good properties, including high stability against radiation, heat resistance, coloring visibility, and low cost [3-5]. In addition, because of their low coloring and opacity, oxide pigments are not suitable for incorporation in paint and plastics [6]. Sulfate and nitrate pigments have lower heat resistance than oxide pigments and also require harmful and/or combustible gas to synthesize. Furthermore, it is difficult to obtain sulfide and nitrate pigments with repeatability [7, 8]. Therefore, novel inorganic pigments with suitable properties and facile production methods are demanded.

Several kinds of inorganic red pigments are available for use, e.g., red iron oxide, red lead, cadmium red, vermilion, and cinnabar [9-12]. However, they all suffer from several disadvantages. For instance, red iron oxide exhibits only limited colorfulness, while other pigments contain harmful metals such as lead, cadmium, and mercury. Therefore, a novel red pigment that is economical and does not contain any harmful metals is required. We focus on the natural ore natrophilite (NaMnPO4), because it contains low-toxicity metals [13, 14]. Natural ores have high stability against radiation and heat resistance. Furthermore, they exist in solid phase, which allows applications in plastics, paint, ceramics, etc. Natrophilite contains bivalent manganese ion. The valence of manganese is important to prepare these novel red pigments. Here, novel inorganic red pigments NaMnPO4, imitating natrophilite, were synthesized by heating a mixture of raw materials. The products were subsequently analyzed.

EXPERIMENTAL

Samples (2 g) imitating natrophilite (NaMnPO4) were prepared as follows. Manganese carbonate was mixed with sodium dihydrogen phosphate through the following
reaction:

\[
\text{MnCO}_3 + \text{NaH}_2\text{PO}_4 \rightarrow \text{NaMnPO}_4 + \text{CO}_2 + \text{H}_2\text{O} \quad (A)
\]

To improve the reaction, 5 mL water was added to the mixture and was left for 24 h. Subsequently, the mixture was heated between 400 and 800 °C for 1, 3, and 6 h. The volume of water was varied from 10 to 20 mL to determine its effect. To obtain the novel red pigment, similar compositions were studied through the following equations:

\[
2\text{NaH}_2\text{PO}_4 + 3\text{MnCO}_3 \rightarrow \text{Na}_6\text{Mn}_3(\text{PO}_4)_4 + 3\text{CO}_2 + 3\text{H}_2\text{O} \quad (B)
\]

\[
2\text{NaH}_2\text{PO}_4 + \text{MnCO}_3 \rightarrow \text{Na}_4\text{Mn}_2(\text{PO}_4)_2 + \text{CO}_2 + 2\text{H}_2\text{O} \quad (C)
\]

\[
\text{KH}_2\text{PO}_4 + \text{MnCO}_3 \rightarrow \text{K}_4\text{Mn}_3(\text{PO}_4)_2 + 3\text{CO}_2 + 3\text{H}_2\text{O} \quad (D)
\]

\[
2\text{KH}_2\text{PO}_4 + 2\text{MnCO}_3 \rightarrow \text{K}_6\text{Mn}_3(\text{PO}_4)_4 + 3\text{CO}_2 + 3\text{H}_2\text{O} \quad (E)
\]

\[
2\text{K}_2\text{HPO}_4 + \text{MnCO}_3 \rightarrow \text{K}_4\text{Mn}_3(\text{PO}_4)_2 + \text{CO}_2 + 3\text{H}_2\text{O} \quad (F)
\]

All chemicals were of commercial purity (Wako Chem. Ind., Osaka, Japan) and were used without further purification. The chemical compositions of these materials were determined by X-ray diffraction (XRD) analysis and infrared (IR) spectroscopy. The XRD patterns and IR spectra of the samples were recorded using an X-ray diffractometer (MiniFlex, Rigaku, Japan) with monochromatic CuKα radiation and an IR spectrometer (FT-IR 720, Horiba, Japan) using the KBr disk method, respectively. The color of the phosphate pigments was evaluated based on ultraviolet-visible (UV-vis) reflectance spectra (UV2100, Shimadzu, Japan; reference compound: BaSO_4). The color of the pigments was also described using a color analyzer (TES135 Plus, TES Electr. Electron., Taiwan). The L* value represents the whiteness of powder, in which 100 is white, while 0 is black. The a* value signifies the redness of the material, with positive (maximum +60) and negative (-60) values corresponding to red and green, respectively. The b* value denotes yellow intensity, in which positive (maximum +60) and negative (-60) values correspond to yellow and blue, respectively.

**RESULTS AND DISCUSSION**

*Imitated NaMnPO₄:* Fig. 1 shows the XRD patterns of the samples prepared at various temperatures. Samples heated at 500-800 °C indicated the peaks of NaMnPO₄. These peaks became narrow and evident on increasing the heating temperature. In contrast, the sample heated at 400 °C had ambiguous peaks. Therefore, the formation of NaMnPO₄ required heating at over 500 °C. Fig. 2 shows the IR spectra of the samples prepared at various temperatures. All samples had peaks at 560, 590, 610, 940, 1000, and 1060 cm⁻¹, corresponding to the phosphate anion. Samples

![Figure 1: XRD patterns of samples prepared at various temperatures (for 1 h, with 5 mL water): a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; and e) 800 °C.](example_image1.png)

![Figure 2: IR spectra of the samples prepared at: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; and e) 800 °C (for 1 h, with 5 mL water).](example_image2.png)
prepared at 500 and 600 °C contained small amounts of condensed phosphate indicated by a peak at 730 cm⁻¹, which was associated with P-O-P bonding [15]. However, heating at 700 °C removed this condensed phosphate.

Fig. 3 shows photographs of the samples prepared at various temperatures. The sample prepared at 400 °C resulted in a dark red powder. By heating at a higher temperature, the sample powder exhibited a lighter tone. The sample prepared at 800 °C resulted in yellowish dark red powder, different from other samples.

![Figure 3: Photographs of the samples prepared at: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; and e) 800 °C (for 1 h, with 5 mL water).](image)

Table I - Color of sample powders prepared under various conditions.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Water content (mL)</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>1</td>
<td>5</td>
<td>40.08</td>
<td>7.34</td>
<td>2.10</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
<td>5</td>
<td>42.32</td>
<td>8.18</td>
<td>1.60</td>
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<tr>
<td>600</td>
<td>1</td>
<td>5</td>
<td>44.96</td>
<td>8.48</td>
<td>5.26</td>
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<tr>
<td>700</td>
<td>1</td>
<td>5</td>
<td>46.82</td>
<td>10.07</td>
<td>5.30</td>
</tr>
<tr>
<td>800</td>
<td>1</td>
<td>5</td>
<td>49.91</td>
<td>7.55</td>
<td>7.87</td>
</tr>
<tr>
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</tr>
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<td>6</td>
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<tr>
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<td>1</td>
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<td>50.94</td>
<td>11.92</td>
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<td>20</td>
<td>42.94</td>
<td>12.99</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Fig. 4 shows the UV-vis reflectance spectra of the samples prepared at 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; and e) 800 °C (for 1 h, with 5 mL water). By heating at 700 °C for 3 and 6 h, high values of a* and low L* were obtained. In addition, a larger volume of water produced higher a* values. However, samples prepared with 20 mL water had a low L* value. The heating temperature, time, and volume of water affected the color phase of the phosphate powders.

![Figure 4: UV-vis reflectance spectra of the samples prepared at: a) 400 °C; b) 500 °C; c) 600 °C; d) 700 °C; and e) 800 °C (for 1 h, with 5 mL water).](image)

Other compositions: to obtain the novel red pigment, the effects of relative amounts of the constituents were also studied. High sodium and potassium ratios result in bright
CONCLUSIONS

Novel red phosphate pigments imitating natrophilite were obtained by heating a mixture of manganese carbonate with various phosphates. Samples prepared over 500 °C indicated an XRD pattern associated with NaMnPO$_4$. The sample powder color became light when heated at a higher temperature. The UV-vis reflectance spectra of the samples prepared at 500 and 600 °C had a peak at 660 nm. A high reflectance at over 660 nm was observed in the spectrum of the sample prepared at 700 °C. The suitable condition to obtain high L* (lightness) and a* (redness) values is heating of the sample prepared at 700 °C. The suitable condition to obtain high L* and a* values is heating of the sample prepared at 700 °C. The suitable condition to obtain high L* and a* values is heating of the sample prepared at 700 °C.

REFERENCES


(Rec. 22/05/2018, Ac. 13/07/2018)