SYNTHESIS OF NOVEL MANGANESE PHOSPHATE VIOLET PIGMENT

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Abstract: Novel violet pigments were synthesized from manganese oxide and phosphoric acid by heating at several temperatures. The obtained materials were investigated by X-ray diffraction analysis (XRD), infrared spectroscopy, X-ray photoelectron spectroscopy, ultraviolet–visible reflectance spectroscopy, and L*a*b* color space. Samples synthesized in this study did not show the XRD peak pattern for certain compounds. At P/Mn = 2/3 and 1/1, samples heated at 500 °C showed high a* value and low b* value, corresponding to violet color. On the other hand, at P/Mn = 2/1, the sample heated at 400 °C had the most violet powder.

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 fields1,2. 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 cost3-5. In addition, because of their low coloring and opacity, oxide pigments are not suitable for incorporating in paint and plastics6. Sulfate and nitride 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 nitride pigments with repeatability7,8. 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 cinnabar9-12. 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 metals13,14. 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.

In previous works, we try to obtain manganese phosphate red pigments by heating, however only brown pigments were obtained as a result15,16. Therefore, we synthesize the inorganic pigments by further changing the mixing conditions, a red pigment was not obtained, however a violet pigment could be obtained. In this paper, we report the preparation of this violet pigment.

EXPERIMENTAL

The 2 mL of phosphoric acid (14 mol/L) was diluted with 10 mL of water. Manganese dioxide was mixed with this phosphoric acid in the molar ratio of P/Mn = 2/3. This mixture was kept for 1 day under room temperature, and then heated at 300, 400, 500, 600, and 700°C for 1, 3, 6 hours. The ideal chemical equation was follows.

3MnO₂ + 2H₃PO₄ → Mn₃(PO₄)₂ + 3H₂O + 3/2O₂ (1)

This chemical reaction is related to the preparation method of NaMnPO₄ in the previous works15,16. Further, to obtain various kinds of pigments, we synthesized the materials at P/Mn = 1/1 and 2/1 in the same method. The expected chemical reactions are as follows.
\[ \text{MnO}_2 + \text{H}_3\text{PO}_4 \rightarrow \text{MnHPO}_4 + \text{H}_2\text{O} + 1/2\text{O}_2 \]  
\[ \text{(2)} \]
\[ \text{MnO}_2 + 3/2\text{H}_2\text{O} + 1/4\text{O}_2 \rightarrow \text{MnPO}_4 + 3/2\text{H}_2\text{O} + 1/4\text{O}_2 \]  
\[ \text{(3)} \]
\[ \text{MnO}_2 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Mn(HPO}_4)_2 + 2\text{H}_2\text{O} \]  
\[ \text{(4)} \]
\[ \text{MnO}_2 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Mn(HPO}_4)_2 + 2\text{H}_2\text{O} \]  
\[ \text{(5)} \]
\[ \text{MnO}_2 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Mn(HPO}_4)_2 + 2\text{H}_2\text{O} \]  
\[ \text{(6)} \]

All chemicals were of commercial purity (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) and were used without further purification.

The chemical compositions of these materials were estimated 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 Corp., Akishima, Japan) with monochromatic CuKα radiation and HORIBA FT-IR 720 (Horiba Ltd., Kyoto, Japan) using the KBr disk method, respectively. Furthermore, for the optimum material, the valence of manganese was evaluated by X-ray photoelectron spectroscopy (XPS, JPS-9010; JEOL Ltd., Akishima, Japan).

The color of the phosphate pigments was evaluated based on ultraviolet–visible (UV–Vis) reflectance spectra (UV2100; Shimadzu Corp., Kyoto, Japan) (reference compound: BaSO₄). The color of the pigments was also described using a TES135 plus color analyzer (TES Electrical Electronic Corp., Taipei, 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; +128) and negative (-128) values corresponding to red and green, respectively. The b* value denotes yellow intensity, in which positive (maximum; +128) and negative (-128) values correspond to yellow and blue, respectively.

RESULTS AND DISCUSSION

Samples synthesized in P/Mn = 2/3

Figure 1 shows the XRD patterns of the samples prepared at various temperatures. Samples heated at 300 °C and 400 °C showed the peaks of manganese dioxide, and samples heated at higher temperature showed unknown peaks. It can be judged that the temperature of the heating at 400 °C is too low because the raw material remains. Figure 2 shows the IR spectra of the samples prepared at various temperatures. Samples heated at 500 °C showed the absorption peaks at 925, 1050 and 1240 cm⁻¹. Samples heated at 300 °C and 400 °C had broad peaks, and their spectra were different from those of the samples heated above 500 °C. This tendency was the same as the result of XRD patterns.

Figure 3 shows the photographs of the samples prepared at various temperatures. Samples heated at 300 °C and 400 °C were a black powder due to the black color of the remaining manganese dioxide. Sample heated at 500 °C became violet powder, darkened when heated at 600 °C, and sample heated at 700 °C became yellowish.

![FIGURE 1 XRD patterns of samples prepared at various temperatures](image)

![FIGURE 2 IR spectra of samples prepared at various temperatures](image)
Figure 4 shows the UV-Vis reflectance spectra of the samples prepared at various temperatures. It can be seen that most of the samples have a small change in reflectance with respect to a change in wavelength and have little color. Among them, the reflectance of the sample heated at 500 °C varied with wavelength (Fig. 4(c)). This sample reflected light of violet wavelength (380-450 nm). It was also violet because it reflected light of blue wavelength (450-485 nm) and red wavelength (625-800 nm) and absorbed light of green wavelength (500-565 nm). Since this result had the same tendency as the compound containing trivalent manganese, it was considered that the sample heated at 500°C contained a large amount of trivalent manganese. On the other hand, in the sample heated to 700°C, the reflectance decreased as the wavelength became shorter (Fig. 4(e)). This change tended to be the same as the reflectance spectrum of divalent manganese compounds in previous papers. This sample was considered to include a large amount of divalent manganese.

Table 1 shows the L*a*b* values of samples prepared under various conditions. Sample heated at 500 °C indicated high a* value and low b* value, corresponding to violet color. Sample heated at 700 °C showed a high b* value, corresponding to yellow. In addition, we also examined samples with a long heating time at 500 °C, however the color of sample powder became unclear gray. In Table 1, the samples heated for 3 or 6 hours showed low a* values and b* values close to zero. Finally, at P/Mn = 2/3, the optimum condition to obtain a violet pigment was at 500 °C for 1 hour.

Samples synthesized in P/Mn = 1/1 and 2/1

At P/Mn = 2/3, there was some manganese dioxide.
FIGURE 6 XRD patterns of samples prepared at various temperatures (P/Mn = 2/1), (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C, \( \text{Mn}_2\text{P}_4\text{O}_{12} \).

FIGURE 7 Photographs of samples prepared at various temperatures (P/Mn = 1/1), (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C.

remaining without reaction, therefore, samples with a reduced manganese dioxide ratio were synthesized. Figures 5 and 6 show the XRD patterns of samples prepared at P/Mn = 1/1 and 2/1, respectively. The weak peaks of \( \text{Mn}_2\text{P}_2\text{O}_{7} \) were observed in XRD pattern of the samples prepared at P/Mn = 1/1 and then heated to 600ºC and 700ºC\(^{19}\). It was considered that \( \text{MnHPO}_4 \) formed by the equation (2) was dehydrated and condensed to form \( \text{Mn}_2\text{P}_2\text{O}_{7} \).

\[
2\text{MnHPO}_4 \rightarrow \text{Mn}_2\text{P}_2\text{O}_{7} + \text{H}_2\text{O} \quad (7)
\]

At P/Mn = 2/1, the XRD peak pattern of manganese (II) cyclo-tetraphosphate was observed by heating at 600°C and 700°C\(^{20}\). It was considered that \( \text{Mn(H}_2\text{PO}_4)_2 \) formed by the equation (6) was dehydrated and condensed to produce \( \text{Mn}_2\text{P}_4\text{O}_{12} \).

\[
2\text{Mn(H}_2\text{PO}_4)_2 \rightarrow \text{Mn}_2\text{P}_4\text{O}_{12} + 4\text{H}_2\text{O} \quad (8)
\]

In both compositions, the samples heated below 500 °C had unknown peaks or were amorphous.

Figure 7 shows the photographs of samples prepared at P/Mn = 1/1. Sample heated at 500°C became the most violet, and sample heated at 700 °C showed a yellowish tint. This change was the same as the samples heated in P/Mn = 2/3. Figure 8 shows the photographs of samples prepared at P/Mn = 2/1. Sample heated at 300 °C was viscous due to excess phosphoric acid. Samples heated at 400 °C became the most violet, and samples heated at 600 °C and 700 °C became a light colored powder.

Table 2 shows the \( \text{L}^*\text{a}^*\text{b}^* \) values of phosphate materials prepared in P/Mn = 1/1 and 2/1. In the material prepared in P/Mn = 1/1, sample heated at 500 °C showed the highest \( \text{a}^* \) value and the lowest \( \text{b}^* \) value. Sample heated at 700 °C showed a high \( \text{b}^* \) value, corresponding to a yellow tint. Among the samples prepared in P/Mn = 2/1, sample heated at 400 °C indicated the highest \( \text{a}^* \) and lowest \( \text{b}^* \) values.

TABLE 2 \( \text{L}^*\text{a}^*\text{b}^* \) values of sample powders synthesized at various conditions (P/Mn = 1/1 and 2/1)

| P/Mn | Temp. °C | \( \text{L}^* \) | \( \text{a}^* \) | \( \text{b}^* \) |
|------|----------|----------------|--------------|--------------|
| 1/1  | 300      | 37.44          | 6.35         | 2.02         |
| 1/1  | 400      | 35.65          | 6.04         | -2.60        |
| 1/1  | 500      | 47.72          | 7.32         | -7.30        |
| 1/1  | 600      | 34.35          | 4.03         | -1.79        |
| 1/1  | 700      | 39.63          | 3.41         | 5.41         |
| 2/1  | 300      | -              | -            | -            |
| 2/1  | 400      | 36.98          | 8.30         | -7.80        |
| 2/1  | 500      | 33.08          | 8.03         | -5.47        |
| 2/1  | 600      | 56.57          | 6.78         | -7.38        |
| 2/1  | 700      | 52.48          | 2.23         | 2.74         |

\( ^- \); unmeasurable
FIGURE 9 XPS spectra of samples, (a) Mn powder, (b) MnCO$_3$, (c) MnO$_2$, (d) sample prepared at P/Mn = 2/1 and then heated at 400ºC.

Samples heated at 600 ºC and 700 ºC showed relatively high L* value, which corresponded to light color.

Figure 9 shows the XPS spectrum of the optimum sample in this work. For comparison, the spectra of manganese powder (manganese: +0), manganese carbonate (+II), and manganese oxide (+IV) are shown. Since the manganese peak in the sample was wide and weak, it was found that various valences of manganese were mixed. However, samples showed the peaks of divalent manganese compounds in XRD patterns had lost the violet color. In addition, sample in which manganese (+ IV) dioxide, which is a raw material, remained, became close to black. It was considered necessary to form a trivalent manganese compound in order to obtain violet color.

CONCLUSION

Novel manganese phosphate violet pigments were obtained by heating a mixture of manganese dioxide and phosphoric acid at various temperatures. Samples synthesized in this study did not show the XRD peak pattern for certain compounds. At P/Mn = 2/3 and 1/1, samples heated at 500ºC showed high a* value and low b* value, corresponding to violet color. On the other hand, at P/Mn = 2/1, the sample heated at 400 ºC had the most violet powder. The violet color in this study is darker, and future research requires lightness.

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