Effect of SiO₂ and Al₂O₃ on the synthesis of Fe₂O₃ red pigment

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Fe₂O₃ red pigments, especially hematite particles have been widely utilized in many technologies, such as pigments, catalysts, coatings, flocculants, cosmetics, electronic materials and abrasives. There are many commercially available Fe₂O₃ powders for use as red pigment for Japanese porcelain enamel. However, the tone of red color of Fe₂O₃ pigments was strongly influenced by synthesized temperature. It was important that the color-stable pigments, which were not affected by morphology and dispersal behavior, were synthesized for use as thermally stable red pigments. The present work was to study the possibility of synthesizing red inorganic pigments by composite of Fe₂O₃, Al₂O₃ and SiO₂.

Key-words : Red pigment, Fe₂O₃, Al₂O₃, SiO₂, Spinel, Hematite, Corundum

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Inorganic pigments are excellent in terms of chemical and temperature stability, compared to organic pigments. However, the number of colors of inorganic pigments available is limited compared with those of organic pigments. In particular, very few colors of ceramic pigments are available.¹⁾

Many inorganic pigments are synthesized as a solid solution of a mother crystal with coloring transition metal oxides as chromophore. For instance, reddish ceramic pigments, such as chromium doped alumina pink pigments, which consist of little quantity of chromium doped into alumina (corundum) and zinc-aluminum spinel (granite), are prepared on the basis of the color of a ruby.²⁾

It is known that the color of a pigment can be changed by the addition of a very small amount of an additive.³⁾ This additive is generally a heavy metal.

Recently, the influence of heavy metals on the human body has been reported. Lead and cadmium are already regulated by food hygiene laws.

The heavy metal is hard to be generally drained in the outside the body. Therefore, users must be warned of the toxicity. For example, selenium red, which includes cadmium, is bright red in color. However, inhalation of the selenium compound included in it may cause poisoning symptoms. When using selenium red pigment, an isolated place as well as a mask and gloves are necessary. Furthermore, it must not be dumped into sewage.

From the viewpoint of workplace safety and protection of the environment, a safe pigment is needed.

Among the heavy metals, iron is the only safe metal.

Hematite⁴⁾ (Fe₂O₃) has been widely used for reddish ceramic pigments for a long time. However, the red color tone of Fe₂O₃ pigments is strongly influenced by thermal action. Thus, a study was conducted to identify the coloring mechanism in the synthesis of Fe₂O₃ pigments, and to obtain reddish ceramic pigments that are stable at high temperatures.

The chemical compositions of the pigments are shown in Table 1. The pigments were synthesized from Fe₂O₃ (95.0

Table 1. Chemical Compositions of Fe₂O₃-Al₂O₃ and Fe₂O₃-Al₂O₃-SiO₂ Pigments (molar ratio).

Sample No.	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂
F2A	2	1	0
FA	1	1	0
FA2	1	2	0
F2AS3	2	1	3
FAS2	1	1	2
FA2S3	1	2	3

mass%, Wako Pure Chemical Industries, Ltd.), high purity alumina (99.99 mass%, Taimei Chemicals Co., Ltd.), and SiO₂ (single product, Wako Pure Chemical Industries, Ltd.). The mixture of raw materials was wet-mixed by planetary ball milling for 20 min. After drying, the mixture was synthesized at 1250, 1300, 1350, and 1450°C for 30 min in air.

The pigments were kneaded with water-soluble synthetic resin paint (Washin), and painted on a transparent film. Reflectance spectra were measured in the wavelength range of 400 to 780 nm by a spectrophotometer (Color Analyzer TC-1800, Tokyo Denshoku). The reflectance was converted into absorbance by following the remission function, $f(R) = (1 - R)^2 / 2R$, where R is the reflectance.⁵⁾

The crystalline phases of the synthesized pigments were identified by powder X-ray diffractometry (XRD; Mac science Co., Ltd. MXP3).

Microstructures of the pigments were observed with a scanning electron microscope (SEM; Hitachi Ltd. S-2400).

Figure 1 shows the absorbance of the pigments. As-received Fe₂O₃ powder had high absorbance between 410 and 560 nm, and low absorbance between 580 and 780 nm. Its color was Cinnabar red.

Between 410 and 560 nm, the absorbance of the pigment

synthesized at 1250°C was lower than that synthesized at 1300°C. The absorbance from 580 to 780 nm tended to increase with an increase in Fe₂O₃ at all temperatures. High Fe₂O₃ content pigments turned blackish-red, and low Fe₂O₃ content one turned cinnabar red. The curves of the pigments synthesized at 1350 and 1450°C were almost flat, and their color was black or blackish red-brown. As the content of Fe₂O₃ in pigments synthesized at 1450°C increased, the curve of the spectra resembled the curve of Fe₃O₄ (spinel).⁶⁾ Therefore, the blackening of the pigments with a rise in the synthesized temperature and an increase in Fe₂O₃ content is considered to be caused by the generation of the spinel.

CIELAB L*a*b* of the FA2 pigments is shown in Table 2. FA2, whose composition is Fe₂O₃:Al₂O₃=33:67, showed the highest value of a* at all synthesis temperatures. The same result was obtained for all values of C*. Of all the pigments with a composition of Fe₂O₃:Al₂O₃=33:67, the pigment synthesized at 1300°C showed the highest value of a*.

In a preliminary experiment, we found that this composition was the most stable at all temperatures.

Fig. 1. Absorbance spectra of the pigments synthesized at (a) 1250, (b) 1300, (c) 1350, (d) 1450°C and as-received Fe₂O₃ and Fe₃O₄. The composition of FA2 is Fe₂O₃:Al₂O₃ = 1:2 (molar ratio).

Figure 2 shows the XRD patterns of FA2 and FA2S3 pigments synthesized at 1300°C. The FA2 pigment was composed of double phases of hematite solid solution and corundum solid solution. As a result, phase diagrams of Fe₂O₃-Al₂O₃⁷⁾ was obtained.

Spinel peaks were not detected, which may be because they were present in very small amounts. The fact that these pigments turned into a reddish cast when ground more finely suggested that some undetected particles may exist in the spinel.

As for the ratio of hematite solid solution and corundum solid solution, because it obeys the principle of leverage, it seemed that the difference in color was controlled by the ratio of the composition. The phase diagrams of Fe₂O₃-Al₂O₃ indicate almost the same amount of both hematite and corundum solid solutions in the FA2 pigment.

CIELAB L*a*b* of the Fe₂O₃-Al₂O₃, Fe₂O₃-Al₂O₃-SiO₂ and as-received Fe₂O₃ are shown in Table 3.

The pigment with a composition of Fe₂O₃:Al₂O₃=33:67 showed a higher value of a* than the pigments with no added SiO₂.

Figure 3 shows the absorbance spectra of Fe₂O₃-Al₂O₃-SiO₂ and Fe₂O₃-Al₂O₃ pigments synthesized at 1300°C, and as-received Fe₂O₃. These spectra resembled each other closely, but the absorbance at wavelengths between 580 and 780 nm was different. The value of a* was affected by these differences.

Table 2. CIELAB L*a*b* of FA2 Pigments Synthesized at 1250, 1300, 1350, and 1450°C Composition of FA2 is Fe₂O₃:Al₂O₃ = 1:2 (molar ratio)

Synthesized temperature	L*	a*	b*	C*
1,250°C	35.10	22.86	17.14	28.57
1,300 °C	30.56	24.37	16.34	29.34
1,350 °C	34.17	13.40	12.42	18.27
1,450 °C	22.90	6.210	3.780	7.27

Fig. 2. XRD patterns of Fe₂O₃-Al₂O₃ and Fe₂O₃-Al₂O₃-SiO₂ pigments synthesized at 1300°C. a) Fe₂O₃-Al₂O₃ (FA2), b) Fe₂O₃-Al₂O₃-SiO₂ (FA2S3)

The absorbance at wavelengths in the neighborhood of 580 nm caused the FA2S3 pigment to turn into a yellowish cast. This result agreed with the increase of the value of b^* .

The absorbance spectra of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ pigments resembled those of as-received Fe_2O_3 . Therefore, the absorbance at wavelengths in the neighborhood of 580 to 780 nm decreased, and the pigments turned into a reddish cast. Although this absorbance was controlled by the addition of Al_2O_3 , the influence of SiO_2 increased.

With the addition of Al_2O_3 in the pigments, the absorbance at the wavelengths from 400 to 560 nm decreased.

The absorbance at the wavelengths from 580 to 780 nm was controlled by the addition of SiO_2 to a coloring pigment. However, the effect was not similar to that of as-received Fe_2O_3 .

It was supposed that spinel generation was controlled by the addition of Al_2O_3 and SiO_2 .

On the other hand, the absorbance between 580 to 780 nm decreased with a decrease in the quantity of Fe_2O_3 .

It is not evident whether the cause of the color change was the addition of Fe_2O_3 , Al_2O_3 , or SiO_2 .

It is reasonable to suppose that the effect is due to a com-

bination of Fe_2O_3 , SiO_2 , and Al_2O_3 .

Figure 2 shows the XRD patterns of the $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ pigments synthesized at 1300°C . The pigments consisted of phases of hematite solid solution, corundum solid solution, quartz, and cristobalite. This result showed that SiO_2 and Al_2O_3 did not generate a new crystal.

Figure 4 shows the features of FA2 and FA2S3 pigments synthesized at 1300°C .

Elemental analysis by electron probe X-ray microanalysis (EPMA) revealed that small particles were present in the corundum solid solution, and slightly larger particles were present in hematite solid solution (Fig. 4a). The larger particles (Fig. 4b) were SiO_2 and the surrounding particles were present in a solid solution of corundum and hematite.

It is clear that the added SiO_2 did not form any crystal, such as mullite, and that the form of the solid solution of corundum and hematite was affected by the presence of SiO_2 .

With the addition of Al_2O_3 to Fe_2O_3 , the pigment showed stable color development when it was heated at a high temperature. The pigment became bright red when SiO_2 was

Table 3. CIELAB $L^*a^*b^*$ of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ Pigments and as-received Fe_2O_3

	L^*	a^*	b^*	C^*
As-received Fe_2O_3	33.79	29.13	21.07	35.95
F2A	24.68	18.63	10.88	21.57
FA	26.55	21.47	13.80	25.52
FA2	30.56	24.37	16.34	29.34
F2AS3	31.89	25.87	21.84	33.85
FAS2	32.82	28.12	25.37	37.87
FA2S3	36.72	28.97	28.48	40.62

Fig. 4. SEM photographs of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ synthesized at 1300°C . a) $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ (FA2), b) $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ (FA2S3)

Fig. 3. Absorbance spectra of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$, $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ synthesized at 1300°C and as-received Fe_2O_3 . a) $\text{Fe}_2\text{O}_3\text{:Al}_2\text{O}_3 = 2\text{:}1$, b) $\text{Fe}_2\text{O}_3\text{:Al}_2\text{O}_3 = 1\text{:}1$, c) $\text{Fe}_2\text{O}_3\text{:Al}_2\text{O}_3 = 1\text{:}2$
 -----: $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$, —: $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$,: as-received Fe_2O_3

added, and SiO₂ did not form any crystal.

With the addition of SiO₂, the color became redder. However, the data obtained was insufficient to discuss the behavior of the SiO₂ added to these pigments.

It has been reported that the red tone of Fe₂O₃ pigments is strongly influenced by the particle size, morphology, and the aggregation of the pigments.⁸⁾

The possibility that SiO₂ controlled the grain size of Fe₂O₃ or generation of the spinel was suggested.

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