The physical and optical properties of newly synthesized, environmentally friendly, highly reflective green–black (HRGB) pigments \( \text{(CoO}_x\text{MgO})_{1-x}\text{n}[(\text{Al}_2\text{O}_3)_{x}\text{(Fe}_2\text{O}_3)]_{1-y} \) \( (x = 0.5, y = 0.75, \text{and } n = 1) \) calcined at various temperatures were studied. The pigments were prepared from \( \text{Fe}_2\text{O}_3, \text{Al(OH)}_3, \text{Mg(OH)}_2, \text{and CoCO}_3 \) by a novel modified solid solution method. The physical and optical properties (lower magnetization and higher total solar reflectance) of the HRGB pigments were superior to those of related pigments with the same chemical structure. Dependence of physical and spectroscopic properties of the HRGB synthesis was performed at a reduced calcination temperature with lower energy consumption than the standard methods. The physical and optical properties (lower magnetization and higher total solar reflectance) of the HRGB pigments was also studied. Mixed with \( \text{TiO}_2 \), a highly reflective black pigment, synthesized similarly to the HRGB pigment and possessing similar physical properties, exhibited 80% higher reflectivity than a standard black pigment similarly mixed with \( \text{TiO}_2 \).

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1. Introduction

Recently, environmentally friendly technologies that reduce heat island phenomena by reflecting the near-infrared (NIR) component of sunlight have attracted great interest. IR-light reflecting dark black pigments composed of spinel-type composite oxides containing \( \text{Cr}^{3+}, \text{Mn}^{3+} \) and rare earth metals are extensively used in roof materials because of their high reflectivity and longevity. However, environmental and supply stability issues have necessitated the development of Cr-free materials and substituents for rare earth metals. Therefore, we synthesized highly reflective green–black (HRGB) pigments, \( \text{(CoO}_x\text{MgO})_{1-x}\text{n}[(\text{Al}_2\text{O}_3)_{x}\text{(Fe}_2\text{O}_3)]_{1-y} \), which are spinel-type composite oxides, by an environmentally friendly solid solution method. The method is novel because it synthesizes \( \text{Fe}_2\text{O}_3 \) by a wet process and at a lower calcination temperature (with lower energy consumption) than the standard method.15

Despite their black color, the developed pigments absorbed little sunlight; instead, they selectively reflected in the 780–2500 nm region when applied to a white surface. They also reflected 20% of sunlight in the 300–2500 nm region. Therefore, they could reduce the temperature increase of a black surface exposed to sunlight. The HRGB pigments comprised a mixed system of four elements, \( \text{Fe, Al, Mg, and Co} \) derived from \( \text{Fe}_2\text{O}_3, \text{Al(OH)}_3, \text{Mg(OH)}_2, \text{and CoCO}_3 \) respectively. A wide-angle X-ray diffraction (WAXD) study indicated a spinel structure of the HRGB pigment, with the general formulation \( \text{AB}_2\text{O}_4 \) (where \( \text{A} \) is a \( 2+ \) cation and \( \text{B} \) are \( 3+ \) cations).16

One novelty of this study was the synthesis of HRGB pigments by an environmentally friendly method that requires less energy than standard methods. No \( \text{Cr}_2\text{O}_3 \) was used, and the HRGB pigments constitute a spinel \( \text{CoO-MgO-Al}_2\text{O}_3-\text{Fe}_2\text{O}_3 \) system rather than the typical \( \text{CoO-MgO-Al}_2\text{O}_3-Cr_2\text{O}_3-\text{Fe}_2\text{O}_3 \) system.17 The calcination temperature was also 200–400°C lower than the conventional calcination temperature.

In our previous report,16 calcination reaction of the HRGB pigments was qualitatively and quantitatively monitored by NIR spectroscopy.16 The bands in the NIR electronic spectra of the HRGB and related pigments (similar components but calcined at lower temperatures (500–900°C) were assigned by comparing the spectra with those of spinel structured \( \text{AB}_2\text{O}_4 \) and \( \text{AB}_2\text{O}_4 \) to that of \( \text{(A}_1\text{B}_2\text{)}\text{B}_2\text{O}_4 \) \( (\text{A} = \text{Co, Mg and } \text{B} = \text{Fe, Al}) \), which possesses an inverse spinel structure.16 The HRGB pigments also showed distinctive spectroscopic, optical, and physical properties.

Herein, we report the synthesis, function, and properties (i.e., spectroscopic, optical, and physical) of the HRGB pigments, and compare them with the corresponding properties of related pigments. The effect of calcination temperature on these properties is also discussed. In particular, the pigment was found to have better physical properties than pigments with the same structure \( \text{(CoO}_x\text{MgO})_{1-x}\text{n}[(\text{Al}_2\text{O}_3)_{x}\text{(Fe}_2\text{O}_3)]_{1-y} \), including low sinterability, good dispersion distribution, and 10% lower reflectivity in the visible (Vis) region. The dark black pigments highly reflected NIR radiation near 1000 nm and had a total solar reflectance (TSR) of 0.33. Finally, this study discusses the effect of mixing with \( \text{TiO}_2 \). Gray paints are frequently desired for roof coatings. However, when mixed with \( \text{TiO}_2 \), which strongly reflects in the NIR region, the reflectance of conventional black pigments was reduced, while that of the new pigment was retained. The sunshine reflectance (TSR) of a highly reflective black (HRB) pigment prepared similarly to the HRGB pigment but with a brown–black color increased by 60% after mixing with \( \text{TiO}_2 \). This increase was significantly higher than that achieved by a mixture of other black pigments and \( \text{TiO}_2 \).
2. Materials and methods

2.1 Raw materials

The HRGB pigment was synthesized from the following raw materials: Fe₂O₃ (particle size 0.6 µm and purity 98.8%), Al(OH)₃ (particle size 1.58 µm and purity 99.6%), Mg(OH)₂ (particle size 3.94 µm and purity MgO 66.6%), CoCO₃ (particle size 1.18 µm and purity Co 48.4%), and TiO₂ (JR-701, particle size 0.27 µm, and purity 93%). These raw materials obtained from Toda Pigments Co. Ltd., Sumitomo Chemicals, Co. Ltd., Konoshima Chemicals, Co. Ltd., Seidou Chemicals, Co. Ltd., and Tayca Corporation, respectively, were used without further purification. Notably, a conventional wet process was employed for Fe₂O₃ synthesis, thereby reducing the energy consumption and increasing the productivity, as detailed in the Results and Discussion.

Table 1 summarizes the colors and reflectivities of the raw materials and their oxides (obtained by the heat treatment of the raw materials at 900°C). Figure 1 displays the Vis–NIR spectra from 300 to 2600 nm of the raw materials and their oxides. From Table 1 and Fig. 1, probably, Co₃O₄ alone shows an intense feature in the NIR region, and therefore exhibits low reflectivity.

2.2 Characterization methods of the developed pigments

2.2.1 WAXD

WAXD data were measured for the synthesized pigments in the scanning angle range (2θ = 5–90°) with a step width of 0.02°, using a Rigaku RINT 2500 X-ray diffractometer with a scintillation detector. Radiation of wavelength 1.5406 Å (Cu Kα) was employed at a generator power of 40 kV and 300 mA.

2.2.2 Fluorescence X-ray analysis

The quantity of each metal in the synthesized pigments was determined by a Rigaku RIX2100 fluorescence X-ray analysis instrument.

2.2.3 Measurement of primary particle shape, average particle size, surface area, and magnetization

The shape of the primary particles was observed by a Hitachi High Technology Series S-4800 scanning electron microscope (SEM). Average particle sizes were measured using a JEOL Helos High Technology Series S-4800 scanning electron microscope with a JEOL Helos Inlammation detector. Radiation of wavelength 1.5406 Å (Cu Kα) was employed at a generator power of 40 kV and 300 mA.

2.2.4 Color features of the pigments (L*, a*, and b* values)

The hues of the synthesized pigments were measured as follows: each sample (0.5 g) was thoroughly kneaded with castor oil (0.5 µl) using a Hoover Muller mill, yielding a paste. To this paste a clear lacquer (4.5 g) was added, and the mixture was thoroughly kneaded into a paint. The obtained paint was applied to a cast-coated paper using a 150-µl applicator. The thickness of the coating film was approximately 30 µm.

The hue of the film on the coated piece was measured by a chroma meter (CR-300; Minolta Co., Ltd.) and expressed by the typical color specification indices (L*, a*, and b* values) according to JIS Z 8732.

2.2.5 Vis–NIR spectra measurement and reflectivity measurements

The Vis–NIR spectra and reflectivities (300–2600 nm) of the coating films prepared for color measurement were measured in a Hitachi U-4100 spectrometer. The raw materials were evaluated in the same way. A BaSO₄ pellet was employed as a reference. The reflectivities are presented as the average reflectivities in the 300–780, 780–2500, and 300–2500 nm regions, as described in “Determination of the reflectance of solar radiation by a paint film (JIS K 5602).” The transparency of castor oil and the lacquer in the NIR range was not considered; light scattering at the lacquer pigment boundary is possible and must be investigated in the future.

Table 1. Colors and reflectivities of raw materials

| Raw material | Heat treatment temperature °C | Hue color | L*  | a*  | b*  | Reflectivity |
|--------------|-------------------------------|-----------|-----|-----|-----|--------------|
|              |                               |           |     |     |     | Vis           |
|              |                               |           |     |     |     | 300–780 nm   |
| Mg(OH)₂      | —                             | white     | 91.9| -0.4| 5.6 | 81.47        |
| Al(OH)₃      | —                             | white     | 89.9| -0.2| 4.5 | 80.74        |
| Fe₂O₃        | —                             | red       | 37.4| 31  | 24.2| 9.86         |
| CoCO₃        | —                             | pink      | 53  | 31  | -9.6| 59.41        |
| MgO          | 900                           | white     | 91  | 0.4 | 6.4 | 80.44        |
| Al₂O₃        | 900                           | white     | 90  | -0.2| 4.5 | 81.05        |
| Fe₂O₃        | 900                           | red       | 34  | 27.5| 18.4| 9.58         |
| Co₃O₄        | 900                           | black     | 25.6| -0.6| -0.3| 5.49         |

L*, a*, and b* indicate the brightness direction, on a scale from 0 (black) to 100 (white). a* and b* indicate the color directions (where a* indicates the green-red axis and b* indicates the blue-yellow axis).
3. Results and discussion

3.1 Synthesis of HRGB pigments

The pigments were synthesized by the method proposed by Ohtsuka,\textsuperscript{13} with three novel modifications. First, the method avoided the use of Cr2O3, which presents a hazard to the environment. Second, synthesis was achieved at a lower calcination temperature, with considerable reduction in energy consumption, than that required for conventional synthesis. Third, the synthesis of Fe2O3 by a wet process, which further reduced energy consumption and increased productivity (see below). Finally, the HRGB pigments were prepared by an environmentally friendly method.

Usually, spinel-type pigments constituting a CoO–MgO–Al2O3–Cr2O3–Fe2O3 system, which are typically used in ceramic glazes, are calcined at a high temperature of 1400°C and then crushed.\textsuperscript{17} The crushed pigments are mixed with glazes and further heat-treated at 1300°C. In this process, the more Cr3+ incorporated into the pigments, the more stable the spinel structure; consequently, the more indestructible the pigment.

In the method presented here, Cr2O3 was not used, and a CoO–MgO–Al2O3–Fe2O3 spinel system was synthesized instead of the conventional CoO–MgO–Al2O3–Cr2O3–Fe2O3 system.\textsuperscript{17} While the conventional method uses raw materials such as CoO, Cr2O3, MgO, Fe2O3, and Al(OH)3, the new method uses CoCO3, Mg(OH)2, Fe2O3, and Al(OH)3. In addition, the main raw material, Fe2O3, is conventionally synthesized by a dry process, but was synthesized by a wet process prior to incorporation into the new pigments.\textsuperscript{18} In the wet process, Fe2O3 particles were produced by neutralization at pH 5 using aqueous solutions of 0.24 mol/L ferrous sulfate with sulfuric acid and 0.24 mol/L sodium hydroxide. The resulting ferrous oxide particles were washed, dried at 100°C, and heat-treated at 600–950°C. This technique allows the physical properties of the particles, such as size and crystalline structure, to be controlled by changing the synthesis conditions, such as pH and temperature.

Fe2O3 prepared by the wet process yielded a narrow particle distribution with no large particles. The early-stage dispersion was also superior to that in existing methods, thus enabling high speed dispersion. Therefore, wet process synthesis of Fe2O3 facilitated the productivity and labor costs of paint manufacturing. Furthermore, Fe2O3 processed in this manner dispersed more readily when wet-mixed with CoCO3, Mg(OH)2, or Al(OH)3, thus facilitating the productivity and labor costs of paint manufacturing. Among the 11 pigments shown in Tables 2, 3, and 4, SA8, SAA, HRB, HRGB, HRB, and AlB were newly developed.\textsuperscript{15,20} The main pigment was HRGB. The chemical composition of all samples was (CoO)(MgO)y·n[(Al2O3)x·(Fe2O3)y]·z, (x/y/n = 0.5/0.75/1; n denotes the molar ratio). Notably, all samples were Cr-free and contained no rare metals, characterizing them as environmentally friendly materials. Colors ranged from pure black (A8 and SAA) to brownish (HRB), greenish (HRGB), and bluish–green (HRG). The CoO content of the five dark pigments was relatively low, which is desirable from an economic viewpoint. All these pigments had a spinel structure.

Although HRG\textsuperscript{20} was more reflective than HRGB, it was also less blackish. The five dark pigments were prepared with varying Al2O3 and Fe2O3 content as follows: SA8 contained no Al2O3, HRB contained a moderate quantity, HRGB contained a relatively high quantity, HRG contained the highest quantity of Al2O3 but low quantities of Fe2O3, and HRBL contained the highest content of Al2O3 but no Fe2O3. In this manner, the molar ratios of Al2O3 and Fe2O3 were varied while maintaining the CoO and MgO ratios at 1. In Fig. 4, the reflectivity in both the regions (300–780 and 300–2500 nm) is observed to increase with increasing Al2O3 content, while the black color and magnetization weaken with decreasing Fe2O3 content.

| Sample number | Sample name | (CoO)y·(MgO)z·n[(Al2O3)x·(Fe2O3)y] | Raw material ratios |
|---------------|-------------|-----------------------------------|---------------------|
|               |             | CoO: 73.5 | MgO: 9.0 | Al2O3: 0 | Fe2O3: 66.3 | CoO: 9.1 | MgO: 32.6 | Al2O3: 33.4 | Fe2O3: 16.8 |
Figure 3 shows that the primary particles of HRGB are granular, with narrow powder size distribution, as reported for other well-dispersed iron oxides such as HRV.14) Although some aggregated components were present, as indicated by the nonzero magnetization results (Table 4), no sintering was observed in HRGB; the particles were well dispersed. Figure 5 shows the Vis–NIR spectra of SA8, HRB, HRGB, HRG, HRBL, and MAT305 at 300–2600 nm. From this figure, the reflectivities of HRBL and HRG around 500 nm are determined as 55% and 17%, respectively, consistent with their respective blue and blue–green colorations. In addition, although the reflectivity of the paint prepared with HRBL and HRG changed steeply at the
border between the Vis and NIR regions, and both pigments exhibited low reflectivity in the 1200–1600 nm region (Fig. 5), their sunshine reflectivities were excellent (42.67 and 51.35, respectively) over the entire region (Table 3). Conversely, the reflectivities of HRGB, HRB, and SA8 in the Vis region were 10% smaller. These dark black pigments reflected near 1000 nm, and their sunshine reflectivities over the entire region were 23.9, 25.5, and 33, respectively. Therefore, the TSR of these pigments was significantly higher than that of normal black pigments such as MAT305 (L° = 23, a° = 0.3, b° = -0.2, and TSR = 5.4).

3.3 Spectroscopic properties of the developed pigments

With the exception of MAT305, all pigments exhibit a broad feature in their Vis–NIR spectra from 1100 to 1800 nm (Fig. 5). This blunt peak is assignable to the d–d transition, 4A2→4T1, of Co (II). In Fig. 5, the three components of the d–d transition band in the 9000–6000 cm⁻¹ region undergo a wavelength shift that depends on the Fe₂O₃ molar ratio. Specifically, the reflectance below 1000 nm decreases with increasing Fe₂O₃ content. In fact, the peaks shift significantly upon transition from HRG to HRGB and from HRGB to HRB, suggesting that the structure surrounding Co (II) significantly differs between HRG and HRGB and between HRGB and HRB. Because the reflectance in this region was highly sensitive to the crystal structure, this region could be used to monitor the crystal structures of the black pigments containing Co (II). Another notable point in Fig. 5 is the broad feature from 950 to 1150 nm in the spectrum of SA8, which contained the highest Fe₂O₃ content. This feature is
attributable to the foot of the charge-transfer band of Fe₂O₃. The intensity of this band decreases with decreasing Fe₂O₃ content, and is absent in the spectrum of HRBL, which contains no Fe₂O₃.

3.4 Effect of calcination temperature on the physical and spectroscopic properties of HRGB

The effects of calcination temperature on the color and reflectivity of the paint prepared with HRGB are summarized in Table 5. As the temperature was increased, the pigment color altered from red–black to brownish–black and ultimately to greenish–black. The reflectivity was maximized at a calcination temperature of 1100°C.

Figure 6 shows the Vis–NIR spectra from HRGB calcined from 500 to 1200°C. In this figure, the reflectivity is flat and neutral in the visible light region (400–700 nm); thus the mixture appears as gray achromatic. However, in the NIR region (780–2500 nm), a broad feature near 1000 nm and a valley in the vicinity of 1500 nm develop with increasing TiO₂ content.

Figure 7 plots the sunshine reflectivities (TSR) in the 780–2500 nm and 300–2500 nm regions as a function of L* values. The red line indicates the relationship between the L* value and the sunshine reflectivity of a highly reflective pigment that satisfies the JIS standards for a roof coating material (JIS K5675). Notably, the sunshine reflectivity of the paint prepared with the HRB and TiO₂ mixtures in the 780–2500 nm region exceeded that specified by JIS K5675. In addition, for the mixture with L* = 51.3 (HRB 40% and TiO₂ 60%), the sunshine reflectivity (in the 300–2500 nm region)

| Calculination temperature (°C) | Hue color   | L*  | a*  | b*  | Vis Reflectivity 300–780 nm | Vis–NIR Reflectivity 300–2500 nm |
|--------------------------------|-------------|-----|-----|-----|---------------------------|---------------------------------|
| 500                            | red         | 27.2| 5.7 | 5.7 | 5.99                       | 9.83                            |
| 600                            | red         | 27.6| 5.1 | 5.4 | 6.06                       | 9.71                            |
| 700                            | brownish–black | 27.6| 4.5 | 5.1 | 6.08                       | 14.06                           |
| 800                            | black       | 25.9| 2.5 | 2.5 | 5.43                       | 17.24                           |
| 900                            | black       | 25.3| 2.5 | 1.4 | 5.32                       | 24.69                           |
| 1000                           | black       | 26  | 2.2 | 1.6 | 5.63                       | 29.55                           |
| 1100                           | greenish–black | 27.5| 0.9 | 2.8 | 7.2                        | 33                              |
| 1200                           | greenish–black | 26.9| 0.6 | 2.1 | 6.15                       | 31.08                           |

Fig. 6. Vis–NIR spectra of HRGB calcined from 500 to 1200°C.

Fig. 7. Reflection spectra of HRB mixed with TiO₂. Mixing ratios of HRB to TiO₂ were 0, 1, 5, 10, 20, 30, 40, 50, and 100%.

Fig. 8. Sunshine reflectivity (TSR) as a function of L* value (HRB + TiO₂ mix).
was expected to be 40% higher than that specified by the Osaka Heat Island Certification Standard (blue line).21) Mixed with TiO₂ (a typical white pigment), the new HRB pigment satisfies the requirements of both JIS K5675 and Osaka Heat Island Certification Standard, and is therefore suitable as a commercial coating material.

4. Conclusion

HRGB pigments were synthesized by an environmentally friendly method with lower energy requirements than the conventional method. The main advantages of the new method are threefold. First, the synthesis involves no Cr₂O₃ or rare metals. Second, Fe₂O₃ was synthesized by a wet process. Third, the calcination temperature was 200–400°C lower than that required in the conventional method. These advances not only address the environmental issues and resource problems associated with the conventional method but reduce the energy consumption and improve the efficiency of producing pigments.

The HRGB pigments prepared by this method possess superior physical properties. Although black, they absorb little sunlight and display high reflectivity when applied to a white surface. Furthermore, the TSR of the pigments is considerably increased by mixing with TiO₂, a commonly used paint additive.

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