Synthesis of Co-free inorganic blue pigments based on turquoise blue glaze

Keiji KUSUMOTO¹,³

¹National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan

Glass mixtures based on turquoise blue glaze were synthesized by the conventional ceramic method, and their color properties were investigated as environmentally friendly Co-free inorganic blue pigments. Samples showed coloring from light blue to black depending on their compositions. The bluest color was observed for 0.60 BaO·0.20 Li2O·0.20 Na2O·0.45 Al2O3·2.50 SiO2 in a 20 wt% CuO sample heated at 900°C, which had the following color parameters: (L* a* b*) of L* = 41.9, a* = −4.5, and b* = −14.2. The a*, b* values are comparable to those of commercial Co-based blue pigments. Since the glass mixtures do not include cobalt oxide as a raw material, it should be an attractive alternative to conventional Co-based inorganic blue pigments.

Key-words : Pigment, Blue, Cobalt oxide, Copper oxide, Glaze

Synthetic inorganic pigments are widely used for various products, such as paints, ceramics, glasses, and plastics, because they possess high thermal, chemical, and UV stability compared to organic pigments. Inorganic blue pigments are in particular demand due to their wide applicability.

At present, Co-based blue pigments such as CoAl2O4, (Co, Zn)2SiO4 are used for industrial applications due to their superior color performance.¹⁻⁶ These pigments contain toxic and pollutant oxides such as CoO and ZnO, however, that can adversely impact the environment and human health. For this reason, attention has been directed largely to the synthesis of new inorganic compounds with a vivid blue color called cobalt blue for use as pigments.

Among existing synthetic inorganic blue pigments other than Co-based pigments, vanadium blue pigment (V:ZrSiO4) is especially well known.⁷ The color of vanadium blue pigment is a light blue color called turquoise blue, however, not cobalt blue. As environmentally friendly inorganic blue pigment candidates, calcium scandium silicate garnet (Ca5Sc2Si3O12) and YIn₁₋ₓMnₓO₃ compounds have been reported.⁸⁻⁹ These candidates exhibit a blue color similar to that of Co-based pigments, but they are not attractive as replacements for Co-based pigment, since expensive raw materials such as Sc₂O₃, Y₂O₃, and In₂O₃ are required to synthesize them. A novel blue pigment that can replicate Co-based pigments is therefore required from the viewpoint of environmental protection.

In the field of glazes for pottery products, it is known that turquoise blue glaze exhibits a light blue color. The turquoise blue color in these glazes is attributed to microparticles of copper oxide. It is especially well known that the color of copper oxide changes from light blue to dark blue with increases in the barium oxide content in the glaze. Although barium compounds are known as deleterious substances, it has been suggested that their toxicity to biological tissues is substantially less than that of cobalt and vanadium compounds. Thus, the use of barium compounds for this study appears to present no problem.

In this study, glass mixtures based on turquoise blue glaze have been synthesized and investigated for their color properties to search for a novel environmentally friendly inorganic blue pigment.

Li2CO3 (Wako Pure Chemical Industries Ltd., 99.9%), Na2CO3 (Kanto Chemical Co., Inc., 99.5%), CaCO3 (Yoneyama Yukuhin Kogyo Co., Ltd., 99.5%), BaCO3 (Wako Pure Chemical Industries Ltd., 99%), Al2O3 (Wako Pure Chemical Industries Ltd., 99.9%), and SiO2 (Wako Pure Chemical Industries Ltd., 99.9%) were used for preparation of the basic glaze. Basic copper(II) carbonate [CuCO3·Cu(OH)2·H2O, Wako Pure Chemical Industries Ltd., as CuO 48–56%] was used as the copper oxide source for the coloring material in the glaze.

These powders were thoroughly mixed in an agate mortar with a pestle for 10 min and then heated at 800–1100°C in air for 60 min (heating rate 200°C/h). After heating, the resulting mixtures were thoroughly milled in an agate mortar with a pestle for 10 min. The crystalline phases were identified using an X-ray diffractometer (Rigaku Denki Co., Ltd., RINT-2550). In order to test
the color performance of the powders as pigments, pastes were prepared by mixing the powders with silicone resins (Cemedine Co., Ltd.) with 25 volume percent powder. The resulting pastes were applied to a white hard paper by a die-coating method. The thickness of the coated films obtained were approximately 0.2 mm. The color parameters \((L^*a^*b^*)\) were measured using a spectrophotometer (Konica Minolta Sensing Inc., CM-700d). The parameter \(L^*\) represents the brightness or darkness of a color relative to a neutral grey scale, while the parameters \(a^*\) (the green-red axis) and \(b^*\) (the blue-yellow axis) express the color qualitatively.

According to the literature on turquoise blue glaze,\(^{10}\) the glaze has been prepared by heating mixtures consisting of \(0.50 \text{BaO} \cdot 0.10 \text{CaO} \cdot 0.20 \text{Li}_2\text{O} \cdot 0.20 \text{Na}_2\text{O} \cdot 0.45 \text{Al}_2\text{O}_3 \cdot 2.50 \text{SiO}_2\) with around 2 wt % \(\text{CuO}\). Thus, we began by investigating the glaze formation conditions by heating mixtures consisting of \(0.50 \text{BaO} \cdot 0.10 \text{CaO} \cdot 0.20 \text{Li}_2\text{O} \cdot 0.20 \text{Na}_2\text{O} \cdot 0.45 \text{Al}_2\text{O}_3 \cdot 2.50 \text{SiO}_2\) with 2 wt % \(\text{CuO}\) at various temperatures.

**Figure 1** shows photographs of powders prepared by heating compositions of \(0.50 \text{BaO} \cdot 0.10 \text{CaO} \cdot 0.20 \text{Li}_2\text{O} \cdot 0.20 \text{Na}_2\text{O} \cdot 0.45 \text{Al}_2\text{O}_3 \cdot 2.50 \text{SiO}_2\) with 2 wt % \(\text{CuO}\) at 800–1100°C.

As can be seen from the photographs, powders with light gray color and light blue color were obtained from mixtures heated at 800°C and 900°C, respectively. On the contrary, samples were welded to the crucible when heated at 1000°C or above. From these results, it was found that recovery of the sample was difficult for mixtures heated at 1000°C or above. The heating temperature of mixtures were therefore set fixed at 900°C to enable easy sample collection.

**Figure 2** shows X-ray diffraction patterns (XRD) of samples heated at 800 and 900°C.

Analysis of the XRD of a sample heated at 800°C confirmed that the peaks of \(\text{BaO} \cdot 2\text{SiO}_2\), \(\text{CaO} \cdot \text{SiO}_2\), and an unknown crystal that are considered compounds consists of \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\). On the other hand, analysis of the XRD of a sample heated at 900°C confirmed that the peaks of the unknown crystal were clearly decreased. Since a halo pattern peculiar to glass is shown at around 26° in the XRD, it seems that glass is formed in samples heated at 900°C or above. From these results, it was found that glass mixtures consisting of glass, \(\text{BaO} \cdot 2\text{SiO}_2\), \(\text{CaO} \cdot \text{SiO}_2\), and small amounts of an unknown crystal are formed when mixtures are heated at 900°C or above. To investigate the effect of \(\text{CuO}\) content in glaze on the color of the samples, mixtures were prepared at various \(\text{CuO}\) contents.

**Figure 3** presents photographs of powders produced by heating mixtures consisting of 0.50 \(\text{BaO} \cdot 0.10 \text{CaO} \cdot 20 \text{wt} \% \text{CuO}\) at 900°C.

**Fig. 1.** Photographs of powders prepared by heating compositions of 0.50 \(\text{BaO} \cdot 0.10 \text{CaO} \cdot 0.20 \text{Li}_2\text{O} \cdot 0.20 \text{Na}_2\text{O} \cdot 0.45 \text{Al}_2\text{O}_3 \cdot 2.50 \text{SiO}_2\) with 2 wt % \(\text{CuO}\) at 800–1100°C.

**Fig. 2.** XRD of samples heated at 800 and 900°C.

**Fig. 3.** Photographs of powders produced by heating mixtures consisting of 0.50 \(\text{BaO} \cdot 0.10 \text{CaO} \cdot 0.20 \text{Li}_2\text{O} \cdot 0.20 \text{Na}_2\text{O} \cdot 0.45 \text{Al}_2\text{O}_3 \cdot 2.50 \text{SiO}_2\) with 2–20 wt % \(\text{CuO}\) at 900°C.
Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ with 2–20 wt % CuO at 900°C. The color parameters (L* a* b*) of the samples are given in Table 1. The low a* and low b* values indicate the degree of green and blue coloring of the samples, respectively.

As can be seen from the photographs, the color of the powder changed from light blue to dark blue with increases in the content of CuO in the glaze. The b* values clearly decreased when the CuO content increased from 2 to 10 wt %. As for the increase of b* value in the sample with 20 wt % CuO, it is not discussed here since the colors of the sample are affected by the BaO content in the glaze as described below. Although the color of CuO powder is usually black, it is empirically known that CuO particles show a blue or green color in glaze containing BaO. As for this phenomena, it is considered that the color of CuO particles is affected by the properties of the created ligand field surrounding the particles.11)

To investigate the effect of BaO content in glaze on the changes in color of the CuO particles, samples were prepared at various ratios of BaO/CaO content in the glaze composition. Specifically, samples were prepared by heating of the mixtures consisting of 0.60 (BaO + CaO)·0.20 Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ compositions with 20 wt % CuO followed by observation of the color performance of the samples.

Figure 4 offers representative photographs of powders prepared by heating of mixtures consisting of 0.60 (BaO + CaO)·0.20 Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ with 20 wt % CuO.

It is evident from the photographs that samples with BaO-rich compositions show a dark blue color. The color of the samples changed from dark blue to dark green with decreases in BaO content in glaze. Moreover, the color of the samples becomes black in compositions without BaO as a raw material. These results indicated that the colors of CuO particles are affected strongly by the presence of BaO in glaze. From the viewpoint of color data of the samples, the bluest sample was obtained by heating compositions of 0.60 (BaO + CaO)·0.20 Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ with 20 wt % CuO, which had color parameters (L* a* b*) of L* = 41.9, a* = −4.5, and b* = −14.2.

As for the relationship between BaO and CuO in glaze, a study by Berke on blue pigments used in ancient times is useful for understanding of the changing colors of the samples. Berke reported that a blue pigment called China blue is made of a BaCuSi₄O₁₀ (BaO·CuO·4SiO₂) compound.3) Thus, in the mixtures consisting of BaO, CaO, Li₂O, Na₂O, Al₂O₃, SiO₂, and CuO, there is a possibility that a BaCuSi₄O₁₀ compound is formed in the glaze. The XRD of samples made by heating mixtures 0.60 BaO·0.20 Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ with 20 wt % CuO were therefore examined from the viewpoint of forming BaCuSi₄O₁₀ compounds in the glaze.

Figure 5 shows the XRD of a sample produced by heating mixtures of 0.60 BaO·0.20 Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ with 20 wt % CuO at 900°C.

Table 1. Color parameters (L* a* b*) of samples prepared by heating of mixtures consisting of 0.50 BaO·0.10 CaO·0.20 Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ with 2–20 wt % CuO at 900°C

| CuO content (wt %) in glaze | L*  | a*  | b*  |
|-----------------------------|-----|-----|-----|
| 2                           | 77.6| −11.2| −8.2 |
| 6                           | 61.3| −12.5| −10.3|
| 10                          | 53.7| −12.6| −14.6|
| 20                          | 40.6| −6.2 | −11.3|

Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ with 2–20 wt % CuO at 900°C. The color parameters (L* a* b*) of the samples are given in Table 1. The low a* and low b* values indicate the degree of green and blue coloring of the samples, respectively.
by heating of a BaO-rich glaze mixture. Berke also reported that pure BaCuSi₄O₁₀ is difficult to prepare by the solid-state reaction method, because stable SiO₂ and CuO resist reaction without a flux compound. On the other hand, in the glass mixtures prepared in this study, it seems that the easy formation of BaCuSi₄O₁₀ occurred because the glass matrix served the function of flux. For preparation of BaCuSi₄O₁₀ powder by the solid-state reaction method, the process of eliminating the flux compound is required. On the other hand, the synthesis method in this study has the merit of making it easy to fabricate blue glass mixture powder, including BaCuSi₄O₁₀, simply in large volume.

The color parameters (L*,a*,b*) of conventional inorganic blue pigments and representative samples prepared from 0.60 BaO·0.20 Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ compositions with 20 wt% CuO are given in Table 2.

As mentioned above, the low b* values indicate the degree of blue color of the samples. On the contrary, the low a* values indicate the degree of green color of the samples. From the viewpoint of color data, it can be seen that vanadium blue pigment (V₂ZrSiO₄) is a bright greenish blue color, since the pigment shows large L* and low a* values. On the other hand, it can be seen that the colors of samples prepared in this study are similar to those of Co-based blue (CoAl₂O₄) pigments, since the L*,a*,b* values are the numerical values of an approximation. It seems, therefore, that glass mixtures based on turquoise blue glaze have the potential for use as substitute, taking into consideration the ecology in comparison with the conventional Co-based blue pigments. In particular, this pigment candidate is expected to be used for coating materials, since the powder can be fabricated in large quantities by a simple process.

Glass mixtures based on turquoise blue glaze have been synthesized in the search for novel environmentally friendly inorganic blue pigments. Analysis of the XRD of the samples confirmed that glass formed by heating of mixtures at 900°C or above and glaze consist of glass, BaO·2SiO₂, CaO·SiO₂, and a small amount of unknown compounds. It was found that the color of the CuO particles is affected strongly by the presence of BaO content in the glaze. Samples showed coloring from light blue to black depending on the CuO and BaO content in the glaze. The bluest color was obtained by heating mixtures of 0.60 BaO·0.20 Li₂O·0.20 Na₂O·0.45 Al₂O₃·2.50 SiO₂ with 20 wt% CuO, which had color parameters (L*,a*,b*) of L* = 41.9, a* = −4.5, and b* = −14.2. The a*, b* values are comparable to those of a commercial Co-based blue pigment.

Table 2. Color parameters (L*,a*,b*) of conventional inorganic blue pigments and representative samples

| Sample                  | L*  | a*  | b*  |
|------------------------|-----|-----|-----|
| V₂ZrSiO₄               | 70.1| −13.1| −14.5|
| CoAl₂O₄               | 44.5| −6.5| −11.7|
| Ba-based glaze with CuO| 41.9| −4.5| −14.2|

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