Kütahya Dumlupınar University
Institute of Graduate Studies

Journal of Scientific
Reports-A
E-ISSN: 2687-6167
Number 47, June 2021

RESEARCH ARTICLE

THE USE of BLACK COLORANT OBTAINED from DOMESTIC SOURCES in LEADED and BORON GLAZES

Hale YILDIZAY [1], Fikret AYDOĞDU[2]

[1]Kütahya Dumlupınar University, Kütahya Fine Arts Vocational School, Department of Tile Art and Design, Kütahya, hale.yildizay@dpu.edu.tr, ORCID: 0000-0002-3896-9912
[1]Kütahya Dumlupınar University, Kütahya Fine Arts Vocational School, Department of Tile Art and Design, Kütahya, fikret.aydogdu@dpu.edu.tr, ORCID:0000-0001-8514-0405

Received Date:16.05.2021 *Accepted Date:29.09.2021*

ABSTRACT

In this study, the usability of the black colorant obtained by mixing of MHP composite produced from laterittic nickel, chromite and magnetite ores in certain proportions, in boron and leaded glazes was investigated. Prepared black colorant was added to leaded and boron glaze in varying proportions. The color properties of the colored glazes were measured by spectrophotometer and their values are expressed as “L * a * b *”. It has been determined that the color values of this colorant used in leaded and boron glazes are quite similar to commercially used black pigments. As a result, black colorants with high added value were produced with the use of domestic resources and positive results were obtained in their use in leaded and boron glazes.

Keywords: *Boron glaze, Leaded glaze, Raw material, Coloring, Characterization*

1. INTRODUCTION

The glaze is a glass or glassy structure that melts on the ceramic body surface covering it in a thin form [1]. Specially prepared inorganic synthetic pigments containing natural raw materials, metal oxides or multiple metal oxides are used in the coloring of ceramic glazes. Pigments do not melt in glaze composition and disperse in small grains in the glaze, maintaining their crystal structure [2].

Black color has a 25% share in total pigment consumption in the world [3]. The use of pure oxides in the production of black pigments increases the cost of black colored glazes (4). There are some studies on the production of black pigments with natural raw materials (5) and / or wastes containing precious metals (6) that are cheaper than pure oxides in order to reduce the pigment cost (7). The color performances of black pigments produced in these studies were examined in different glazes.

The production of black pigments used in glazes usually consists of mixtures of iron, cobalt, chromium, nickel, magnesium, and copper oxides in certain proportions (8). Cr-Fe hematite pigments are widely used for black color in some of the glazes (9), while Co-Fe-Cr, Fe-Mn (10) and Ni-Fe-Cr spinel pigments (11) with high thermal and color stability are used in others.

For this purpose, in our study, a new coloring composition was prepared by mixing MHP composite, magnetite and chromite mineral which produced in our country. MHP composite is preferred in the study because it contains high levels of nickel and cobalt oxide. The MHP composite used in the study is produced in our country by acid dissolving (HPAL) method under high pressure, which is the state-of-the-art application of the most efficient hydrometallurgical acquisition method [12].

In this study, the effects of adding the inorganic black colorant obtained by mixing the MHP composite obtained from laterittic nickel ore extracted, chromite, and magnetite mineral in our country to leaded and boron glazes were examined.

2. EXPERIMENTAL METHOD

2.1. Raw Materials

In the production of colorants; magnetite mineral as iron oxide source was provided from Ferromad mining company in Kutahya, Hisarcik district. Chromite mineral as chromium oxide source was provided from Hayri Ogelman mining company located in Bursa Harmancik district.

In addition, the MHP composite, which guides the study differently; it was used as source of nickel and cobalt oxide and supplied as raw material from Meta Nickel Cobalt company in the Manisa Gördes region. Leaded, boron glazes and their bodies used for colorant trials were obtained from Sedef Handicraft.

The commercial black pigment CK13074 (Ferro Corporation), CP 30 (Itaca S.A.) used in ceramic and tile coloring are taken as reference pigment in this study.

2.2 Chemical Analysis Results

Chemical analysis (XRF) before starting to work on the raw materials used, melting of samples was carried out in panalytical Eagon 2 model device, chemical analysis was carried out on Panalytical brand Axios MAX model device (Table 1).

Table 1. Chemical analysis of raw materials used in colorant production

Oxides (%)	Chromite	Magnetite	MHP composite
SiO_2	10,61	2,98	0,6
Al_2O_3	5,22	0,95	0,34
Fe_2O_3	20,57	89,93	0,3
CaO	0,23	1,51	
MgO	20,64	3,91	3,91
Co_3O_4	-	-	3,97
CuO	-	-	0,34
Na_2O	-	-	0,07
TiO_2	0,14	0,03	-
Cr_2O_3	39,56	-	-
As_2O_3		0,43	-
V_2O_5		0,27	-
P_2O_5	-	0,09	-
ZnO	0,12	-	0,76
MnO	0,26	-	7,21
NiO	0,17	-	82,5
SO_3	0,02	0,11	-
L.O.I*	0,98	0,57	-

L.O.I*: Loss on ignition

2.3. Colorant Production

In this study, black colorant synthesis was made using magnetite, chromite and MHP composite raw materials. In the first stage the chromite, magnetite and MHP composite were grinded and then dried. It was determined that 40% chromite, 40% magnetite and 20% MHP composite mixture were the most suitable coloring mixture and studies continued in this direction (Table 2).

Table 2. Magnetite, chromite and MHP composite minerals used in colorant production. (%)

	Magnetite	Chromite	MHP composite
Colorant (%)	40	40	20

This raw coloring mixture prepared were added to the leaded and boron glazes in proportions of 10%, 15 and 20% and mixed and homogenized for 15 minutes using alumina balls in a jet mill. The coloring effect of leaded glaze and boron glaze is seen in the Figure 1 and Figure2, respectively.

JSR A
Journal of Scientific Reports

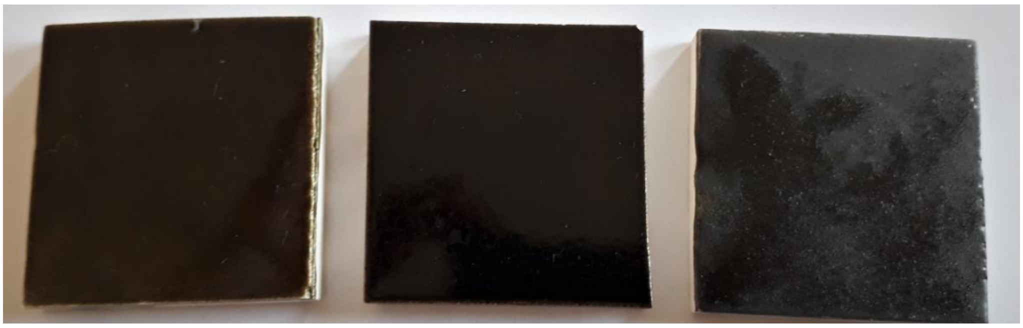


Figure 1. 10%, 15% and 20% colorants addition into leaded glaze, respectively.

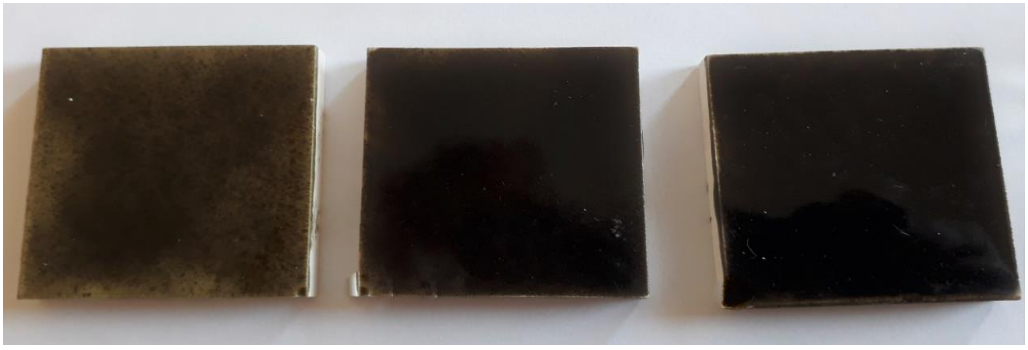


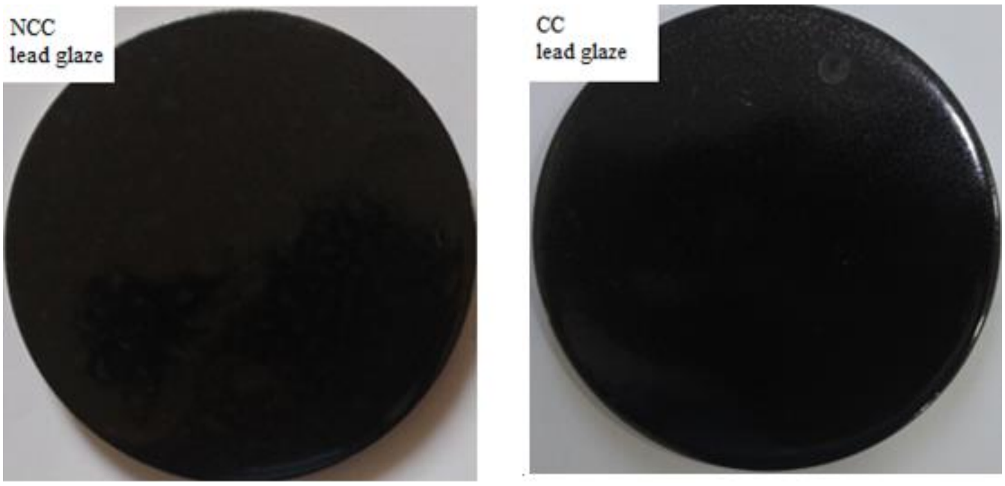
Figure 2. 10%, 15% and 20% colorants addition into boron glaze, respectively.

It has been observed that 15% and 20% colorant additions have a good effect on the formation of black color. Therefore, it is thought that 15% mixture is sufficient. Since it is thought that the use of excess colorants will lead to a cost increase, in the study were continued with the addition of 15% colorant.

The colorant obtained by applying heat treatment (calcination) to the colorant, which has a certain chemical composition and crystal structure, was stabilized. When heat is applied, the materials used in the formation of colorants react with each other, forming new chemical compounds and structures.
Sometimes the unstable color table that occurs is due to the inability to adequately complete the reactions necessary for color formation. This instability is eliminated by the calcination process.

In the second stage colorant mixture (Table 2) was calcined at 1200ºC in the electric kiln. Porcelain crucibles were used for the calcination process and grinded after calcination. Then, the colorant was dried in the oven and added to the glazes.
The viscosity of the glazes was determined by using the ford cup viscometer. The viscosity of the prepared glazes is set to 15 sec and litre weight to 1450 g/l. The prepared calcined and non-calcined colorants were added to the glaze at a rate of 15%. These glazes were then applied to the body and fired in the laboratory in an electric kiln in the appropriate firing regime. The color effect of the non-calcined colorant (NCC) on leaded glaze is shown in Figure 3a and color effect of the calcined colorant (CC) on leaded glaze is shown in Figure 3b.

JSR A
Journal of Scientific Reports



(a) (b)

Figure 3. a) Color effect of the non-calcined colorant (NCC) on leaded glaze, b) Color effect of the calcined colorant (CC) on leaded glaze.

The color effect of the non-calcined colorant (NCC) on boron glaze is shown in Figure 4a and color effect of the calcined colorant (CC) on boron glaze is shown in Figure 4b.

(a) (b)

Figure 4. a) Color effect of the non-calcined colorant (NCC) on boron glaze, b) Color effect of the calcined colorant (CC) on boron glaze.

2.3. Microstructural Analysis

The morphological properties of the leaded and boron glaze samples were examined by the FEI NANO SEM 650. EDS analysis was performed with the EDAX-EDS device connected to a scanning electron microscope (SEM).

3. RESULTS

3.1. Color Analysis

Black pigment called Ferro CK13074, a supplier of glaze pigment found in our country, was used to compare the leaded and boron glazes used with black color characteristics. The color characteristics of all glazed bodies were measured. Color measurements of colored samples were made by Konica Minolta–Spectrophotometer CM-700d device. The results obtained are expressed in Table 3 as "L* a * b*" parameters. Based on the L*, a*, b* values of commercial black pigments, it is seen in Table 3 that the black pigment to be produced must have L*<31, a* <1, b* <1 values.

Table 3. Color values of pigment and colorant samples.

Colored glazes	L	a	b
Ferro-CK13074 Leaded glaze	31,06	0,13	-0,58
NCC leaded glaze	30,52	-0,09	-0,45
CC leaded glaze	27,37	0,25	0,18
Ferro-CK13074 Boron glaze	30,47	-0,05	-0,4
NCC boron glaze	28,31	-0,12	0,01
CC boron glaze	26,26	0,4	0,07

3.2. Microstructure Analysis

Microstructural appearance of the distribution of NCC crystals in leaded glaze are given in Figure 5a. In the microstructure images have detected crystals similar to butterfly. Image of butterfly-shaped of crystal in Figure 5b and EDS analysis of crystal is given in Figure 6.

JSR A
Journal of Scientific Reports

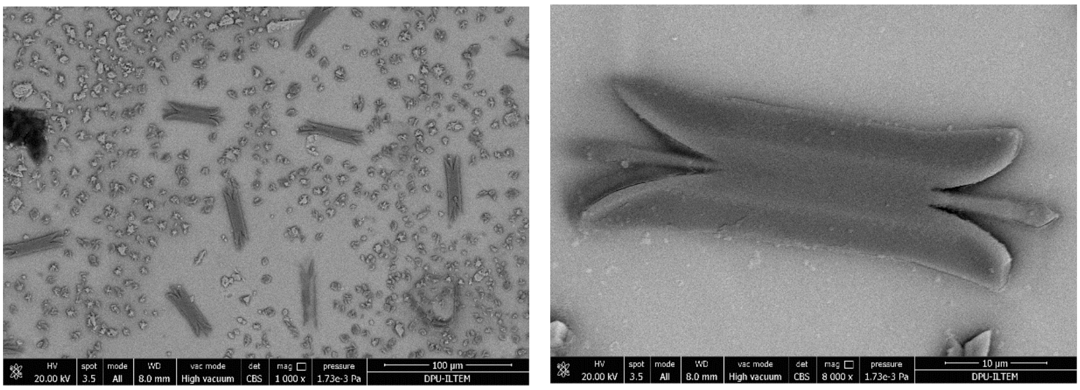
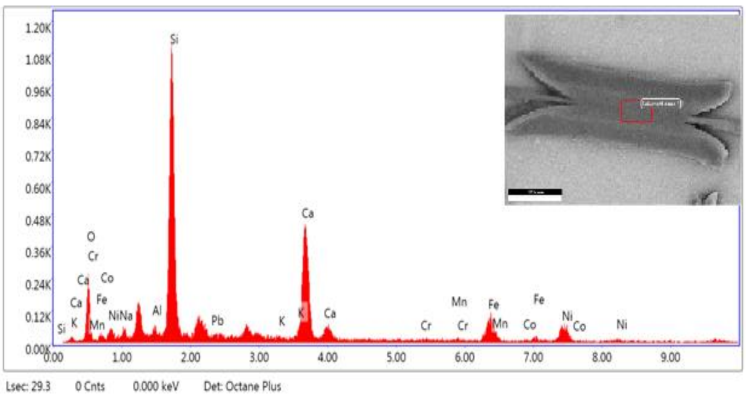


Figure 5. SEM microstructure image a) Distribution of NCC crystals in leaded glaze at the 1000X magnification b) NCC crystal in leaded glaze at 8000X magnification.



Element	Weight (%)
Na_2O	0.63
Al_2O_3	0.67
SiO_2	42.07
PbO_2	0.86
K_2O	0.23
CaO	27.16
Cr_2O_3	0.44
MnO	0.98
Fe_2O_3	14.94
CoO	0.72
NiO	11.31

Figure 6. EDS analysis of NCC crystals in leaded glaze at 8000X (Fe, Cr, Ni, Pb, Mn and Co quantities on the glaze surface).

Microstructural appearance of the distribution of CC crystals in the leaded glaze are given in Figure 7a. In the microstructure images have detected crystals similar to tetragonal structures. Image of tetragonal-shaped of crystals in Figure 7b and EDS analysis of crystals are given in Figure 8.

JSR A Journal of Scientific Reports

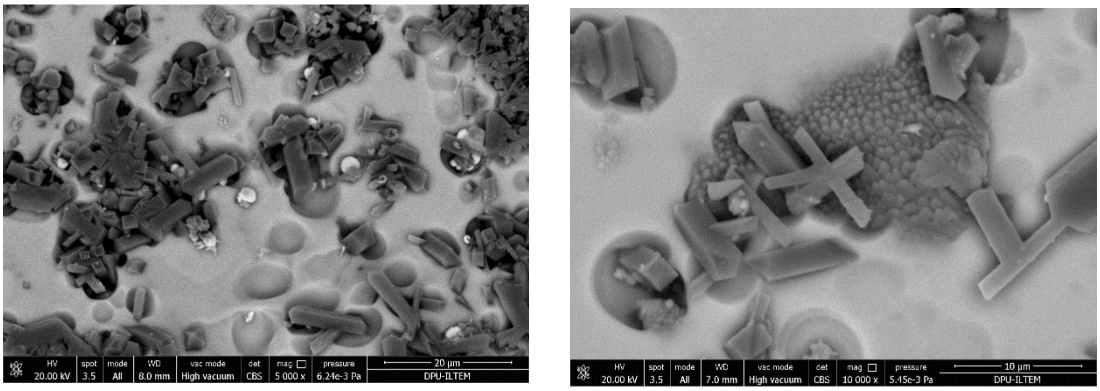
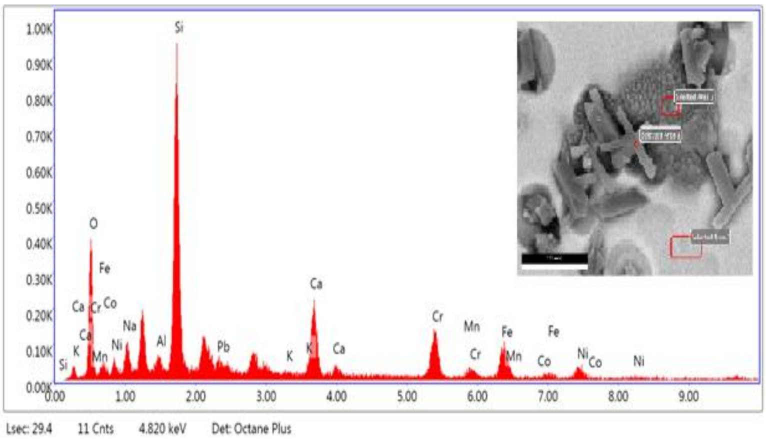


Figure 7. SEM microstructure image a) Distribution of CC crystals in leaded glaze at the 5000X magnification b) CC crystals in leaded glaze at 10000X magnification.



Element	Weight (%)
Na_2O	3.05
Al_2O_3	1.34
SiO_2	38.47
PbO_2	2.92
K_2O	0.27
CaO	13.11
Cr_2O_3	15.96
MnO	1.23
Fe_2O_3	16.33
CoO	0.82
NiO	6.50

Figure 8. EDS analysis of CC crystals in leaded glaze at 1000X (Fe, Cr, Ni, Pb, Mn and Co quantities on the glaze surface).

Microstructural appearance of the distribution of NCC crystals in the boron glaze are given in Figure 9a. In the microstructure images have detected in some of the crystals needle-like structures. The needle-like shaped of crystals image are given in Figure 7b and EDS analysis of crystals are given in Figure 8.

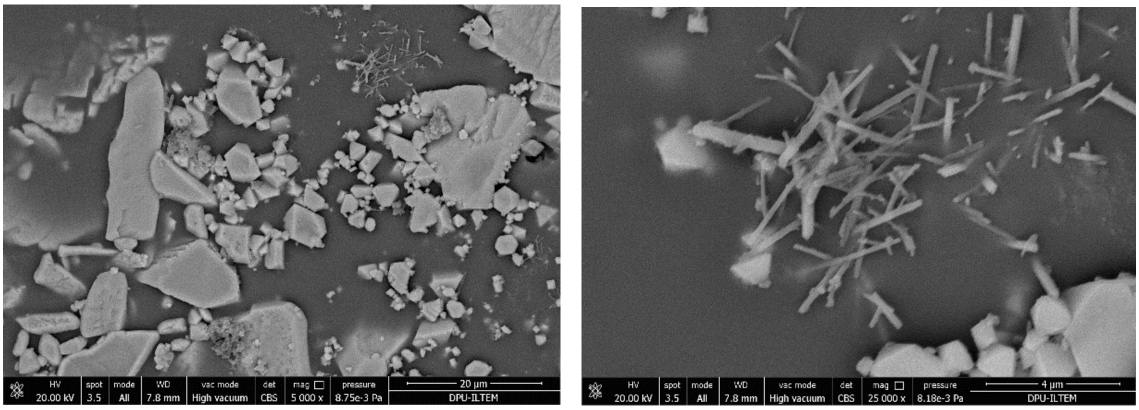
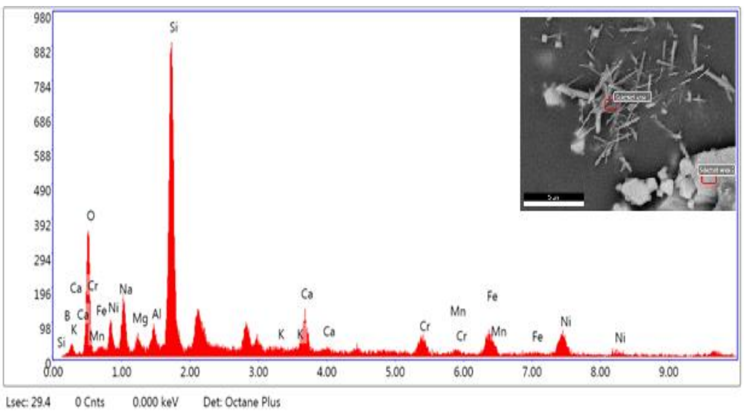


Figure 9. SEM microstructure image a) Distribution of NCC crystals in boron glaze at the 5000X magnification b) NCC crystal in leaded glaze at 25000X magnification.



Element	Weight (%)
B_2O_3	17.42
Na_2O	5.02
MgO	0.61
Al_2O_3	1.61
SiO_2	38.61
K_2O	0.51
CaO	6.34
Cr_2O_3	5.74
MnO	0.66
Fe_2O_3	10.56
NiO	12.91

Figure 10. EDS analysis of NCC crystals in boron glaze at 25000X (B, Fe, Cr, Ni, Mn quantities on the glaze surface).

Microstructural appearance of the occurring NCC crystals in the boron glaze are given in Figure 11a. The image of the crystals is given in Figure 11b and EDS analysis of crystals are given in Figure 12.

JSR A
Journal of Scientific Reports

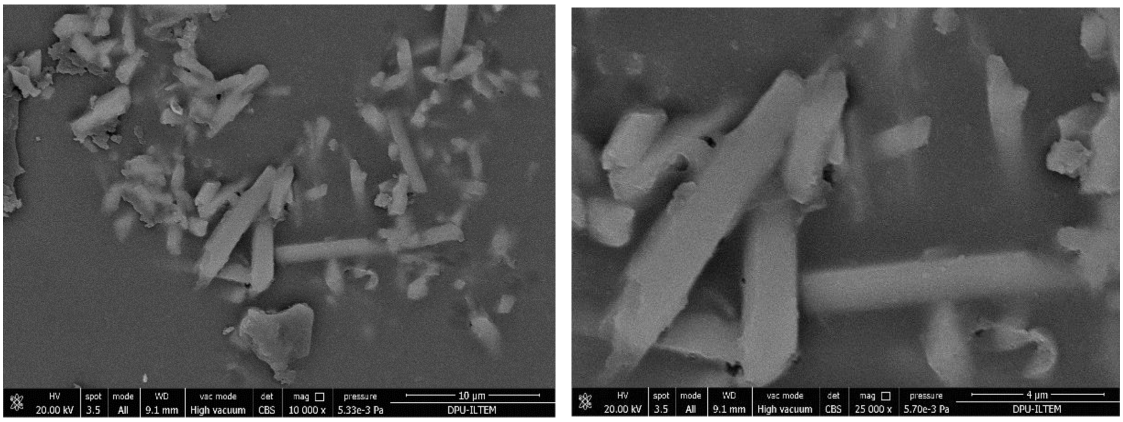
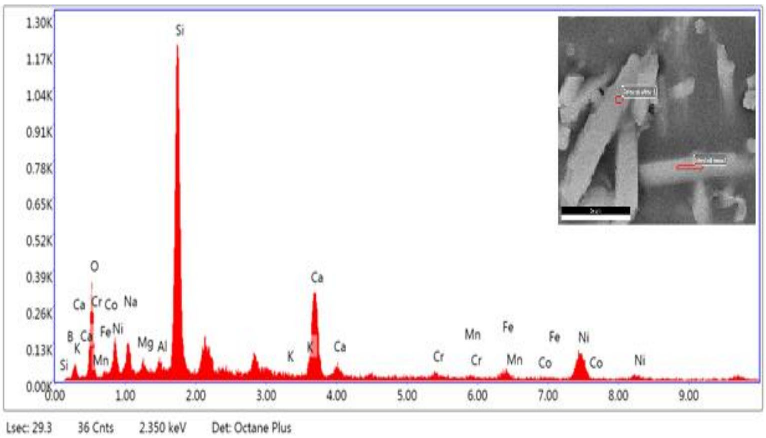


Figure 11. SEM microstructure image a) Distribution of CC crystals in boron glaze at the 10000X magnification b) CC crystal in leaded glaze at 25000X magnification.



Element	Weight %
B_2O_3	15.55
Na_2O	3.20
MgO	0.77
Al_2O_3	1.09
SiO_2	39.49
K_2O	0.50
CaO	16.18
Cr_2O_3	1.57
MnO	0.86
Fe_2O_3	3.86
CoO	0.93
NiO	16.00

Figure 12. EDS analysis of CC crystals in boron glaze at 25000X (B, Fe, Cr, Ni, Co, Mn quantities on the glaze surface).

4. DISCUSSION

In this study, the production ability of black colorants for leaded and boron glazes was examined using industrial products such as chromite, magnetite and laterittic nickel ore, the composition of which is stable.

In the prepared colorants, due to Fe_2O_3, CoO, NiO, and Cr_2O_3 containing of the raw materials used, a decrease in the L* (whiteness) value of the samples used in the leaded glazes compared to the leaded glazes using commercial pigments was observed. The highest decrease in L* value occurred in leaded glaze using calcined colorant, with a decrease of 11.88% compared to the leaded glaze using commercial pigment, and the L* value was measured as 27.37.

A decrease was also observed in the L* (whiteness) value of the samples used in boron glazes. The highest decrease in L* value occurred in boron glaze with calcined colorant with a decrease of 13.81% compared to the boron glaze using commercial pigment, and the L* value was measured as 26.26.
It was observed that the b* (yellowness) value and a* (redness) values showed small change, and the obtained a and b values were less than 1.

Microstructure images and EDS analysis, it is seen that the crystals in the glazes have a heterogeneous distribution. In microstructure analysis, these crystals found in insoluble form within the glassy phase played an effective role in color formation. EDS analyzes show that their crystal structures are rich in Fe_2O_3, NiO, Cr_2O_3 and CoO. SEM-EDS results; the presence of chromium, iron, nickel and cobalt oxide ensured the acquisition of very good black tones in glazes.

As a result, the obtained colorant and calcination applied to this colorant positively affected the color parameters in the glaze compositions where the colorants were used and the color parameters similar to commercial black colorants were found. The colorants added to the glazes covered the body surface perfectly.

ACKNOWLEGMENTS

This study was financially supported by Kütahya Dumlupınar University Scientific Research Projects Co-operative Center with project no. 2017 – 69. We would like to thank our Scientific Research Projects Co-operatorship Center, which provided financial support to the project.

REFERENCES

[1] Arcasoy, A., (1983)., Seramik Teknolojisi. M.Ü.G.S.F. Seramik, İstanbul., ASD Yay., No:2, 13-14.

[2] Eppler, R.A., (2000)., Glazes and Glass Coatings, Am. Ceram. Soc., Westerville, 130-135.

[3] Costa, G., Della, V.P., Ribeiro, M.J., Oliveria, A.P.N., Monros, G., and Labrincha, J.A. (2008). Synthesis of black ceramic pigments from secondary raw materials. Dyes and Pigments, Vol.77, pp.137–144.

[4] Tanisan, B., and Turan, S. (2011). Black ceramic pigments for porcelain tile bodies produced with chromite ores and iron oxide waste. Journal of Ceramic Processing Research, Vol.12, 462-467.

[5] Ozel, E., Kücük, I., and Turan, S., (2002). Synthesis of an iron-chromium ceramic pigment by using limonite and chromite mixtures. Key Eng. Mater., Vol.206-213, 1227-123.

[6] Yang, Y.G., Xu, J.H., Cai, B., Wang, Q.C., Xiu, D.P., Zhao, Z.B., Sun, Q. Z., and Cao, S. L. (2013). Synthesis and applications of black ceramic from recycled industrial wastes. Advances in Applied Ceramics, 112, 146-148.

[7] Tanisan, B., and Turan, S. (2012). Synthesis of Fe-Mn black pigments by using hematite waste and manganese ore mixtures. Trans. Indian Ceram. Soc. Vol.71(1),17-22.

[8] Calbo, J., Sorli, S., Llusar, M., Tena M.A., and Monros, G., (2004). Minimisation of toxicity in nickel ferrite black pigment. British Ceramic Transactions, Vol.103, 3-9.

[9] Özel E., and Turan S., (2003). Production and characterisation of iron-chromium pigments and their interactions with transparent glazes. Journal of the European Ceramic Society Vol.23, 2097-2104.

[10] Dondi, M., Zanelli, C., Ardit, M., Cruciani, G., Mantovani, L., Tribaudino, M., and Andreozzi, G. B. (2013). Ni-free, black ceramic pigments based on Co—Cr—Fe—Mn spinels: a reappraisal of crystal structure, color and technological behaviour, Ceramic Int. 39 (8), 9533–9547.

[11] Schabbach, L.M., Bondioli, F., Ferrari, A.M., Petter, C.O., and Fredel, M.C. (2009). Colour in ceramic glazes: Efficiency of the Kubelka–Munk model in glazes with a black pigment and opacifier, Journal of the European Ceramic Society, Vol. 29, 2685-2690.

[12] http://www.metanikel.com.tr