Kütahya Dumlupınar University
Institute of Graduate Studies

Journal of Scientific Reports-A
E-ISSN: 2687-6167
Number 48, March 2022

RESEARCH ARTICLE

PREPARATION of BLACK COLORANTS for STONEWARE GLAZES with USING Ni-Co COMPOSITE, CHROMITE and IRON OXIDE MIXTURES

Hale YILDIZAY [1*], Fikret AYDOĞDU[2]

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

Received Date:09.03.2022 *Accepted Date:30.03.2022*

ABSTRACT

Black ceramic colorants were prepared from mixing Ni-Co composite, chromite and magnetite mineral as raw materials. The colorant mixture prepared for this purpose was added to stoneware ceramic glazes at 10%,15% and 20% respectively. The prepared colorant added glazes were ground in the jet mill for 15 minutes and sieves. Glazes applied to the stoneware bodies and then fired at 1200 °C in an industrial ceramic kiln. Color values of colorants and colored glazes were measured L*a*b* with a spectrophotometer device. It has been observed that this prepared colorant has similar properties with the color values of the black colorants used in the sector. As a result, it has been shown that the black colorant obtained can be used as a colorant in Stoneware glaze recipes without causing any problems or defects in the final product.

Keywords: *Stoneware, Glaze, Materials, Characterization, Colorant*

1. INTRODUCTION

Stoneware tableware has a wide range of uses today because it has a wide range of colored glazes and is durable. Pure metal oxides can be used in the production of stoneware glazes with different colors, as well as in colorants obtained by mixing raw materials containing appropriate elements in certain proportions and passing them through standard color preparation processes [1,2].

Black colorant is the most preferred color among the colorants used in ceramics. Black colorants have a use of approximately 25% in the ceramic industry [3]. The black color used in ceramics is obtained with two kinds of colorants. First, escolaite—hematite solids $(Cr, Fe)_2O_3$ and secondly, Fe—Cr—Ni—Co—Mn—(Cu—V) system complexes appear as spinel compositions. [4,5]. Eskolait—hematite colorants used in glazes for black color are less stable [6,7]. Therefore, black colorants used in ceramic glazes are mostly preferred in spinel structure [8, 9].

Pure oxides are used to obtain valuable elements such as iron, cobalt, chromium, magnesium, nickel and copper in the spinel structure of black colorants. This increases the final product cost considerably. While the first consideration in colorant production is the selection of suitable raw materials, current trends are towards alternative and cheaper raw materials. In the ceramic industry,

there are studies on the use of different raw materials and wastes to reduce the cost of black color production [10-16].
The aim of this study is to synthesize black color for stoneware ceramic glazes from relatively cheaper raw materials, to determine the color properties and to reveal possible interactions between colorant and stoneware glazes using various ratios of Ni-Co composite, chromite and magnetite mixtures.

2. EXPERIMENTAL METHOD

2.1. Raw Materials

In the production of colorants; Chromite mineral as chromium oxide source was provided from Hayri Ogelman mining company in Bursa Harmancik. Magnetite mineral as iron oxide source was provided from Ferromad mining company in Kütahya Hisarcık district. In addition, the Ni-Co 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.

Ni-Co composite is preferred in the study because it contains valuable elements for black color production such as high amounts of nickel, mangan and cobalt oxide. The Ni-Co composite used in the study is produced by acid dissolving (HPAL) method under high pressure, which is the state-of-the-art application of the most efficient hydrometallurgical acquisition method [17].

Stoneware glazes and their bodies used for colorant trials were obtained from Tulu porcelain company. The commercial black pigments CK13074 (Ferro Corporation), CP 30 (Itaca S.A.) used in stoneware ceramic coloring are chosen as a reference colorant in this study.

The samples of the raw materials used, was melted out in panalytical Wagon 2 model device and XRF (chemical analysis) was carried out on Panalytical brand Axios MAX model device (Table 1).

Table 1. Chemical composition of raw materials.

Oxides (%)	Chromite	Ni-Co composite	Magnetite
SiO_2	10.61	0.6	2.98
Al_2O_3	5.22	0.34	0.95
Fe_2O_3	20.57	0.3	89.93
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

2.2. Preparation of Black Colorants

For the study, black colorant synthesis was made mixing Ni-Co composite, magnetite, chromite and as raw materials. The colorant raw materials used in the study was subjected to wet milled and then dried. In the study, it was determined that 40% chromite, 40% magnetite and 20% Ni-Co composite mixtures.

3. RESULTS and DISCUSSION

3.1. Color Analysis

Black colorant made for this study, were added to the stoneware glazes proportions of 10%, 15 and 20% and mixed and homogenized for 15 minutes using alumina balls in the jet mill. The results obtained by adding 10%, 15%, 20% colorant to the stoneware glaze composition are given in Figure 1. Stoneware glaze is taken from Tulu Porcelain company.

The color characteristics of all stoneware glazes were measured. Color measurements of colorants in stoneware glaze were made with Konica Minolta–Spectrophotometer CM-700d device. The results obtained are shown in Table 2 as L* a * b* parameters. Table 2 is included commercial black pigment of stoneware glaze, Ferro CK13074, for compare colorants.

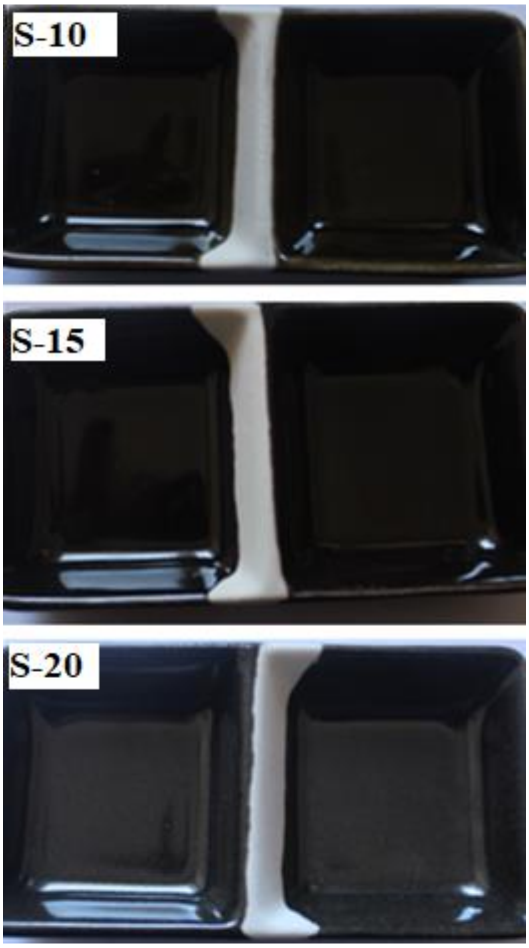


Figure 1. Color effects of 10%, 15% and 20% non-calcinated colorants addition on stoneware glaze, respectively

The results obtained are shown in Table 2 as L* a * b* parameters. Based on the L*, a*, b* values of commercial black pigments, it is seen in Table 2 that the black colorant in stoneware glazes to be produced must have L*<30, a* <1, b* <1 values.

In the Table 2. L a, b values of black colorants in stoneware glazes were measured. It can be seen from the images at the Figure 1, (S-20) that the color turns gray with the addition of 20% colorant in stoneware glaze and the L value increases from (28.18) to (31.54) towards white. The appearance of black color in 15% colorant addition was determined visually and with L,a,b values. 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.

Table 2. L a, b values of black colorants in stoneware glazes.

Colorants in stoneware glaze	L	a	b
Ferro-CK13074	29.9	0.11	-0.23
S-10	28.03	0.11	2.39
S-15	28.18	0.46	0.25
S-20	31.54	0.09	0.82

In the Figure 2, there are images of the pressed samples of black colorant powders that were not heat treated (without calcination), calcined at 1100 and 1200 ºC. L a, b values of black colorant, colorants calcined at 1100°C and 1200°C are given in Table 3.

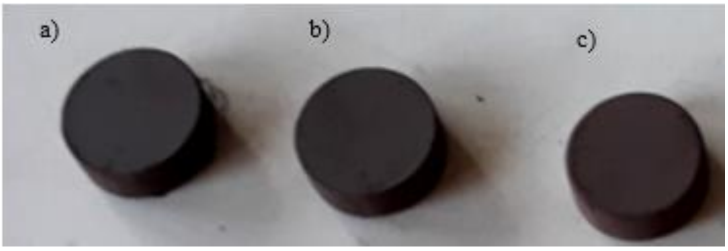


Figure 2. Pressed form of the prepared black colorant powders a) colorant (non-calcinated) b) Colorant calcined at 1100 ˚C for 1 hour c) colorant calcined at 1200 ˚C for 1 hour.

The colorant used in this study was calcined in the electric kiln for 1 hour at a temperature of 1100 ºC and 1200ºC respectively. Porcelain crucibles were used for the calcination process and wet grinding was applied again to the colorants that solidified after calcination. The colorants were sieved and dried.

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

Table 3. L a, b values of Ferro-CK13074, produced black colorant and black colorants calcined at 1100°C and 1200°C .

Colorants	L	a	b
Ferro-CK13074	25.54	-2.75	-4.85
Produced black colorant	28.58	2.05	3.99
Calcinated black colorant 1 hour at 1100°C	29.39	2.13	1.73
Calcinated black colorant 1 hour at 1200°C	24.18	0.63	-0.80

The viscosity of the glazes was determined with using the ford cup viscometer. The viscosity of the prepared glazes is set to 15 sec and litre weights to 1450 g/l. These glazes were then applied on the ceramic bodies by dipping method and fired in the industrial kiln at 1200 ºC. Figure 3 shows the calcinated colorants applied to stoneware glazes and their effect on the bodies and L,a,b values are given in Table 4.

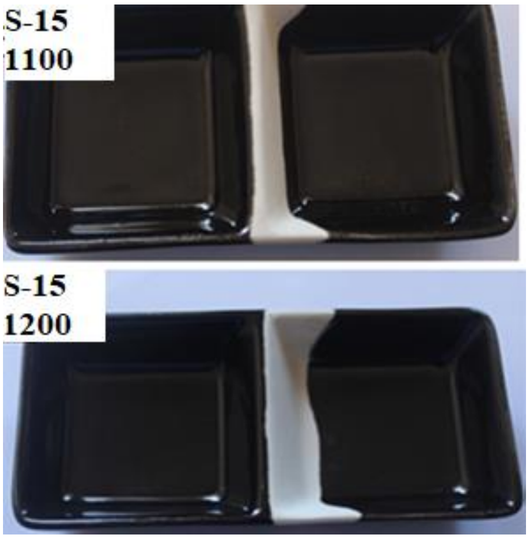


Figure 3. Color effect of the calcined colorants at 1100 ºC and 1200 ºC on the stoneware ceramic glaze respectively.

Table 4. L,a,b values of stoneware ceramic glazes containing Ferro- CK13074 pigment, black colorants calcined at 1100 ºC and 1200 ºC.

	L	a	b
Ferro-CK13074	29.90	0.11	-0.23
S-15 (calcinated 1100 ºC)	26.71	0.61	-0.24
S-15 (calcinated 1200 ºC)	25.94	0.59	0.45

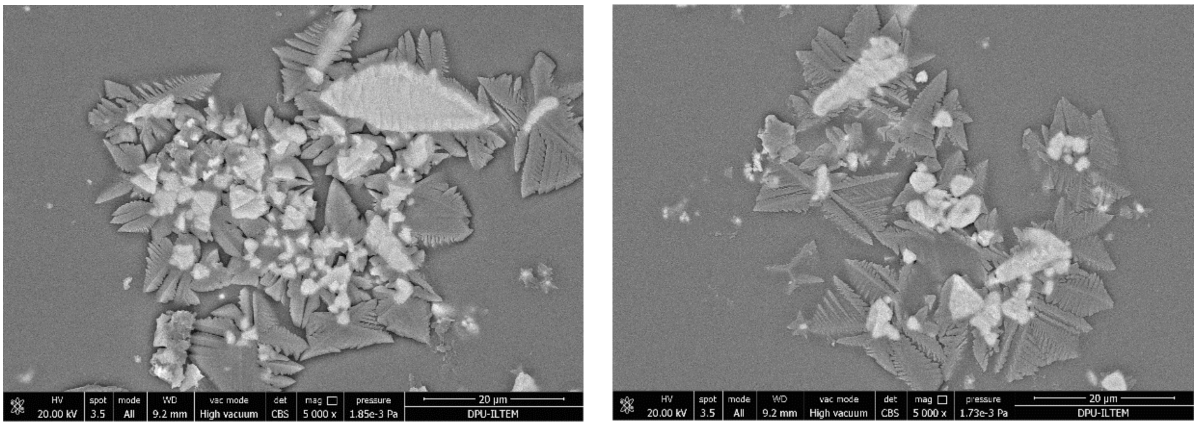
The whiteness value of L was measured as (29.90) in stoneware glazes using commercial black pigments. This whiteness value was measured as (26.71) and (25.94) respectively, by using black colorants calcined at 1100°C and 1200°C in stoneware glazes. The L* value of the black colorants produced by the calcination process decreased compared to the commercial black pigments. This shows us the success of the colorants obtained as a result.

3.2. Microstructure Analysis

The microstructure analysis resulting use of in the glaze the produced colorants was determined with the FEI NANO SEM 650. EDS analysis was performed with the EDAX-EDS device connected to a scanning electron microscope. In the S-15-1100 glaze the occurring crystals and the microstructural appearance are given in Figure 4. In the Figure 5. EDS analysis of crystals in S-15-1100 glaze.

JSR A
Journal of Scientific Reports

Microstructural appearance of the distribution of S-15 (calcinated 1100 ºC) crystals in stoneware glaze are given in Figure 4a and b. In the microstructure images have detected crystals similar to pine leaf. Image of pine leaf shaped of crystal and EDS analysis of crystal is given in Figure 5 and an average oxide composition of the crystals according to EDS in Table 5.



(a) **(b)**

Figure 4. SEM microstructure image and distribution of crystals in stoneware ceramic glaze of S-15-1100. (5000X magnification).

S-15 EDS patterns taken from the glaze crystals of the colorant calcined at 1100 ºC, Fe, Cr, Ni, Co amounts on the glaze surface.

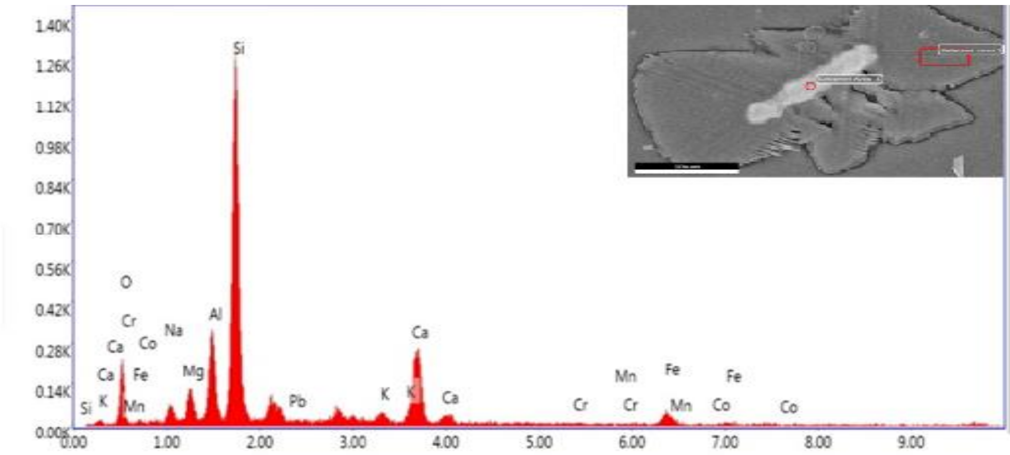


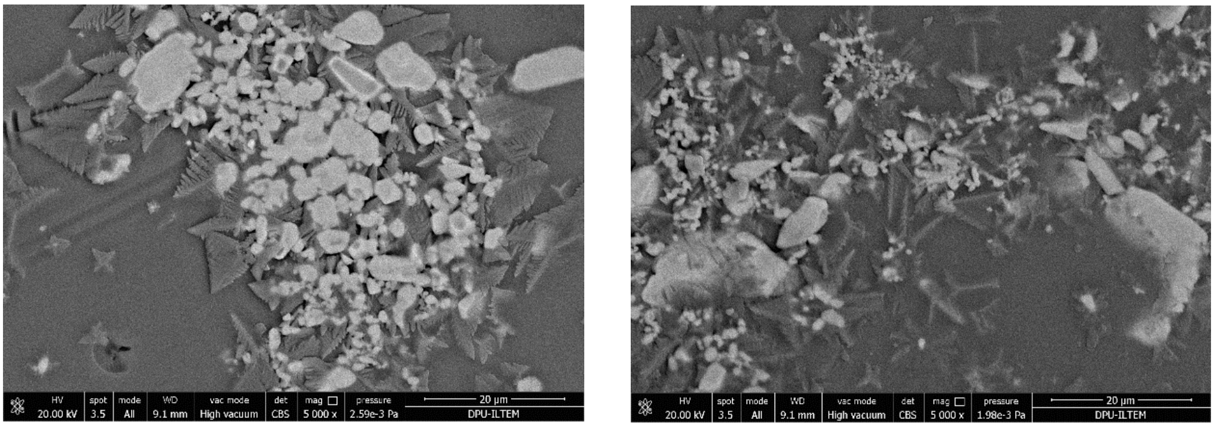
Figure 5. EDS analysis of S-15 (calcinated 1100 ºC) crystals in stoneware glaze at 8000X

(Fe, B, Na, Cr, Ni, Si and Mn quantities on the glaze surface).

Table 5. Average oxide composition of the crystals according to EDS in Figure 5.

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

Microstructural appearance of the distribution of S-15 (calcinated 1200 ºC) crystals in stoneware glaze are given in Figure 6a. In the microstructure images have detected crystals similar to pine leaf. Image of pine leaf shaped of crystal in Figure 6a and 6b. EDS analysis of crystals in glaze is given in Figure 7.



(a) **(b)**

Figure 6. SEM microstructure image and distribution of crystals in stoneware ceramic glaze of S-15-1200. (5000X magnification).

JSR A
Journal of Scientific Reports

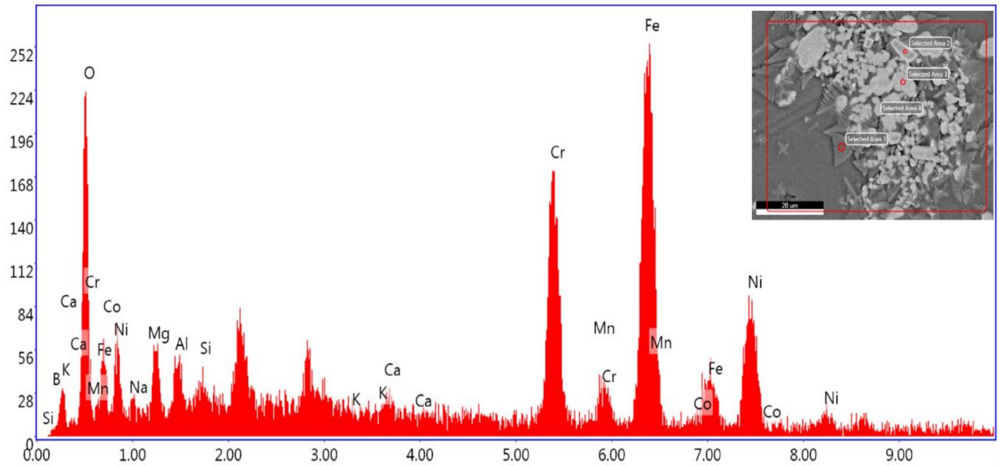


Figure 7. EDS analysis of S-15 (calcinated 1200 ºC) crystals in stoneware glaze at 8000X (Fe, B, Na, Cr, Ni, Co, Si and Mn quantities on the glaze surface).

Table 6. Average oxide composition of the crystals according to EDS in Figure 7.

Element	Weight (%)
B_2O_3	6.99
Na_2O	0.16
MgO	1.04
Al_2O_3	1.04
SiO_2	1.55
K_2O	0.28
CaO	1.04
Cr_2O_3	41.88
MnO	1.53
Fe_2O_3	28.42
CoO	1.34
NiO	14.72

4. DISCUSSION

As a result of this study, it has been determined that using industrial products such as a mixture of Ni-Co composite, magnetite and chromite as a colorant in glazes in which black tones are used in the production of ceramic stoneware glazes, stoneware glazes can be produced without deteriorating their properties and it will contribute economically. The improvement of black tones when the colorant is subjected to heat treatment at different temperatures (1100°C- 1200°C), has created an advantage in the use of this mixture as black color. The obtained colorant and calcination applied to this colorant positively affected the color parameters in the glaze compositions where the colorants were used. The color parameters similar to commercial black pigments were found. The colorants added to the glazes covered the body surface perfectly. As seen in the SEM-EDX results; the presence of chromium, iron, nickel and cobalt oxide ensured the acquisition of very good black tones in stoneware glazes.

ACKNOWLEGMENTS
This study was financially supported by Kutahya Dumlupinar University Scientific Research Projects Co-operative Center with project no. 2017 – 69. We would like to thank our Scientific Research Projects Co-operator Ship 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] Yıldızay H., Taşçı E., (2019). Lateritik Nikel Cevherinden Elde Edilen Nikel-Kobalt Oksit Kompozitinin Stoneware Sırındaki Renk Etkileri. Akü Femübid, Özel Sayı (204-211).

[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] Escribano, P., Carda, J.B., Cordoncillo, E., (2001). Esmaltes y pigmentos cerámicos, Faenza Editrice Iberica, Castellon,

[5] Italian Ceramic Society, (2003). Colour, Pigments and Colouring in Ceramics, SALA, Modena,

[6] Eppler, R.A., (1987). Selecting ceramic pigments. Am. Ceram. Soc. Bull. 66 1600-1604.

[7] Ozel, E., and Turan, S., (2003), Production and characterisation of iron-chromium pigments and their interactions with transparent glazes. J. Eur. Ceram. Soc. 23, 2097–2104.

[8] Eppler, R.A., (1998). “Colorants for Ceramics”; pp. 877–92 in Encyclopedia of Chemical Technology, Vol. 8, Edited by R.E. Kirk, and D.F. Othmer. Wiley, New York,

[9] Maslennikova, G.N., (2001). Pigments of the spinel type, Glass Ceram. 58 5-6.

[10] 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.

[11] 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.

[12] Ozel, E., Turan, S., Çoruh S., and Ergun, O.N., (2006). Production of brown and black pigments by using flotation waste from copper slag. Waste Manage. Res., Vol. 24, pp.125–133.

[13] Costa, G., Della, V.P., Ribeiro, M.J., and Labrincha, J.A., (2008). Forming black spinel pigment from industrial sludge. Am. Ceram. Soc. Bull., Vol.87, No.7, 9101–9107.

[14] 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.

[15] Ozturk, Z.B., Dal, S. (2022). "Characterization of industrial ceramic glazes containing chromite processing waste: Experimental factorial design effects on color parameters", Materials Chemistry and Physics, 282, 125928.

[16] Ozturk, Z.B., Ay, N., (2010). "The effect of ferrochromium fly ash as a pigment on wall tile glaze", Advances in Science and Technology, 88,213-218.

[17] http://www.metanikel.com.tr /mhp-uretiyoruz