

Effect of Kastamonu Red Clay Addition on Color Properties of Ceramic Engobes

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ABSTRACT: Kastamonu province in Northern Turkey found to have new resources of high quality clays which can be used in ceramic industry as raw material. In this study, one type of Kastamonu red clay was selected and its addition effects were studied in ceramic engobe application. This clay was directly used as a colorant agent in the formulation of ceramic engobes. Engobe samples were applied on the surfaces of two different ceramic bodies by casting and then sintering at 1080°C. The ceramic samples were then characterized in terms of surface quality, visible color changes and color parameters measured by chromameter to understand the addition effects of this clay. Depending on the amount of used red clay, gray shades were observed in the measured color parameters. As a general result of the study, it was determined that this type of red clay can be used as a colorant agent in ceramic engobe recipes.

KEYWORDS: Red clay, Engobe, Ceramic, Firing, Color properties

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I. INTRODUCTION

Ceramic products are widely used in building industry and generally are produced from different raw materials such as clays. Clay is one of the important components in the production of industrial and artistic ceramic, glaze, pigment and engobe products. Red clays are one of the common used clayey soils in the production of artistic objects, building materials and structural products [1]. Such clays are also used directly in artistic and industrial ceramics for under-glaze and intra-glaze decoration purposes. Turkey enriched by large resources of clayey minerals, rocks and deposits which have been used in pottery production and building materials for more than a century [2]. Many types of Turkish red clays from different regions were evaluated in the production of engobe and glaze products and the color properties and surface quality were investigated. Engobes are generally used before the glazing of ceramic products to reduce the water permeability, increase the adherence or coloring applications. According to the fabrication process and usage areas, engobes are used as covering the under layers, providing new colors or decoration of the product. Engobe compositions should be designed in a proper way to cover the original color of ceramic bodies, have appropriate density and enough durability during drying, shrinking and sintering. It should melt at lower temperature and remain underneath the glaze layer without fragmentation or peeling [1-2]. Some engobe types can provide special physical properties such as water resistance of the fired ceramic product. Colored clays extracted from nature can be used directly in the engobe production by careful cleaning and filtering processes [3-4]. Raw materials of engobes are generally composed of clay and kaolin, flux, filling material, hardener, binder, opacifier and colorant.

The selection criteria for clays and kaolin used in engobes are commonly whiteness and shrinkage properties. If the high shrinkage is desired, plastic clay is used and for less shrinkage, the amounts of kaolin is increased. In most engobes, the amount of these two materials is ranging between 40-70 wt.% [2]. In the glaze-look engobe, the used clay can be selected according to the desired color and texture properties. Clay materials can be supplied as ferrous clays with low melting temperatures as well as clays with high melting temperatures. The constitution oxides in clay chemical composition have strong effects on the color properties of the final engobe products. For example, small amount of zinc and tin oxides addition can change the color and texture of engobe into white. On the other hand, the color would turn to brown-black by addition of cobalt and iron oxides [5]. Çakır et al. [6] observed that the color of engobes varies from red to brown depending on firing temperature for engobes applied by spraying on stoneware biscuits made of Artvin red clay. The results showed that

cracking and spalling failures were encountered in the bodies fired at 1000 °C. The color of the product, which was sintered at 1100 °C, was slightly darker and a completely cracked surface appeared. Karadeniz et al. [7] reported that engobe samples made of various types of Turkish clays (Aydın, Bolu, Çanakkale, Eskişehir, İstanbul and Nevşehir regions) show wide ranges of colors without using any color additives while giving successful technical results. Karasuet al. [8] stated that iron oxide and iron-containing raw materials, which normally cause undesirable coloration in ceramic industry, can be used to produce different shades as a result of interaction with other colorants. In the study of Güral [3], an engobe made of dam lake clay obtained from Milas region of Isparta province was investigated for the under glaze applications. After firing at 920 and 980 °C, it was observed that the engobe color turns from light brown to dark brown by heating. By addition of other colorant oxides, they reported the formation of gray, red, orange and yellowish tones [3]. In another study carried out by Özenoğlu [4], local Turkish clays from Burdur Ağlasun region were investigated and discussed that how clay samples taken from three different parts of the region effect on surface properties of engobe applied on different ceramic bodies. Various color tones of cream, blue, green, black, brown and red were obtained depending on the amount of used clays and oxides.

The aim of this study is to investigate the possibility and addition effects of red clay obtained from Kastamonu region in Northern Turkey in the production of ceramic engobes. The color properties at different amounts of addition were studied by heating fireclay and stoneware ceramic bodies covered by designed engobes using chromameter.

II. MATERIALS AND METHODS

The main used raw materials for the production of engobe samples were ceramic industry grade kaolin, sodium feldspar, quartz and zircon. A type of red clay obtained from Kastamonu province in Northern Turkey was also selected used as colorant agent to study its effects on color properties and surface quality. This material is generally available in various parts of province and has reddish to grayish color in raw state. This clay was used for a long time in the local handmade pottery products which are famous as red ceramics. The collected sample of red clay was previously purified by washing, screening and passing through a 125 µm sieve. It was dried at 105 °C overnight and then powdered using ball mill. The chemical analysis of the used red clay and other raw materials was investigated by X-ray fluorescence spectroscopy (XRF) on a Xepos 3 machine (Spectro, Germany). For this test, the powders were poured in polymer holders and directly exposed to X-ray. The loss on ignition (LOI) of the materials was calculated by heating of around 1 g sample poured in an alumina crucible at 1050 °C for 1 h in an electric furnace. The chemical analyses of the used raw materials are listed in Table 1.

Table 1. XRF chemical analysis of the used raw materials (wt.%)

Raw Materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	LOI
Kastamonu Red Clay	53.68	23.98	6.94	1.42	0.12	0.34	0.29	2.06	10.03
Kaolin	48.83	35.56	0.89	0.14	0.05	0.35	0.03	2.71	11.30
Sodium feldspar	72.32	16.80	0.05	0.36	0.67	0.26	8.95	0.27	0.32
Quartz	98.15	1.09	0.03	0.02	-	0.05	0.34	0.12	0.21

Table 2 shows the designed formulations of engobe samples. After weighting raw materials according to the specified percentages, each recipe was prepared by mixing the dried powders with 70 ml water, 0.10 wt.% CMC, 0.20 wt.% STTP and then milling in a 500 ml ceramic jar using 200 g balls for 45 minutes. Kastamonu clay was added instead of clay in engobes. After milling, engobe slurries were passed through a 125 µm sieve to reach enough homogeneity before application. Two different ceramic bodies of stoneware and fireclay were selected as substrate for applying engobe samples. These bodies were prepared in the form of 3 cm dia. discs and previously fired at 1000 °C for 2 h in an electric furnace. The prepared engobes were applied by casting to half of all ceramic discs. For final covering of the discs, transparent glaze (Hobby ceramics, Turkey) slurry was used with the same method of casting. After engobe and glaze application, the ceramic discs were dried in an oven at 110 °C for 1 day. After drying, the discs were fired with a heating rate of 5 °C/min at 1080 °C for 30 min followed by cooling with the rate of 10 °C/min. The color parameters of all fired ceramic discs were investigated based on the chromatic coordinates (L, a*, b*) using a CM-2300 chromameter (Konica Minolta, Japan) machine. In this measurement, L* is the aperture axis and L*=0 characterizes black and L*=100 defines whiteness of samples. Other parameters are a* and b* which show green-red and blue-yellow colors, respectively [13].

Table 2. Formulation of engobe samples (wt.%)

Rae Materials	MK3	MK4	MK5	MK7	MK8	MK9
Frit	47	47	47	37	37	37
Kaolin	10	5	0	10	5	0
Quartz	24	24	24	24	24	24
Na-feldspar	14	14	14	24	24	24
Kastamonu red clay	5	10	15	5	10	15

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the color appearances and surface quality of the fired fireclay and stoneware ceramic bodies covered by different engobe formulations. As it is clear in these figures, the surface appearance of the fired ceramic discs at 1080 °C have no trace of cracking or spalling for all applied engobe samples. Engobes are generally low cost products which are mainly prepared from different types of clays. Clays are also wide spread natural raw materials in the earth crust. According to the literature, some of the colorful clays can be applied as colorant in the engobe formulations without further treatment expect of grinding. As it is clear in the figures, Kastamonu clay can be used in the artistic engobes, without causing any problem as a colorant agent and alternative raw material. It is revealed that this clay can be utilized in the production of colored engobes by formation a color change gray tones. This feature could be effective in both aesthetical and technical ceramic linings. Also the peeling and grasping failures were not observed in the engobe and glaze covered fireclay and stoneware bodies fired at 1080 °C.

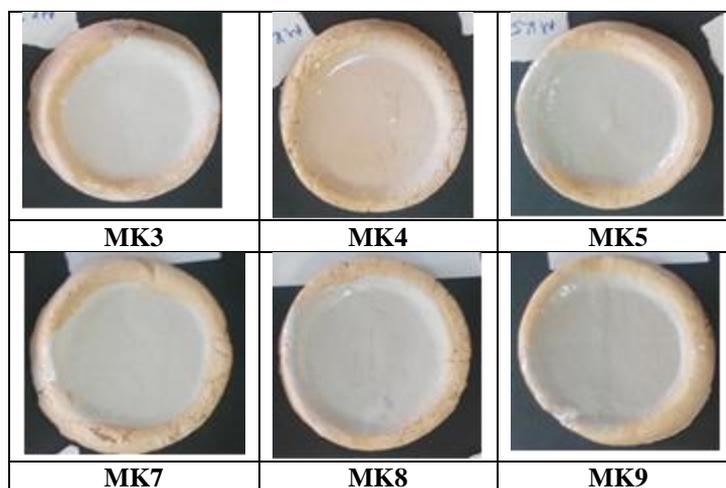


Fig.1. Color appearance of fireclay bodies covered by different engobes

Tables 3 and 4 listed the color parameters of engobe and glaze covered bodies fired at 1080 °C measured by chromameter. According to these results, it is visible that by increasing the amount of the Kastamonu red clay in engobe formulations, the gray color tone increased. As these tables show, L* value which expresses the lightness or darkness of color, decreases due to increase in the amount of red clay, and this makes the color darker. Red clays are vitrifying at different temperatures depending on their compositions. Since they contain high levels of iron and other impurity minerals, they tend to melt at lower temperatures [3]. The lowest L* values of 48.59 and 50.52 were measured by 15 wt.% of Kastamonu clay addition for stoneware and fireclay samples, respectively. The highest value of a* parameter which expresses the redness was measured for lowest additional amount of Kastamonu red clay (5 wt.%) in both fire clay and stoneware bodies. A small increase in b* value was observed due to the increase in the amount of Kastamonu clay. According to the visual appearance of the fired ceramic bodies and measures color parameters, depending on the amount of Kastamonu clay addition, the obtained colors were changed from light gray to dark gray. By increasing the amount of used clay, the colors become darker as seen in Figure 2. For 5 and 15 wt.% of Kastamonu clay addition, light gray and dark gray colors were obtained, respectively. It is clear that this type of Kastamonu red clay can be successfully used as an appropriate material in engobe-glaze applications for artistic purposes at this temperature. According to the XRF chemical analysis of the Kastamonu red clay in Table 1, it is clear that this clay has 6.94 wt.% of iron oxide. It is known that iron content of clayey materials is the main responsible of color changes from light to dark gray in fired glazes and engobes [9-12].

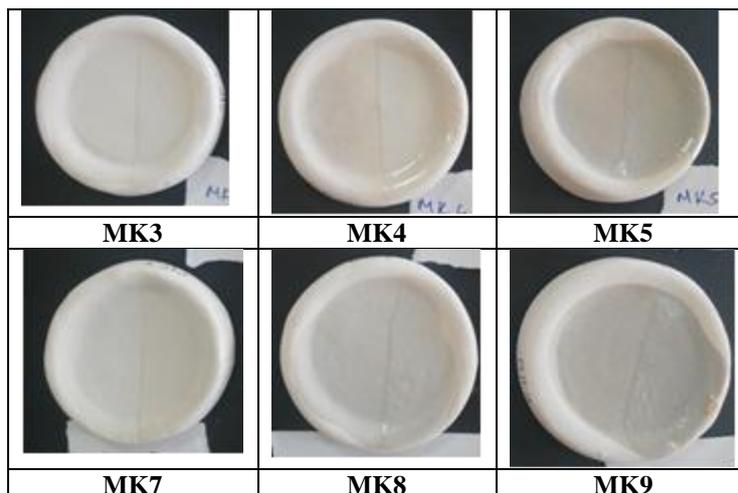


Fig.2. Color appearance of stoneware bodies covered by different engobes

Table 3. Optical parameters of engobes applied on the stoneware bodies

Engobes	L*	a*	b*
MK3	56.41	0.29	17.32
MK4	49.62	-3.97	15.32
MK5	48.59	-5.76	15.01
MK7	64.02	-8.19	16.30
MK8	57.36	-10.72	16.54
MK9	52.25	-11.30	15.38

Table 4. Optical parameters of engobes applied on the fireclay bodies

Engobes	L*	a*	b*
MK3	65.50	-8.01	17.16
MK4	59.54	-9.94	16.79
MK5	52.57	-10.43	15.76
MK7	57.00	3.70	19.35
MK8	49.60	-3.13	15.67
MK9	50.69	-4.91	15.11

IV. CONCLUSION

In this research, a type of red clay from Kastamonu province (Northern Turkey) was investigated as a colorant agent in different percentages in ceramic engobe formulation and its effects were investigated on the color properties of fireclay and stoneware ceramic samples. The applicability of this clay was evaluated as an alternative raw material in ceramic engobes production. According to the appearance of the different fired ceramic bodies covered by the designed engobes, it was shown that there are no effects of glaze failures such as cracking or spalling by using Kastamonu red clay as additive. The color changes with additive amount were also investigated using a chromameter and measuring the variation of L*, a* and b* values. It can be concluded that the designed colorful engobes can be used in ceramic decoration instead of parts of synthetic pigments and dyes.

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