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Color in ceramic glazes: Analysis of pigment and opacifier grain size distribution effect by spectrophotometer

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Abstract

The analysis of the physical interactions between pigments, opacifiers and glazes is fundamental to understand the optical behavior of ceramic glazes. In particular the pigment and opacifier grain size distribution is fundamental to determine the optical properties of the glazes directly changing the color of the product. In this work the influence of the grain size distribution of both zircon ($ZrSiO_4$) opacifier and yellow zircon-praseodymium pigment ($(Zr,Pr)SiO_4$) on the color developed by an opaque glaze was evaluated. The glazes were prepared by addition of zircon opacifier (three different grain size distributions) and yellow Pr-zircon pigment (before and after its micronization) to a commercial frit. The color of the glazes was measured with a spectrophotometer and the absorption and scattering properties of the obtained glazes were explained through the Kubelka–Munk model. The opacifier grain size has the major effect on the scattering of the light while the micronization of the yellow Pr-pigment does not affect significantly the reflectance and thus the color of the evaluated glazes.

Keywords: Color; Spectroscopy; Grain size; Optical properties; Traditional ceramics

1. Introduction

A common problem in the ceramic tile industry is the hue variation between the products that not only impairs the product appearance but also increases stock management costs, and is prejudicial to product competitiveness. This hue variation can be caused by process variables[1] as, i.e. pigment and opacifier preparation conditions that affect the pigments and opacifiers physical and chemical properties.[2–4]

The determination of the hue variation in glazed tiles can be obtained by the analysis of the reflectance curves and the L^*, a^*, b^* parameters provide by a spectrophotometer. In particular, the model developed by Kubelka–Munk[5] supported in reflectance data can be very helpful to explain the color variation. This model relates the reflectance (R) to the absorption (K) and scattering (S) of light by the equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} = f(R) \qquad (1)$$

where R is the fractional reflectance, K is the absorption coefficient, and S is the scattering coefficient at each wavelength of light in the visible region (400–700 nm). This simple relationship can be applied to thick opaque plastics, to paints with a complete hiding, to opaque ceramics.[6] Duncan[7] demonstrated the additivity of the individual contributions of absorption and scattering in a mixture, M, at each wavelength:

$$f(R) = \left(\frac{K}{S}\right)_M = \frac{c_1K_1 + c_2K_2 + c_3K_3 + \cdots}{c_1S_1 + c_2S_2 + c_3S_3 + \cdots} \qquad (2)$$

where c_i refers to the fractional concentration, the subscripts identify the components in the mixture, and the K's and S's are the coefficients for unit concentration. This equation is widely used to predict the color in pigment mixtures.[6–8]

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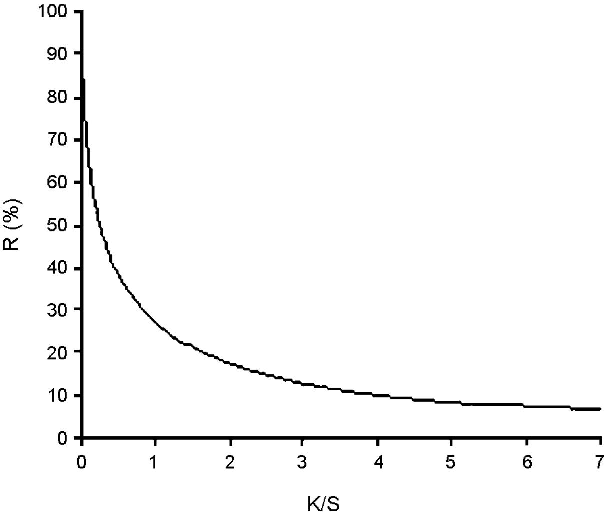

Fig. 1. Graph showing the relationship of reflectance, R_∞, and the ratio K/S according to Eq. (1).[6]

The simple Eq. (1) tells that if the absorption, K, is increased and the scattering, S, is kept constant, the reflectance is decreased. Thus adding a strongly absorbing pigment, such as black, to a system its reflectance decreases; while if S is increased keeping K constant, the reflectance is increased. Thus adding a strongly scattering pigment, such as white, to a system the reflectance increases; if both the absorption and scattering are changed by the same quantity, this will not affect the resulting reflectance or the color (Fig. 1). Thus changing the amount of pigments in a system the reflectance does not change when hiding is complete. Remembering that the nature of the color is described by its spectrophotometric curve and that at each wavelength the Kubelka–Munk model describes how the reflectance is determined, one can visualize how the curve may be modified in a desired way.[6,10]

The reflectance of ceramic glazes is influenced by the grain size distribution and by the refraction index of both pigment and vitreous phase. The grain size distribution has a very important role: pigments with large particle size have, as a consequence, a reduced coating power, whilst smaller particle sizes tend to diminish the intensity of the color and/or to produce different shades tending to easily dissolve into the glaze. Furthermore there is an increase of the white light scattering resulting in a decrease of color saturation.[9–11]

Moreover, the refraction index of the crystal structure is important because both the coloring power and the opacification depend on it. Opacification is a phenomenon that is encountered when a transparent, or partially opaque, phase is dispersed in a transparent medium. White stains are, in reality, transparent crystals with small sizes and high refraction index, immersed in a vitreous phase. The glaze opacification depends on two factors: the particles size and the indexes of refraction of the opacifier and the transparent glass. The larger the difference between these refraction indexes, the larger the phenomenon of matting. The most currently used opacifier is zircon ($ZrSiO_4$). It has a high refraction index (1,96) and is considerably more inexpensive than titanium dioxide, very often used as opacifier too.[9]

Table 1
Chemical composition of the used opaque frit

Oxide	wt%
SiO_2	56.00
ZrO_2	7.40
ZnO	9.60
Al_2O_3	5.07
R_2O ($K_2O + Na_2O$)	3.40
RO (CaO + MgO)	12.80
B_2O_3	5.65
Fe_2O_3	0.08

The influence of the grain size distribution of both opacifier and pigment was evaluated by adding to an opaque glaze a commercial zircon opacifier with three different ranges of particle sizes (micronized (~1 μm), mesh 200 and mesh 100) and yellow Pr-doped zircon pigment before and after its micronization. The color of the obtained glazes were determined by their reflectance curves and L^*, a^*, b^* parameters. The results were explained using the Kubelka–Munk model.[5]

2. Experimental procedure

The grain size distribution of the zircon opacifiers (Ferro) and yellow zircon-praseodymium pigment (Ferro) were measured with a laser granulometer (Fritsh, model Analysette 22). The glazes were prepared in a laboratory ball milling with: 92 wt% opaque frit (chemical composition shown in Table 1), 8 wt% kaolin, 50 wt% water and 5 wt% opacifier at differ grain sizes. For the evaluation of the pigment grain size distribution, glazes with different percentage (range 0.5–5 wt%) of yellow Pr-doped zircon pigment and micronized opacifier were prepared, as shown in Table 2. The total quantity of pigment and opacifier added in the glazes remained constant at 5 wt%. Cylindrical samples (25 mm diameter and 6 mm thickness) of glazes were prepared with a laboratory press humidifyimg the glassy powders with 6 wt% of water. Samples were fired in semi-industrial kiln at 1175 ± 10 °C (total cycle time 40 min). The reflectance curves and the L^*, a^*, b^* parameters of the samples were obtained with a spectrophotometer (Model Datacolor Spectraflash 600) using the optical geometry $d/8$, illuminant D65 and observer 10°.[12]

3. Results and discussion

Fig. 2 shows the difference between the grain size distributions of 100 mesh, 200 mesh and micronized zircon opacifiers. The zircon 100 mesh has the narrow grain size distribution,

Table 2
Glaze compositions prepared in this study

Pigment (wt%)	Opacifier (wt%)
5.0	
2.5	2.5
1.0	4.0
0.5	4.5