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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:

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

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:

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

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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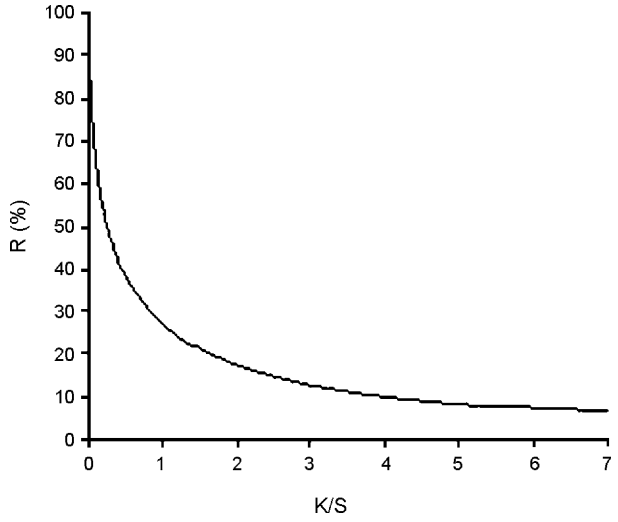

Fig. 1. Graph showing the relationship of reflectance, R_∞, and the ratio K/S according to Eq. (1).[6]

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 $1175 \pm 10\,^{\circ}C$ (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

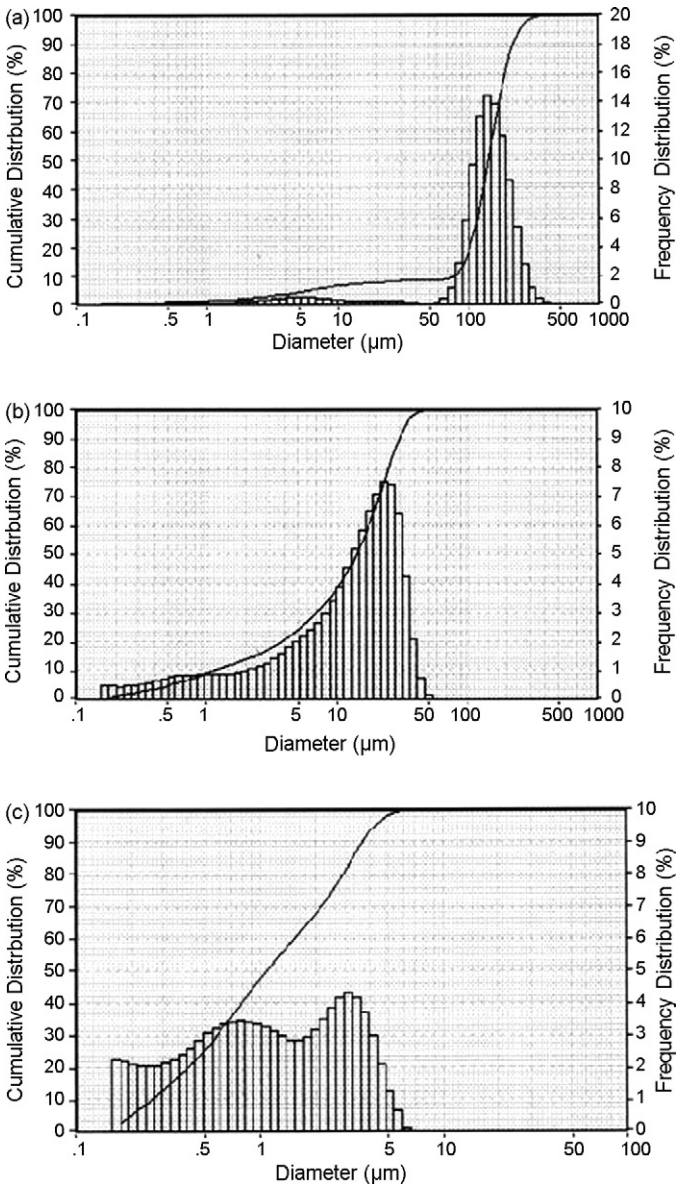

Fig. 2. Grain size distributions of zircon opacifier: (a) 100 mesh, (b) 200 mesh, and (c) after its micronization.

practically monomodal with a medium particle size of 144 μm. The zircon opacifier 200 mesh instead has a deeper grain size distribution with higher percentage of fine particles with main particle size of 14 μm. The micronized zircon opacifier has a bimodal distribution with particles smaller of 5 μm and medium particle size of 1 μm. The chosen opacifiers hence have grain size distributions significantly different. The reflectance curves of the obtained glazes with these three opacifiers are shown in Fig. 3. The L^*, a^*, b^* parameters and the ratio K/S at 420 nm are shown in Table 3. The reflectance curves of the glazes with 100 and 200 mesh zircon opacifier are very similar, without a significative modification even if the medium particle size is drastically reduced by one order of magnitude from 144 to 14 μm. The same occurred with the L^*, a^*, b^* dates and the K/S ratio. A significative increase of the reflectance was observed when micronized zircon opacifier was used. The K/S ratio

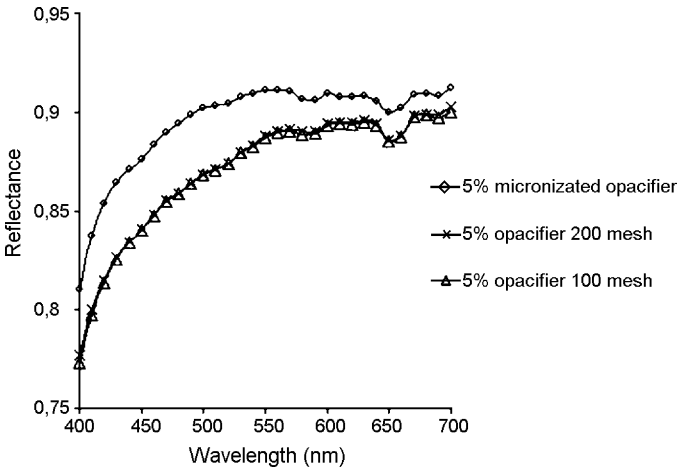

Fig. 3. Reflectance curves of the glazes with 5% zircon opacifier: 100 mesh, 200 mesh and micronized.

was reduced with the increase of the light scattering. Thus the micronization of zircon opacifier (that enables the obtainment of particles smaller than 1 μm) provokes the more effective effect on the light scattering and, as a consequence, on the reflectance and the L^*, a^*, b^* parameters.

In Fig. 4 the grain size distributions of the yellow zircon-praseodymium pigments, as received and after micronization, are reported. The micronization of the yellow zircon-praseodymium pigment displaces the peak of the granulometrical distribution to smaller values leaving it narrower. The medium particles size for the as-received pigment is 9.6 μm while the micronized particle size has a medium value of 3.2 μm. The reflectance curves of the glazes with the yellow zircon-praseodymium pigments are shown in Fig. 5. The figure shows as, in spite of the reduction of the medium particle sizes, the color of glazes is very similar because the reflectance curves have deviations smaller then 1.0%. This behaviour can be explained hypothesizing that the effect of the yellow zircon-praseodymium pigment micronization can be masked by the opacifier added. However, comparing the spectral curves of glazes with only the yellow zircon-praseodymium pigments, before and after its micronization (Fig. 6), the same behaviour is observed, not presenting any significative changes in the reflectance curves. Moreover, L^*, a^*, b^* values do not present any significative changes (Table 4). This behaviour can be explained through the Kubelka–Munk model that relates the absorption (K) and scattering (S) with reflectance (R). Probably the absorption and the scattering of the light provoked by the yellow zircon-praseodymium pigment have been changed by the same quantity

Table 3
L^*, a^*, b^* parameters and K/S ratio of glazes opacified with zircon with differ grain size distribution

5% opacifier	L^*	a^*	b^*	K/S (420 nm)
100 mesh	95.31	−0.27	3.04	0.02
200 mesh	95.27	−0.25	3.07	0.02
Micronized	96.30	−0.73	2.08	0.01

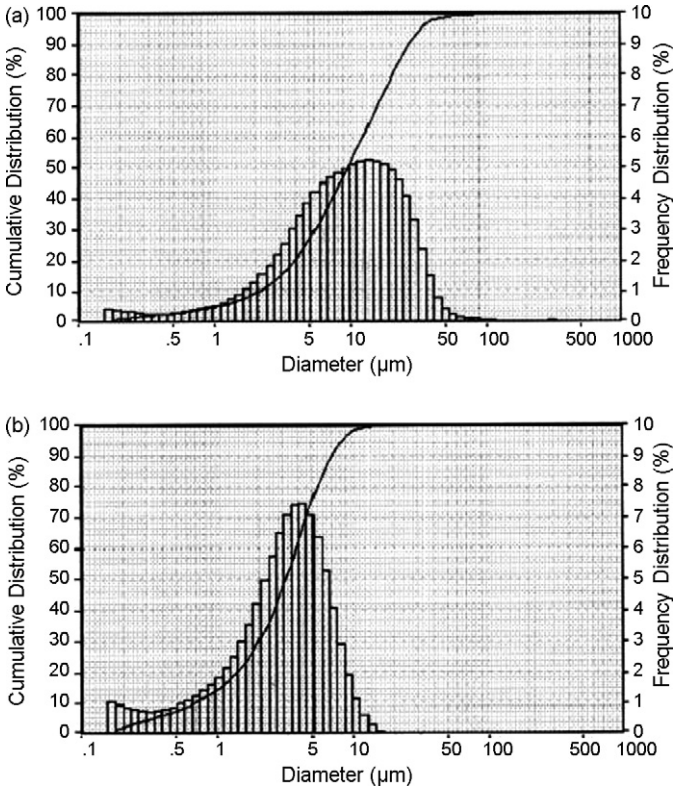

Fig. 4. Grain size distribution of the yellow Pr-doped zircon pigment: (a) before and (b) after micronization.

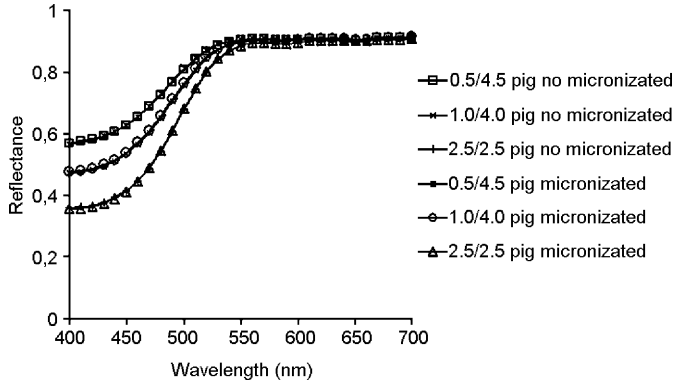

Fig. 5. Reflectance curves of the yellow glazes with different additions of zircon opacifier (mirconized) and yellow pigment.

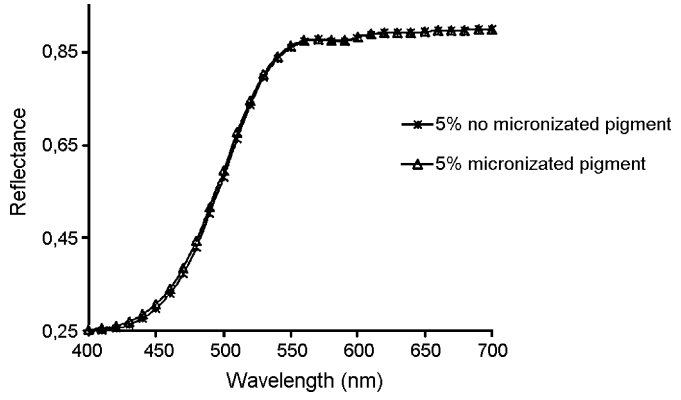

Fig. 6. Reflectance curves of the yellow glazes with 5 wt% of yellow pigment before and after its micronization.

Table 4
L^*, a^*, b^* parameters and *K*/*S* ratio of the glazes containing the yellow pigment before and after its micronization

Pigment (wt%)	Opacifier (wt%)	L^*	a^*	b^*	*K*/*S* (420 nm)
Micronized yellow pigment					
5.0	–	91.00	−3.36	44.90	1.05
2.5	2.5	92.64	−4.05	34.90	0.56
1.0	4.0	94.13	−4.03	24.53	0.27
0.5	4.5	94.83	−3.58	17.97	0.15
Non-micronized yellow pigment					
5.0	–	90.80	−2.99	45.60	1.07
2.5	2.5	92.62	−3.87	34.86	0.55
1.0	4.0	93.98	−3.96	24.79	0.27
0.5	4.5	94.80	−3.45	17.89	0.15

as the yellow pigment particle size is reduced. In fact the higher probability of collision between light and particles, more frequently with the decrease of particle size, can increase the light scattering proportionally to the increase of the absorption, maintaining the *K*/*S* ratio constant, as shown in Table 4. Consequently the reflectance curve and the L^*, a^*, b^* parameters are not affected by the micronization of yellow zircon-praseodymium pigment.

4. Conclusions

The obtained results show, regarding the effect of opacifier particle size on light scattering, that significant changes were observed only with the micronized one.

Moreover, the obtained results showed that the micronization of the yellow zircon-praseodymium pigment do not significantly affect the color of the produced glazes concluding that in this case micronization is not a necessary step.

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