USE OF ZIRCONIA TO ACHIEVE OPACITY IN TRANSPARENT ENAMELS – CHARACTERIZATION USING KUBELKA-MUNK TECHNIQUES

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ABSTRACT

All materials that form a ceramic enamel – frits, pigments, and opacifiers – can change its colour. It is usual to emphasize the role of pigments in this matter, although other components have the same importance in enamel colour development. Particle size, refractive index and volume fraction of the opacifier being used affect the enamel opacity degree. This work deals with the influence of the zirconia (zirconium silicate – $ZrSiO_4$) fraction on the opacity degree of transparent enamel. The glaze opacity characterization was made measuring the samples' spectral reflectance curves by means of a spectrophotometer. The light scattering (opacity degree) was determined using the ratio between light absorption (K) and scattering (S) coefficients, obtained from the Kubelka-Munk theory. From the spectral reflectance curves and Kubelka-Munk K/S ratio measurements it is found that for zirconia fractions above 12% (weight) there are no changes in the enamel opacity degree.

KEYWORDS: Ceramic Enamels; Zirconia; Kubelka-Munk; Spectrophotometry.

INTRODUCTION

The main factors that determine light scattering of a two-phase system (and consequently affect opacity) are particle size, refractive index and volume of the second phase. The opacification of enamels and glass-silicate systems that have a refractive index varying from 1.49 to 1.65 depends on the effectiveness of the opacifier; this must have a substantially different refractive index from those values, an appropriate particle size for the incident light and a high volume fraction [Kingery, 1960].

The zirconia currently used as an opacifier possesses a high refractive index (1.96), high dispersion and is considerably cheaper than commercial titanium oxide also used as an opacifier. Regarding colour measurement, the CIELAB scale (or L*a*b* values) is the most widely used to measure the colour of an enamelled ceramic surface, even though presenting some errors. The L*a*b* values in most cases are not related with the concentrations of pigments and/or opacifiers added to the enamel, making the use of these parameters difficult for colour smoothing. Better results are achieved using the Kubelka-Munk (K/M) theory [Eppler, 1990].

The K/M model relates the coefficients of absorption (K) and scattering (S) with reflectance (R'), in accordance with Equation 1:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad \text{[Eq. 1]}$$

Equation 1 does not consider specular and internal reflectance. Fresnel (1971) made a correction in the equation that considers these factors for ceramic materials:

$$\frac{K}{S} = \frac{0{,}45(1-R)^2}{\left(R^2 + 1{,}36 \quad - 0{,}056\right)} \qquad \text{[Eq. 2]}$$

From the reflectance data, Equation 2 gives the ratio of the K/M parameters (K/S) for any ceramic material [Eppler, 1990].

The objective of this work is to evaluate the effect of the zirconia addition (volume fraction) on the opacification of a transparent enamel by observing the reflectance spectra obtained and K/S parameters.

EXPERIMENTAL PROCEDURE

Transparent enamel suitable for single firing was milled in eccentric mills for 30 min. The enamel consisted of 92% frits (mainly Zn and Ca oxides), 8% kaolin and 50% water, all in weight percent. Enamel opacification was done using zirconia at 500 mesh, the particle size most widely used industrially. The weight percentage of zirconia added in each milling batch varied from 0% to 16%. Table 1 presents the grain size distribution of the zirconia used. The enamels (with previously controlled densities) were applied on tiles coated beforehand with engobe, forming layers 0.6 mm thick.

cumulative %	Particle size (μm)
10	< 0.39
50	< 2.34
90	< 11.15
100	< 23.00

Table 1. Particle size distribution of the zirconia used (LASER diffraction).

The samples were fired in a semi-industrial roller kiln. The maximum firing temperature used was 1170 ± 10 °C in a 35 min cycle. The L*a*b * colour parameters and spectral reflectance curves of the glazed surfaces were measured using a HunterLab ColorQuest spectrophotometer with 45/0 geometry, D65 illuminant and 10° angle, specular component included. The glaze opacification was analyzed by means of the absorption and scattering coefficient (K/S) ratios, calculated from Equation 2 with the spectral reflectance data obtained.

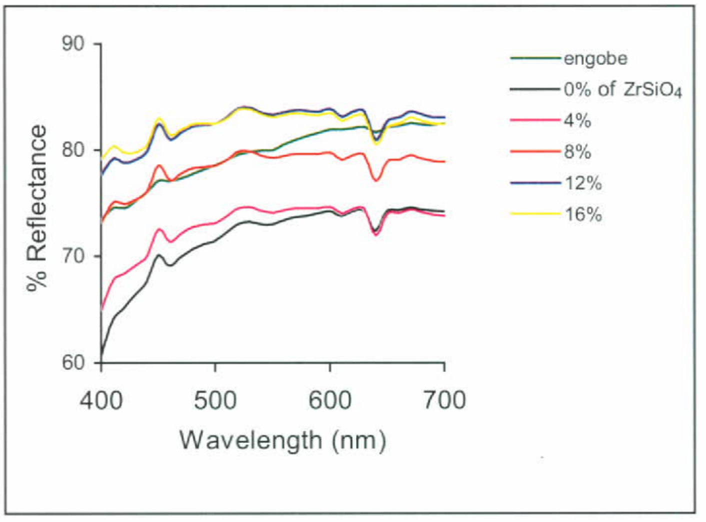
RESULTS AND DISCUSSION

Table 2 presents the measured L*a*b* parameters for both the engobe (after firing) and enamels (glazes with zirconia). The engobe layer was measured as a reference for all enamel formulations. L indicates the luminosity, +a the red tonality, -a the green one, +b yellow and -b the blue one – all in the CIE system.

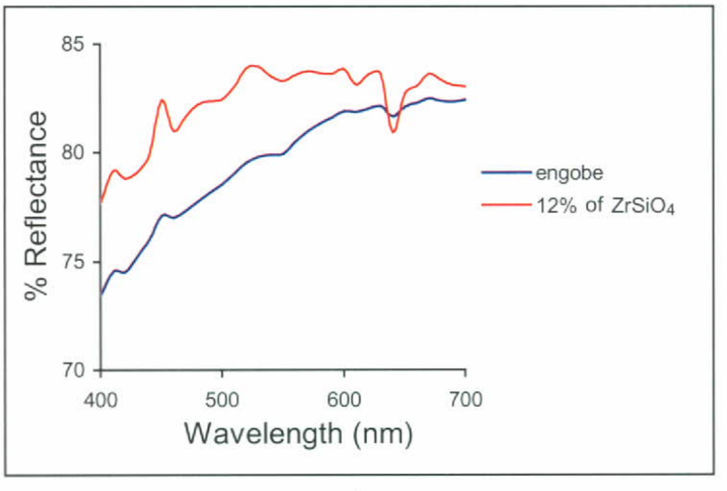
wt% opacifier	L*	a*	b*
engobe	91.8	0.4	2.8
0	88.4	-0.5	3.6
2	89.3	-0.8	3.6
4	88.9	-0.8	2.4
6	90.7	-0.8	2.0
8	91.3	-0.7	1.7
10	91.6	-0.5	1.7
12	93.1	-0.7	1.8
14	92.4	-0.7	1.2
16	93.0	-0.7	1.3

*Table 2. Engobe and enamel measured L*a*b* parameters.*

The engobe and enamel spectral reflectance curves are shown in Figure 1(a). In Figure 1(b) one can compare the reflectance of engobe and enamel with 12 wt% zirconia, showing the reflectance increase.



(a)



(b)

Figure 1. Spectral reflectance curves of engobe and several glazes with zirconia (a), reflectance of engobe and glaze with 12 wt% zirconia (b).

The ratio between the absorption and scattering Kubelka-Munk (K/S) coefficients and the wavelength is presented in Figure 2.

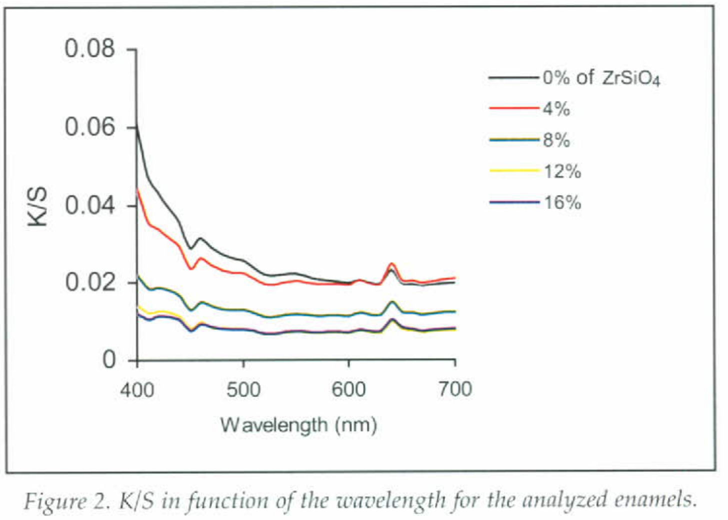


Figure 2. K/S in function of the wavelength for the analyzed enamels.

Figure 3 shows the variation of the ratio K/S in function of the opacifier (zirconia) percentage in the enamel.

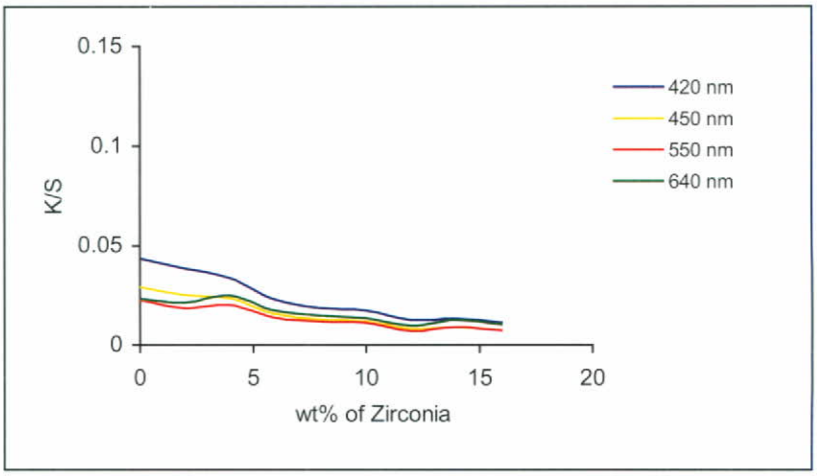


Figure 3. K/S in function of the opacifier percentage in the enamel.

Finally, Figure 4 presents glaze samples with 2 wt%, 8 wt%, 12 wt% and 16 wt% zirconia.

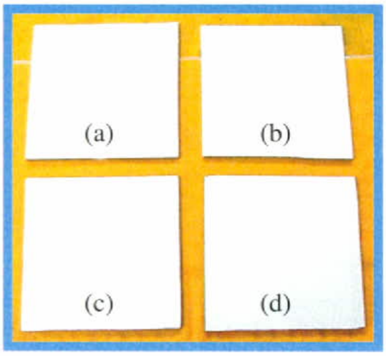


Figure 4. Glaze samples with (a) 2 wt%, (b) 8 wt%, (c) 12 wt% and (d) 16 wt% zirconia.

CONCLUSIONS

L*a*b* parameters provide only indications of colour and opacity, since both are unrelated in a quantitative manner with the opacifier percentages (fractions) in the enamel. Measuring the reflectance spectra and the K/S ratio of Kubelka-Munk, it was verified that, for the transparent enamel used, a larger light scattering (larger opacification) occurred for a 12 wt% zirconia content. Higher percentages (14 and 16 wt%) had not presented significant alteration in opacification using both visual and Kubelka-Munk analysis. The Kubelka-Munk (K/S) parameters (obtained from spectral reflectance curves) provide important information for the development of colours and enamel formulations, since they allow relating the light absorption or scattering to the percentage of a specific opacifier.

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