STUDY OF COLOUR VARIATION IN CERAMIC TILES USING MIXTURE OF PIGMENTS BASED ON TRIAXIAL DIAGRAMS

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1. INTRODUCTION

The increasing evolution of decoration techniques in ceramic tiles has enhanced the possibilities of designing new products. One of the great challenges related to the manufacturing process is to obtain and maintain a standard quality of colours. In agreement to Sánchez et al., the decoration step by serigraphy is the main responsible for colour variations in the products. The serigraphic inks used in the ceramic tile decoration are basically constituted by a mixture of dispersed pigments and milled glass and in aqueous medium. The serigraphic printing is basically a volumetric process. Any factor that can modify the composition and concentration of ink on the surface of a ceramic tile will produce colour variations. In this way, the quantitative effect of a set of factors on the colour variation needs to be known.

The colour is a phenomenon of psychological, biological and physical nature, which depends on the light source, illuminated object and observer. The systems of measurement of colour normally use standard light source and observer. As result, they present a spectre of luminous intensity in function of the wavelength (between 400 and 700 nm). The colour difference can be determined calculating three parameters from the spectre, expressed in a set of Cartesian coordinates X, Y, Z. One of the most common systems is the CIELab, where **L**, **a,** and **b** correspond to the colour coordinates. The calculation of the colour difference in relation to a standard is determined by the parameter ΔE, defined by the Equation A.

$$\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}$$

Equation A

Some researchers observed that the colour difference calculated from Equation A does not represent in a uniform way the perception of a human being. For example, Peñalver et a1. demonstrated that grey, pink, and blue colours present as perception limit, respectively, ΔE = 0.2, 0.4, and 2.0. Studies of pigment formulations using spectral measurements proved to be important tools for predicting colour variations and determining the sensitivity of the composition variation on the ink performance.

2. MATERIALS AND METHODS

Triaxial mixture designs were used for pigment formulation. The measurements of the colour were based on parameters **L**, **a** and **b** of the CIELab system. The present study was carried out with 3 pigments: P1 - Cr, Fe, Co, Ni (grey); P2 - Co, Al (blue); P3 - Co, Si (blue). A serigraphic ink, composed by 66.9% of transparent milled frit and 33.1% of the pigments mixture was applied. The inks were cast on single-fired, white glazed tiles, remaining maintaining a constant ink weight each time. The tiles were fired again at 930ºC for 60 min in an industrial continuous oven. The colorimetric measurements were carried out using a spectrophotometer BYK Gardner with a D65 light source and observation angle of 10°. For each coordinate, an adjustment equation was calculated as a function of the mass fraction of components. The mathematical model that better fits the experimental data was the special cubic.

3. RESULTS AND DISCUSSION

Figure 1A presents the experimental design. Figures 1B, 1C and 1D present the response surfaces obtained, respectively, for **L**, **a** and **b** coordinates.

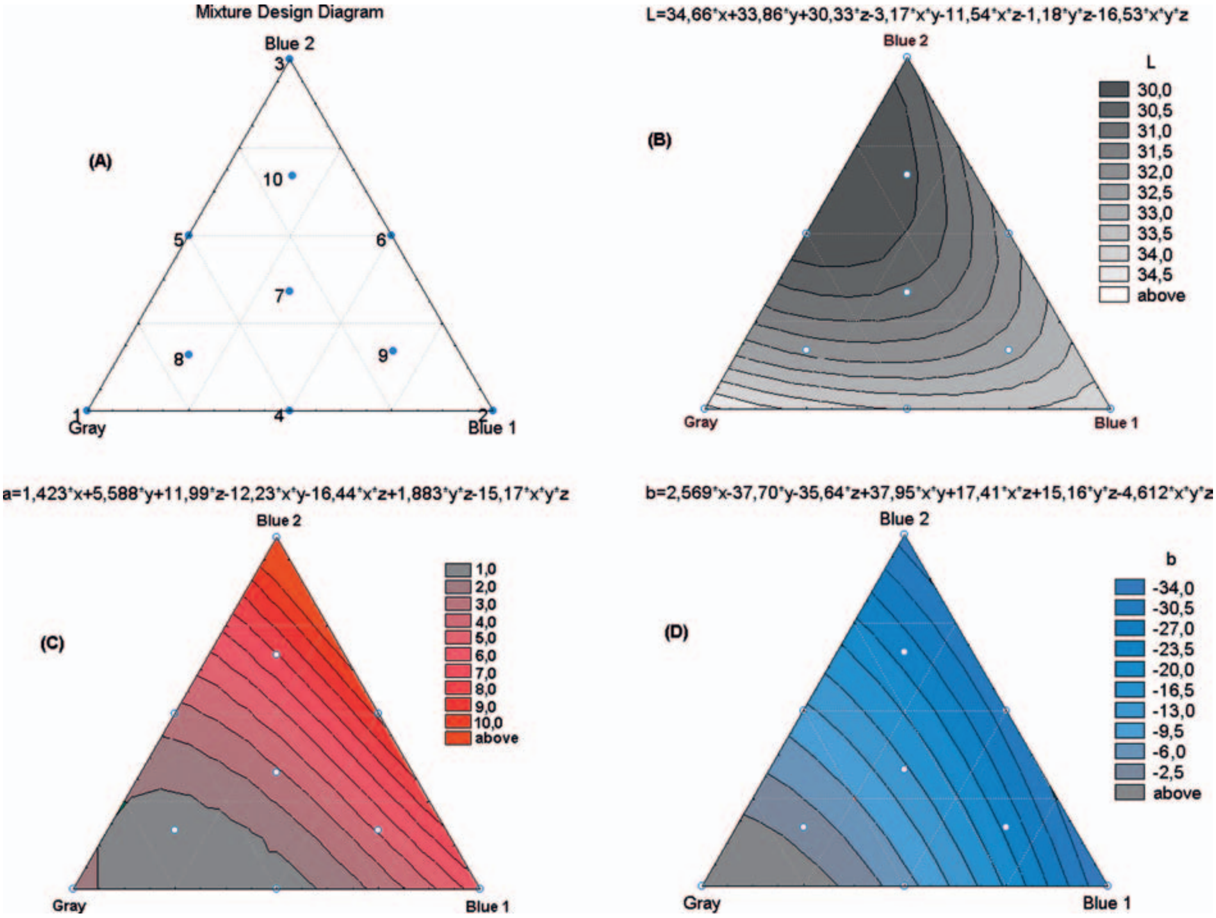

Figure 1. Triaxial diagrams of the studied system: (A) experimental design, and response surfaces for (B) L, (C) a, and (D) b, respectively.

To evaluate the sensitivity of ink in relation to the variation of the pigment composition, ΔE was calculated for a composition area around the central point, i.e. 1/3, 1/3 and 1/3 of each pigment), Figure 2A. A new region of so-called pseudocomponents can be then presented, Figure 2B.

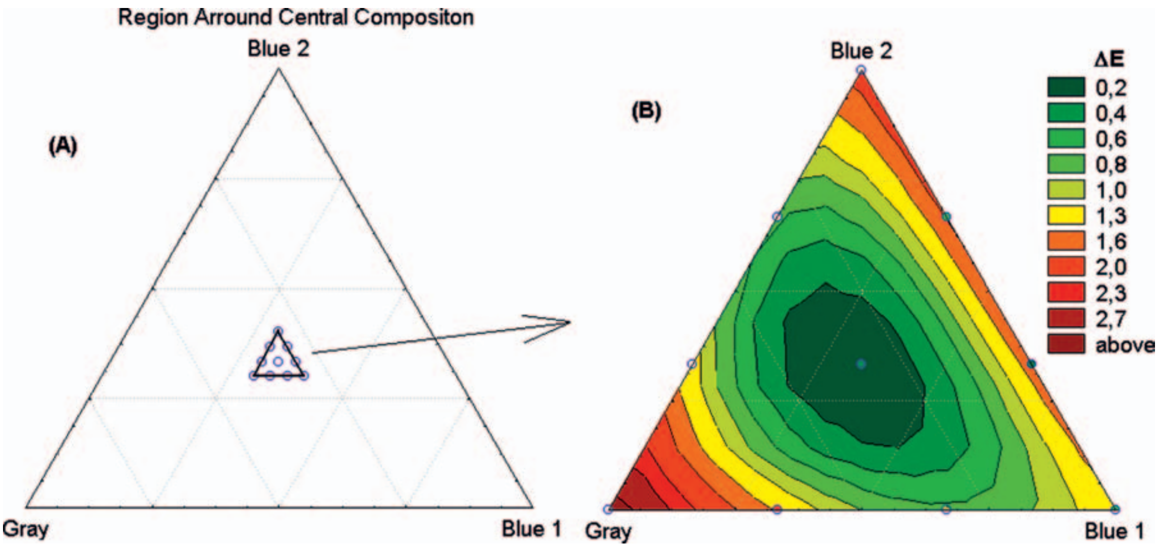

Figure 2

4. CONCLUSION

The pigment system presents higher sensitivity in relation to the amount of grey pigment, since the other two are blue variations. It was quantitatively determined that ± 1% mass variations of the grey pigment causes a DE variation higher than 1. For blue pigments 1 and 2, the limits identified were ± 3% and ± 2%, respectively. Despite the model of experimental adjustment being restricted to the evaluated system, it was possible to quantify the sensitivity of ΔE depending on the relative amounts of components. The higher the difference of the colours in pure pigments the lower tends to be the limits of tolerance in pigments formulation.

REFERENCES

[1] MELCHIADES, F.G. BOSCHI, A.O. Cores e Tonalidades em Revestimentos Cerâmicos. Cerâmica Industrial, 4, 1-6, p. 11-18, 1999.

[2] MORAES, A.C.N. Controle da Variação de Tonalidade na Decoração de Revestimento Cerâmico. Cerâmica Industrial, 4, 1-6, p.32-36, 1999.

[3] PEÑALVER, J. MARTÍ. V. PORTOLÉS, J. NEGRE, P. BARBA, A.GIMÉNEZ, S. MONFORT, E. Estudo das Variáveis de Controle na Aplicação da Serigrafia e sua Influência sobre a Dispersão de Tonalidades nos Revestimentos Cerâmicos. Cerâmica Informação, 4, 5-6, p. 21-26, 1999.

[4] PERIS-FAJARNÉS, G. ALCAÑIZ, M. OLIVARES, M. LENGUA, I. Análise Quantitativa de Variáveis de Impressão Serigráfica que Afetam as Mudanças de Tonalidade em Pisos Cerâmicos Serigrafados, Cerâmica Industrial, 3, 1-2, p. 7-16, 1998.

[5] SANCHEZ, E. SANZ, V. BOU, E. TIRADO, M. Influência da Serigrafia sobre a Variação de Tonalidade de Revestimentos Cerâmicos. Cerâmica Industrial, 4, 1-6, p.19-26, 1999.

[6] SCHABBACH, L.M.Utilização da Espectrofotometria na Caracterização e Predição de Cores de Esmaltes Cerâmicos Monocromáticos Opacos. Tese, Universidade Federal de Santa Catarina, 2004.

[7] SCHABBACH, L.M. FREDEL, M.C. PETTER, C.O. MANFREDINI, T. BONDIOLI, F. Predição da Cor de Esmaltes Cerâmicos Opacos Utilizando o Modelo Kubelka-Munk. Cerâmica Industrial, 9, 4, p. 32-36, 2004.