Dyes and Pigments 95 (2012) 427–430

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Short communication

Tonality variation in ceramic tile silkscreen decoration: Effect of ink density and mesh opening gradient

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A R T I C L E I N F O

Article history:
Received 26 November 2011
Received in revised form
21 February 2012
Accepted 25 April 2012
Available online 3 May 2012

Keywords:
Pigment
Ink density
Silkscreen-printing
Tonality variation
Statistical experimental design
Glazed ceramic tiles

A B S T R A C T

This work aimed to study the effects of ink density and mesh opening on tonality variation of a ceramic glaze decorated by silk-screening. A full factorial experimental design was used in the study, and the control factors were the ink density and the mesh opening; the ink was prepared according a standard ink and it was applied by flexography on a standard glaze. The analysis of variance showed that the screen opening is the factor that most influences the tonality variation of the tiles.

1. Introduction

As the variation of silkscreen ink characteristics can cause tonality variation in tile decoration, one fast and efficient way to control tonality variation in tile decoration is the colorimetric analysis in all development steps. Several factors can influence the development of colors in tile decoration, as metamerism, illuminant, observer and object. The object is the glazed ceramic, a focus of discussion for developers of pigments, silkscreen medium and machinery, among others. Regarding pigments there are some criteria to identify if a specific variation of the pigment will affect its use, such as the color strength, given by the quantity of pigment in ink, with consequences for its use in pure form or in mixtures [1–6].

Silkscreen inks are suspensions with two phases: a solid phase (colored pigment) and a liquid phase (medium). The colored pigments are oxides and the medium is generally an organic mix of polymers or mineral oils. Rheological properties of suspensions are strongly influenced by the medium and by the content of solid particles. The composition of suspensions for silkscreen inks is quite similar to the composition of ceramic glazes; the most important difference is the high oxides content of the silkscreen inks [7,8]. In the case of silkscreen ink it is fundamental to know and be able to control the density and rheological properties besides the pigments used [1–8]. The variation of silkscreen ink rheological and/or storing characteristics will cause tonality variation in tile decoration. One fast and efficient way to control tonality variation in tile decoration is the colorimetric analysis in all development steps.

The colorimetric measurement of parameters dependent on visual comparisons with standards increases the analysis accuracy and eases the formulation and control of the desired colors with greater security, resulting in better use of ceramic pigments. A number of factors can influence the development of colors in tile decoration, as metamerism, illuminant, observer and object. The object is the glazed ceramic, a focus of discussion for developers of pigments, silkscreen medium and machinery, among others [1,2,9].

The formulation of inks for ceramic tile decoration has its beginnings in the development stage of the ceramic design to be produced. Designers are responsible for translating the market trends into wearable tiles, but at the same time the projects must be suitable to the production process at the most practical way possible, providing the desired effect in any produced batch, not varying the design characteristics. When formulating an ink for ceramic tile decoration, the developer should take into account the type of application which is intended: silkscreen, roller decoration,

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0143-7208/$ – see front matter
doi:10.1016/j.dyepig.2012.04.013

injection plotter, inkjet, and others. After setting the type of application, the developer will know the characteristics that the ink should have in order to provide a better workability of the chosen decoration system [10].

As mentioned, the characteristics of the silkscreen inks are usually related to the pigment system and the silkscreen medium, and both influence the rheological behavior of the ink suspension. Forming a solid suspension in a liquid medium, the silkscreen inks require rheological, physical and chemical characteristics as stable as possible in order to maintain color stability during tile decoration. The main aspects for evaluating an ink that meets process and post-consumer requirements are: density, viscosity and tint. These parameters are the most influential in tile decoration process using solid inks [7–10].

Regarding pigments, an inorganic one (ceramic) is defined as a calcined material presenting one or more metallic oxides that, when added to a glaze, confer a uniform color to the ceramic product due the formation of a colored glass coating [11–15]. Structurally, it is formed by a network where both chromophore and modifier elements are combined in order to stabilize or reaffirm the colorant effectiveness. The ceramic pigments are almost always formed by spinel structures [16–24]. The crystalline structure of the spinel group is very complex. Oxygen ions are densely packed forming parallel planes related to the octahedral faces. Divalent cations (for example, Co^{2+}, Mg^{2+}, Fe^{2+}) are bonded with four oxygen ions in a tetrahedral arrangement, while trivalent cations (for example, Al^{3+}, Fe^{3+}, Cr^{3+}) are linked with six oxygen ions pertaining to the octahedral vertices of the structure [15–18]. Each oxygen ion is linked with one divalent and with three trivalent cations. The final product, the enamel, is strongly influenced by both the size distribution and stability of the raw material of which it is composed. Thus, pigment particle size, whether micronized or not, will directly determine the type of chromatic effect after firing [14].

Nowadays most of the Brazilian ceramic tile industry uses the visual comparison method in order to control the tile tonality variation, which is a non adequate method. Therefore, because there are many variables related to the formulation of silkscreen inks for the ceramic industry, the focus of this work was to study by colorimetric analysis the effect of ink density and screen opening in tonality variation of glazed ceramic tiles.

2. Materials and methods

One ink that had the greater degree of color difference was selected from the color palette of a ceramic tile industry after tonality variation analysis by visual perception and by spectrophotometry. In order to study the pigment behavior in silkscreen ink formulations for the decoration of ceramic tiles two variables were selected: screen opening and ink density. Therefore, ink density and screen opening were the factors of a full factorial experiment design. The analysis was made by spectrophotometry using the ΔE parameter, the color difference coordinate, comparing the measures between the color pattern and the color sample. The pigment used was a red Se–Cd oxide and the printing medium (vehicle) was ethylene glycol. A borosilicate glaze was used with 1.5% (mass) pigment addition.

A semi-automatic screen-printing machine was used to apply the ceramic ink regarding the density gradients and the screen openings according to a 3^2 full factorial statistical experimental design with one central point in order to study the implications of these variations in color development, Table 1. The printing machine avoided variations from the speed of application, applicator, spatula tilt, pressure, among others. This type of equipment provides a constant pressure, keeping the application homogeneous regardless of the person to perform the process.

Table 1
Full factorial 3^2 design with a central point.

Run	Mesh gradient[a]	Ink density (g/cm^3)	ΔE (Judds)
1	−10%	1.20	1.1
2	−10%	1.35	2.6
3	−10%	1.50	7.2
4	90 mesh	1.20	1.8
5	90 mesh	1.35	1.4
6	90 mesh	1.50	2.0
7	+10%	1.20	5.3
8	+10%	1.35	3.3
9	+10%	1.50	4.3
10	90 mesh	1.35	1.4

[a] Minor = −10% mesh aperture regarding a 90 ASTM mesh; central = 90 ASTM mesh; major = +10% mesh aperture regarding a 90 ASTM mesh.

Table 1 shows the entire region of the full factorial experimental design, where the studied factors are the density of the ink (g/cm^3) and the screen opening gradient regarding the 90 ASTM mesh, and the levels of each factor are the minor (−10%), central (90 mesh) and higher (+10%) mesh gradient, and ink densities of 1.20 g/cm^3, 1.35 g/cm^3 and 1.50 g/cm^3. These densities were chosen to cover a full range of density variation for flexographic and intaglio printing systems. The mesh size gradient was selected to simulate all decoration conditions used in ceramic printing.

Previously engobed and glazed tiles were silkscreened according the 3^2 experimental design (Table 1). After drying (110 °C, 2 h), five samples for each experiment were fired in a laboratory roller kiln for 21 min at 1180 °C maximum temperature according a single firing cycle. The solid (pigment) and liquid (screen medium) proportions were produced according the experimental matrix. The fired samples were analyzed by spectrophotometry (d8 geometry, 400–700 nm, D65 illuminant) in order to determine the values of ΔL^* (indication of light and dark), Δa^* (green to red) and Δb^* (blue to yellow); the ΔE_{CMC} represents the total change in tonality. It is considered that for shiny surfaces and bright colors a ΔE less than or equal to 0.5 Judd is imperceptible to the human eye, for darker colors and textured surfaces this difference may be 1 Judd.

The spectrophotometry readings were performed according to the experimental matrix (Table 1, three variations of densities and three gradients of application).

3. Results and discussion

Table 1 also shows the results for tonality variation of the tiles according the mesh size gradient and ink density used for all 10 experiments. The results for ink density and mesh size gradient variations show the effect of the silkscreen ink printed over the glaze. The variation in ink density and mesh gradient (screen opening) changes the concentration of pigments in the ink printed over the glaze, resulting in color differences in the fired tiles regarding the ΔE values. The results showed in Table 1 were

Table 2
Analysis of variance (AVOVA) for the color differences (ΔE).

Factor	SS	dF	MS	F test	p test
Mesh gradient (linear)	0.67	1	0.67	0.22	0.66
Mesh gradient (quadratic)	10.64	1	10.64	3.54	0.12
Ink density (linear)	6.51	1	6.51	2.16	0.20
Ink density (quadratic)	2.75	1	2.75	0.91	0.38
Error	15.04	5	3.01		
SS_{total}	36.02	9			

Where: SS is the sum of squares; dF is the degree of freedom; MS is the mean squares; F is the Fisher test; and p is the probability test ($1-\alpha$).

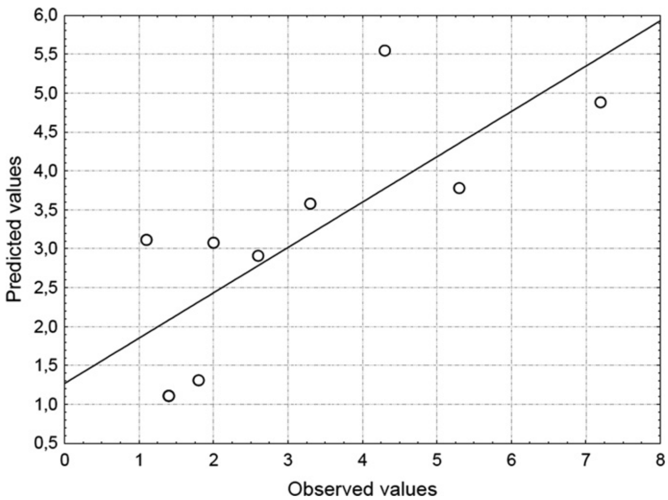

Fig. 1. Observed values versus predicted values for the adjustment to the model.

analyzed by analysis of variance, for determining the most significant effects of the experiment, Table 2.

In Table 2, the factors of study are the mesh gradient and ink density; SS is the sum of squares of main effects (factors), d*F* are the degrees of freedom, and MS the quadratic means. F is the test of statistical significance: the higher the value, the greater the effect of the factor being studied. Finally, *p* is the factor of reliability of the results, where reliability is given by 100 $(1-p)$. Analyzing the data for tonality variation measured by ΔE the most significant factor is the gradient of the mesh size (screen opening) for the quadratic model ($F = 3.54$), and the results have a statistical reliability of 88% ($p = 0.12$). The results have a coefficient of only 53% of the global model analysis, Fig. 1.

To ease the analysis of the effect of the factors on the results, i.e., the effect of mesh gradient and ink density on tonality variation of the silkscreened tiles, response surfaces or contour curves can be used, Fig. 2. 101 code represents the lower mesh gradient, 102 represents the central mesh and 103 the highest. Analyzing the response surface becomes clear that the smallest change in tone occurs for an ink density bellow 1.30 g/cm^3 and the central mesh opening, with tonality values corresponding to ΔE near 1.0.

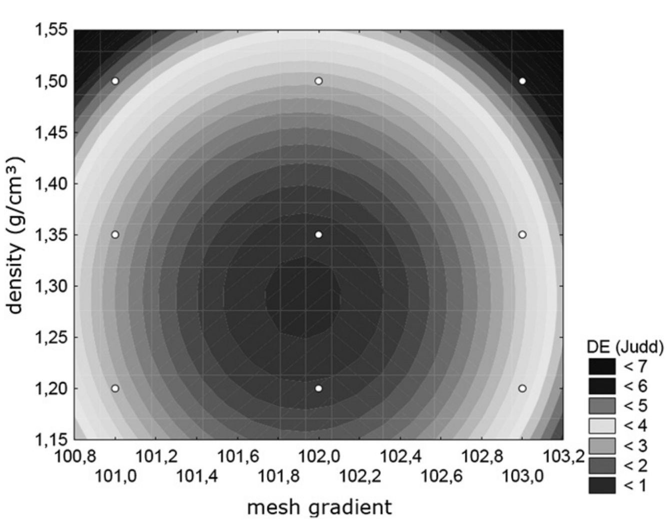

Fig. 2. Contour curve for the effect of mesh gradient and the ink density on tonality variation.

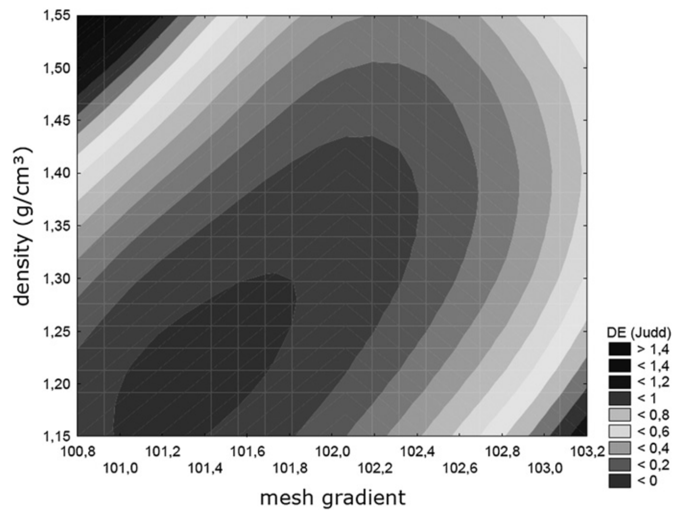

Fig. 3. Desirability contour curve for the effect of mesh gradient and the ink density on tonality variation (Spline fit method).

The fitting equation of the contour curve of Fig. 2 is given by:

$$\Delta E_{\mathrm{CMC}} = 22267.1 - 435.4x + 2.1x^2 - 124.4y + 48.3y^2 \qquad (1)$$

where *x* is the ink density and *y* is the screen opening (mesh gradient).

It is possible to predict the tonality variation, i.e., set the ΔE value to zero, for example. Therefore, defining a desirability contour curve for the tonality variation in function of ink density and screen opening; the result is given in Fig. 3, for the Spline fit method. Using the desirability contour curve the analysis changes: the tonality variation is null ($\Delta E = 0$) for the small screen opening (smaller mesh gradient) and for smaller ink densities, Fig. 3.

The development of inks for ceramic decoration by silkscreening is relatively simple, at least at the laboratory level. However, a good control of the ink composition, screen-printing parameters, drying and firing process, is often necessary to obtain a layer compacity adapted to the desired properties [9,14]. As silkscreen inks are suspensions with two phases, the colored pigment (solid phase) and the medium (liquid phase, generally an organic mix of polymers or mineral oils), the rheological properties of the silkscreen inks are strongly influenced by the medium and by the content of solid particles [7].

Because the composition of suspensions for silkscreen inks is quite similar to the composition of ceramic glazes, the most important difference is the high oxides content of the silkscreen inks. Therefore, the ink density and the way the ink is applied over the glaze layer – the amount of ink, in other words, the screen opening – are the factor that most affect the tonality variation in ceramic decoration by silk-screening.

Intended optical effects such as directed reflection, multiple reflection, interference and color travel (all strong angle-dependent optical effects) are used for functional or decorative purposes, such as security printing or optical filters, cosmetics, plastics, printed products, industrial coatings or car paints. Usually they are achieved by using specially designed effect pigments that are incorporated in parallel alignment in an application system such as an organic medium [14]. But in the ceramic industry that is not the case and the optical effect – tonality variation – showed in Figs. 1 and 2 and modeled by equation (1) is undesirable.

4. Conclusions

The variation in ink density and mesh size gradient (screen opening) changes the concentration of pigments in the ink printed over the glaze, resulting in color differences in the fired tiles regarding the ΔE values. The most significant factor is the gradient of the mesh size for the quadratic model with a statistical reliability of 88%. The smallest change in tone occurs for an ink density bellow 1.30 g/cm^3 and the central mesh opening, with tonality values corresponding to ΔE near 1.0.

However, it is possible to predict the tonality variation. Using a desirability function the tonality variation can be set to zero ($\Delta E = 0$) in this study for the small screen opening (smaller mesh gradient) and for smaller ink densities.

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