INFLUENCE OF SOME PROCESS VARIABLES ON SHADES IN INKJET-DECORATED TILES

M.J. Vicente, F.J. García-Ten, M.C. Bordes, M.C. Segarra, J. González, M.R. Pérez

Instituto de Tecnología Cerámica (ITC). Asociación de Investigación de las Industrias Cerámicas (AICE). Universitat Jaume I. Castellón. Spain.

ABSTRACT

A common problem in decorated ceramic tile manufacture is the difficulty of keeping the same shade in tiles from different lots. In the case of inkjet-decorated tiles, the problem is more pronounced owing to the small particle size of the pigments used in the inks (below 1 µm) and the tiny amount of deposited material (about 10 g ink/m^2). These singular features of inkjet printing can cause little changes in the usual process or substrate variables in industrial production to lead to considerable changes in the resulting shade.

This study examines the influence of some manufacturing process variables on the emergence of shades, with a view to determining which of these most affect the appearance of this problem, and which need to be focused on for control, by implementing the relevant corrective measures.

1. INTRODUCTION

The absence of shades among decorated tiles of the same model is a key requirement for ceramic tile manufacturers when it comes to maintaining appropriate product reproducibility and satisfying the high standards of quality required by an increasingly demanding market.

In recent years, inkjet printing technology has become a widely implemented ceramic tile decoration method. Although the technology is able to suitably reproduce a shade within the same lot, reproducing the same shade across different lots is not so simple and leads to delays in putting the different models to be made into production. It is, therefore, of great importance to understand the relationship that exists between the ceramic process variables and the resulting tile colour.

Studies are available in the literature that focus on in-depth analysis of the influence of inkjet ink characteristics and different printer variables on the characteristics of the deposited drops [1]–[4]. Research has also been conducted into the influence that some process variables can have on the final appearance of the decorated tile [5] [6]. However, few studies relate these variables to the appearance of shades and, in addition, when they do so, they usually do not reproduce the industrial conditions of the inkjet decoration process or the deviations in process and composition variables that customarily occur in industrial practice.

Consultation with several tile manufacturing companies revealed that there was no consensus on which process and composition variables most influenced the generation of shades. This study was, therefore, undertaken to evaluate the influence that different variables relating to the substrate and firing stage have on the resulting shades of inkjet-decorated porcelain tiles. To do so, measurements were made of colour differences among inkjet-decorated test pieces and the printed dots were observed before and after firing.

2. EXPERIMENTAL

2.1. MATERIALS

The study was performed on a glaze substrate, used in porcelain tile manufacture, which was applied onto the body with a slide applicator and yielded an opaque, matt finish. A brown industrial ink, formulated from low-polarity solvents of an organic nature, was chosen because brown tones are among the most widely used colours in industry and, according to information provided by the companies, are among the ones which give rise to the greatest shade problems.

2.2. STUDIED PROCESS VARIABLES

The following variables were studied:

- Variables relating to the substrate (glaze): Temperature, moisture content, particle size distribution, and presence and amount of rheological behaviour-modifying additives.
- Variables relating to the firing stage: peak firing temperature (Tmax) and residence time at peak temperature (tp).

The tested variation range for each variable is set out in the Results section. The influence of each variable was evaluated by comparing the results obtained under standard (STD) conditions, which reproduced industrial manufacturing conditions.

Note that, except when the influence of substrate moisture content was evaluated, all the prints were made on a dry substrate in order to isolate the influence of this variable. It may furthermore be noted that no protective glaze coating was deposited on the decoration, as is typical in floor tile manufacture, to keep the variables relating to this coating from biasing the conclusions. The influence of the protective coating will be analysed in a subsequent study.

2.3. CHARACTERISATION OF THE DECORATED TEST PIECES

The influence of each variable in the appearance of shades was evaluated by quantifying the differences in colour among the test pieces and observing the deposited drops (before and after firing) in an optical microscope.

Colour measurements were made with a spectrophotometer equipped with a small window that allowed the measurement area to be visualised, using a D65 illuminant and 10º observer. The measurements were used to determine the colour difference associated with each variable according to the CIE 2000 expression (Eq. 1), a more complex expression than that customarily used in the ceramic sector, which dates back to 1976 (Eq. 2), but which better represents the perception of the human eye [7]:

$$\Delta E^*_{2000} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \quad \text{(Eq. 1)}$$

$$\Delta E^*_{1976} = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad \text{(Eq. 2)}$$

The printed dots were observed by optical microscopy, micrographs of the printed patches being obtained at 20 magnifications.

3. RESULTS

3.1. DETERMINATION OF THE ERROR ASSOCIATED WITH THE REPRODUCIBILITY OF THE METHOD FOR OBTAINING DECORATED CERAMIC TILES

In order to be able to quantify the influence of each process variable considered in the appearance of shades, it was necessary previously to determine the measurement method error, which included both test piece preparation and colour measurement. To do so, standard, STD, conditions were defined, (Figure 1) and five fired pieces were prepared, applying different ink percentages under these conditions.

To calculate the value of ΔE associated with the measurement method, for each applied ink percentage, the values of the chromatic coordinates of the 5 pieces were first measured. The average value of these coordinates (L^*_m, a^*_m, and b^*_m) were then calculated and the colour difference (ΔE_1, ..., ΔE_5) of each of the 5 pieces relative to the average values was determined by Equation 1. The 5 values of ΔE (ΔE_m) were then averaged and their error (ε) was determined considering a confidence level of 95%. Finally, the measurement method error (ΔE_{STD}) was defined as follows:

$$\Delta E_{STD} = \Delta E_m + |\varepsilon| \quad \text{(Eq. 3)}$$

The values of ΔE_m are plotted in a solid line and those of ΔE_m in a dashed line for each ink percentage in Figure 1. The latter value represents the colour variation associated with method reproducibility when process variables remained constant and includes both the colour measurement error and that corresponding to small imperceptible changes in the process variables. It may be observed that method reproducibility was good at low applied ink percentages and slightly worse when higher ink percentages were deposited. In all cases, though the values of ΔE were higher than the value customarily used to define shades in neutral colours (0.5), they were below 2, the value of ΔE starting at which two colours are usually deemed to be perceivably different in the CIELab space [6][8].

Substrate (glaze)	Residue at 40 μm = 2.0% Deflocculant (TPP): 0.2% Glaze thickness: 300 μm Substrate moisture content: <1% Substrate temperature: 50ºC
Ink	Brown
Print	Printhead: Xaar 1001 GS12 10 patches. (4, 8, 12, 20, 30, 50, 70, 85, 95, and 100%)
Firing	Tmax: 1190ºC tp: 6 minutes

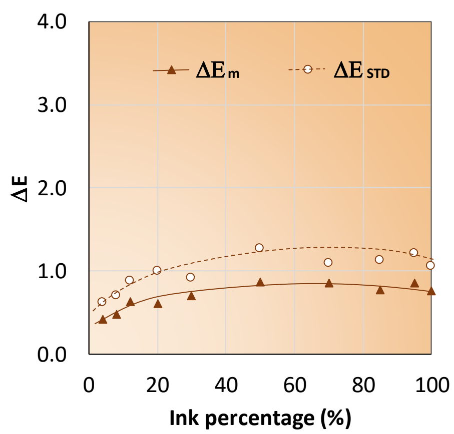


Figure 1. *STD conditions (left) and error associated with the measurement method (right)*

3.2. INFLUENCE OF THE VARIABLES RELATING TO THE SUBSTRATE

3.2.1. INFLUENCE OF SUBSTRATE SURFACE MOISTURE CONTENT

Substrate surface moisture content on printing was measured using an infrared sensor. To be able to quantify this variable, it was necessary to calibrate the instrument to enable the sensor signal to be related to substrate surface moisture content. To do so, the mass loss undergone by a thin layer of glaze and the sensor signal at each moment were continuously and simultaneously recorded. The glaze layer was applied onto a non-porous body, so that the loss of surface moisture content detected by the sensor was exclusively due to evaporation and not to suction by the body.

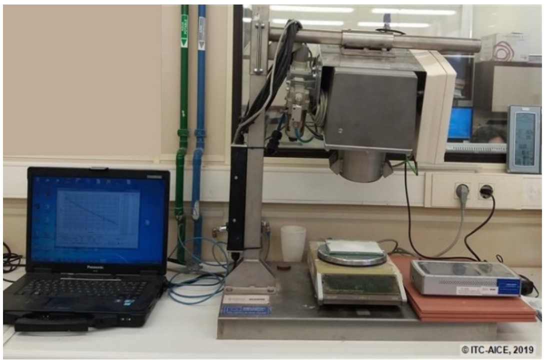


Figure 2. *Set-up used to calibrate the infrared sensor.*

To perform prints on the substrate at different moisture contents, applications were made on test pieces with a slide applicator, the glazed pieces being placed under the sensor for different times, after which they were printed. The preceding calibration enabled determination of substrate surface moisture content at the moment of printing. Two surface moisture contents were tested: 4% and 10% (referenced H4 and H10, respectively). The results obtained were compared with those corresponding to the piece decorated under standard conditions, in which surface moisture content was below 1% (referenced H1, STD).

The effect of substrate moisture content on the definition of the unfired printed dot is shown in Figure 3. It may be observed that, the larger the surface moisture content of the glaze film at the moment of printing, the greater was the dot spread on the unfired piece. This was because, on the one hand, the water contained in the glaze occupied part of the existing voids between the particles of the resulting layers and, on the other, the use of an ink formulated using low-polarity solvents of an organic nature, which were therefore insoluble in the residual surface moisture content of the pieces, favoured the spreading mechanisms of the deposited ink, while concurrently inhibiting ink absorption and imbibition (suction) processes [5].

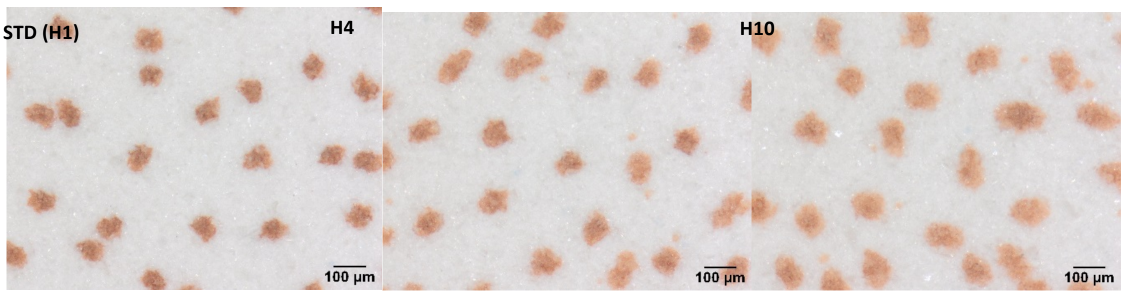
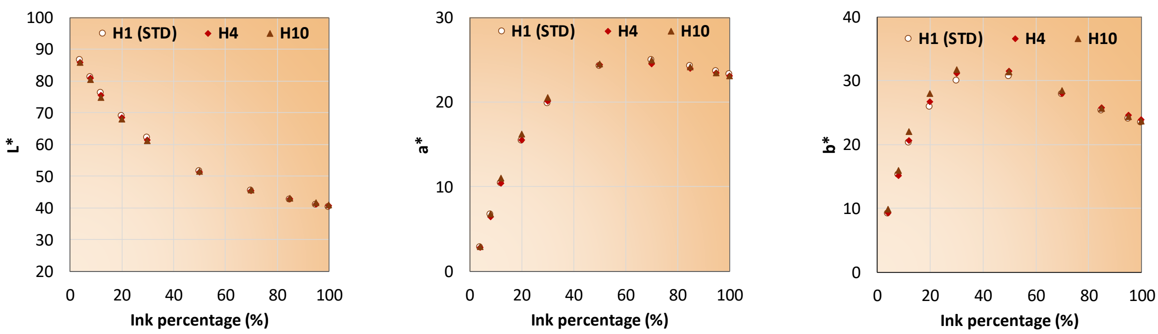


Figure 3. *Influence of substrate moisture content on dot definition. Unfired piece.*

The effect of substrate moisture content on the chromatic coordinates as a function of applied ink percentage is plotted in Figure 4. It shows that, for the three tested moisture contents, an increase in the amount of deposited ink entailed a reduction in chromatic coordinate L* (lower lightness), owing to the rise in ink-occupied substrate surface area. However, the increase in the amount of printed ink did not lead to a continuous rise in coordinates a* and b*, as might have been expected, but a maximum was obtained at intermediate ink percentages (40–50%). Above this percentage, the value of these coordinates decreased anew, particularly in the case of coordinate b*. This occurred because the colour of the fired piece depended both on the surface area occupied by the ink and on the degree of pigment interaction with the glaze. Thus, at low ink percentages, an increase in the deposited amount led to a greater proportion of the substrate surface being occupied by the ink. However, at ink percentages above 40%, at which practically the entire substrate had already been covered, deposition of more ink entailed drop overlapping. In the SEM observation (Figure 5) it may be noted that, in the case of the patch with the smallest amount of ink (4%), the pigment particles located at the edges of the printed dots were fully integrated into the glaze and partly dissolved. This did not occur at high applied ink percentages, at which the entire surface was taken up by the pigment, so that there was less interaction between the surface pigment particles with the glaze, which might explain the decrease in a* and, particularly, in b*.



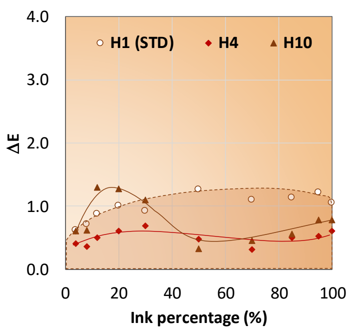


***Figure 4**. Influence of substrate moisture content on the chromatic coordinates and variation in colour.*

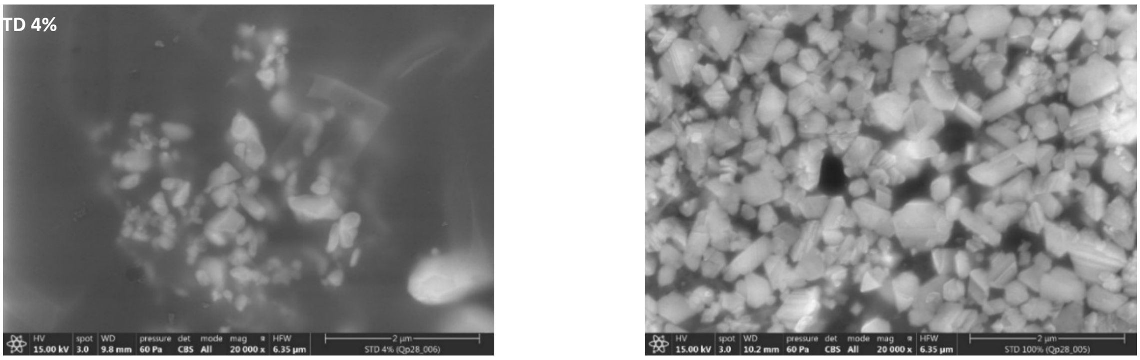


Figure 5. *Surface viewed in the SEM of the patches printed with 4% (left) and 100% (right) ink under standard conditions (STD).*

In regard to the evolution of the chromatic coordinates with substrate moisture content, (Figure 4) small variations were observed owing to the scale used, though it may be noted that an increase in moisture content lowered the values of coordinate L* and increased those of coordinates a* and b* at low ink percentages, which could be related to the greater spread of the printed dots after firing as a result of the greater applied drop spread. Thus, an increase in substrate surface moisture content led to a rise in the covered area at low ink percentages owing to the greater dot spread (drop in coordinate L* and rise in coordinates a* and b*). At higher test amounts of ink, due to overlapping of the deposited drops, these differences were not visually noticeable.

As for the shades generated on modifying substrate moisture content, it was observed that the effect of moisture content was only significant at high moisture contents (H10) and low ink percentages (up to 30%), as may be deduced from Figure 4 in which the values of ΔE_{STD} corresponding to the measurement method error have been represented in a shaded area.

3.2.2. INFLUENCE OF SUBSTRATE TEMPERATURE

Two substrate temperatures at the moment of printing were tested: 50ºC (standard temperature, representative of industrial conditions) and 25ºC. In both cases, the substrates had been previously dried in an oven to keep moisture content from influencing the results.

Figure 6 depicts the micrographs corresponding to observation of the dots printed on the unfired pieces. They show that, under the conditions used, the reduction of substrate surface temperature at the moment of ink printing from 50°C (T50) to 25ºC (T25) did not lead to any substantial changes in deposited dot spread, indicating that the process of drop-to-printed dot conversion did not change, corroborating the conclusions drawn in the literature [5][6]. As there were no substantial changes in the degree of dot spread on the substrate, no significant changes in colour were observed in the fired pieces either, the detected differences in colour being below the ΔE_{STD} values, as may be observed in Figure 6.

However, it should be taken into account that, in industrial production, the decrease in substrate temperature (usually due to production line stoppages) is associated with a change in substrate surface moisture content, so that, at industrial level, changes in shade associated with variations in substrate temperature could develop as a result of changes in substrate moisture content.

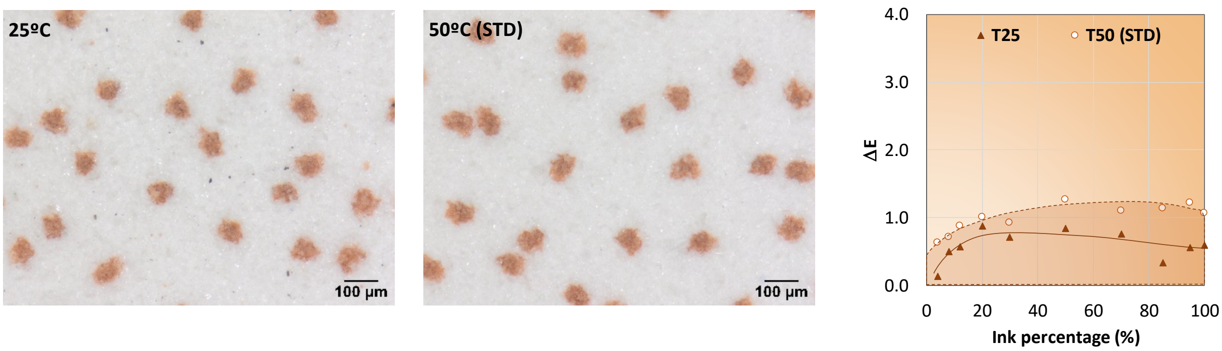


Figure 6. *Influence of substrate temperature on unfired dot definition (left and centre) and on colour variation (right).*

3.2.3. INFLUENCES OF GLAZE PARTICLE SIZE

Two glaze suspensions were prepared, modifying milling time to obtain a residue at 40 µm of 4% (R4) and below 1% (R1), respectively. The variations tested in this study, of the order of those found in industrial practice, did not lead to substantial changes in the degree of deposited drop spread. This contrasts with other studies [9][10] that report differences in ink penetration with glaze particle size, though in those studies the deposited ink volume and differences in particle size were much greater, which significantly affected the microstructure of the substrate (volume and pore size). After firing, no significant variations in colour were observed among the pieces, though changes were noted in other glaze properties that affected fired glaze appearance (gloss and roughness).

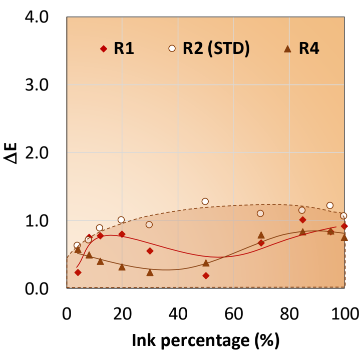


Figure 7. *Influence of glaze particle size on colour differences.*

3.2.4. INFLUENCE OF GLAZE RHEOLOGY

In this section, glaze rheology was modified by reducing deflocculant content, TPP, from 0.2 % (STD) to 0.05% (F) and by adding 0.3% bentonite (B). The changes in viscosity resulting from these changes are summed up in Table 1.

	STD	F	B
Viscosity Ford Cup (s)	54	103(*)	159(*)
Viscosity γ=0.1s^{-1} (cP)	11000	29000	31000
Viscosity γ=1000s^{-1} (cP)	270	290	300

(*) Very high viscosity for industrial glaze application

Table 1. *Glaze viscosity*

The variations in the chromatic coordinates and colour are plotted, in relation to standard conditions, caused by the change in rheological behaviour of the glaze suspension, in Figure 9. It shows that, under the test conditions, the lower degree of glaze deflocculation (F) as a result of a lower deflocculant content did not lead to changes in the degree of dot spread on the substrate (Figure 8) and, hence, nor in the developed colour.

The added bentonite (B), however, owing to its morphology (small particle size and plate-like shape) tended to orient itself horizontally on the substrate surface [11], adversely affecting ink suction and facilitating ink spread. The greater spread of the deposited drops entailed a rise in chromatic coordinates a* and b* in the fired piece, a higher value of ΔE than ΔE_{STD} being obtained at low ink percentages, which indicates that the bentonite addition in the tested proportion could give rise to shades. High values of ΔE were not observed in the patches corresponding to ink percentage above 30% owing to dot overlap.

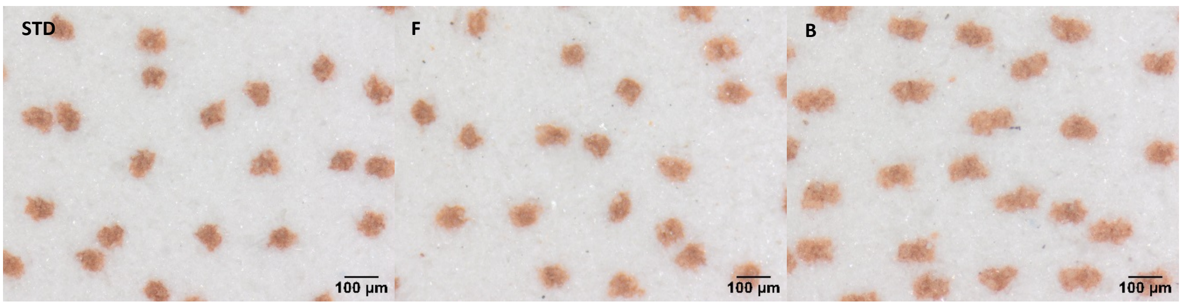


Figure 8. *Influence of glaze rheology on unfired dot definition.*

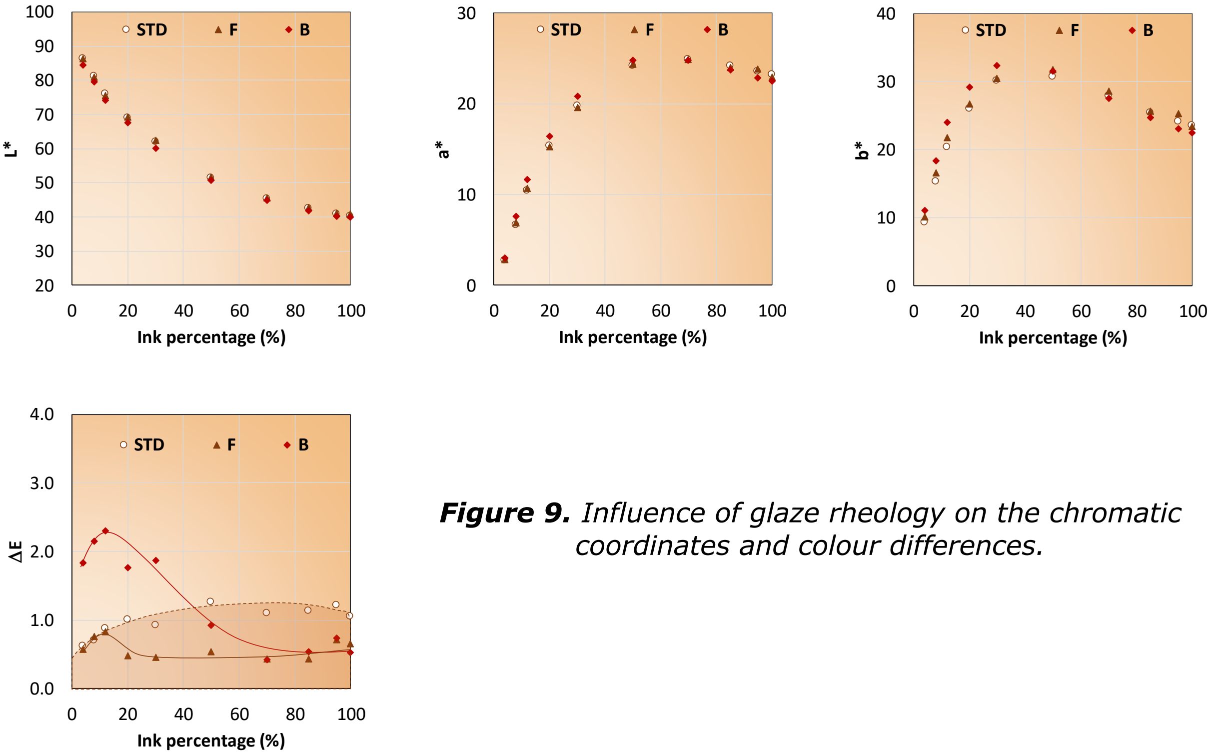


Figure 9. *Influence of glaze rheology on the chromatic coordinates and colour differences.*

3.3. INFLUENCE OF THE FIRING VARIABLES

Analysis of the firing variables must take into account, in addition to the change in the pigment's chromatic coordinates owing to its interaction with glaze, the change in the substrate's own colour. In the tested substrate, it was observed that an increase in the degree of firing, whether because of a rise in Tmax or tp, considerably lowered the three chromatic coordinates, particularly L* and b*.

The effect of the firing variables, Tmax and tp, on the chromatic coordinates of the decorated pieces may be observed in Figure 10. It shows that both variables had a pronounced effect on the three chromatic coordinates, raising coordinate L* as the degree of firing of the pieces increased, both by the rise in Tmax and in tp. This indicates that, as the degree of firing increased, lighter colours, which were not assignable to the change in substrate colour, were obtained.

Coordinates a* and b* did not display the same trend. Thus, as Tmax and tp rose, coordinate a* decreased, indicating that the pieces had a lower red component, except in the range of high amounts of applied ink, at which the values practically coincided. This effect cannot be attributed to the change in substrate coordinate a* because, though this decreased, it did so to a much lower extent.

Coordinate b* increased with Tmax, this effect being most visible when high percentages of ink were applied. The effect of tp on coordinate b* was more complex because, at low applied ink percentages, it decreased when tp rose, this trend reversing at ink percentages above 30%. Again, these colour changes were not due to the variation in substrate chromatic coordinates on modifying the degree of firing.

Observation in the optical microscope of the pieces (Figure 11) only indicated that, on raising the degree of firing, the colour was less intense, which matched the measurements of the chromatic coordinates. This was due to progressive integration of the pigment into the glaze during firing of the pieces, particularly at the edges of the printed dots (Figure 12).

With regard to shade generation, as was to be expected, the variation of both firing variables significantly modified the values of ΔE, these lying above ΔEm (Figure 13). This effect was of the same order when Tmax increased or decreased in relation to STD temperature (1190°C), but it was much more pronounced when the value of tp decreased than when it increased.

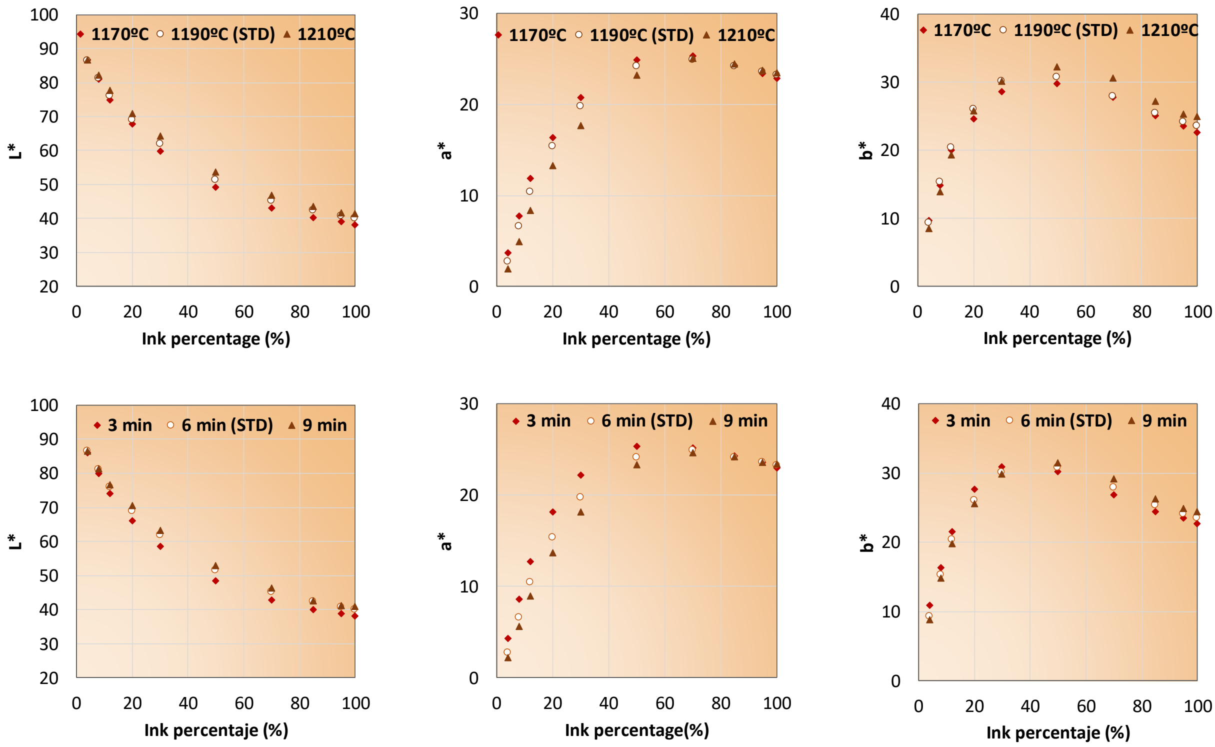


Figure 10. *Influence of Tmax (top) and tp (bottom) on the chromatic coordinates.*

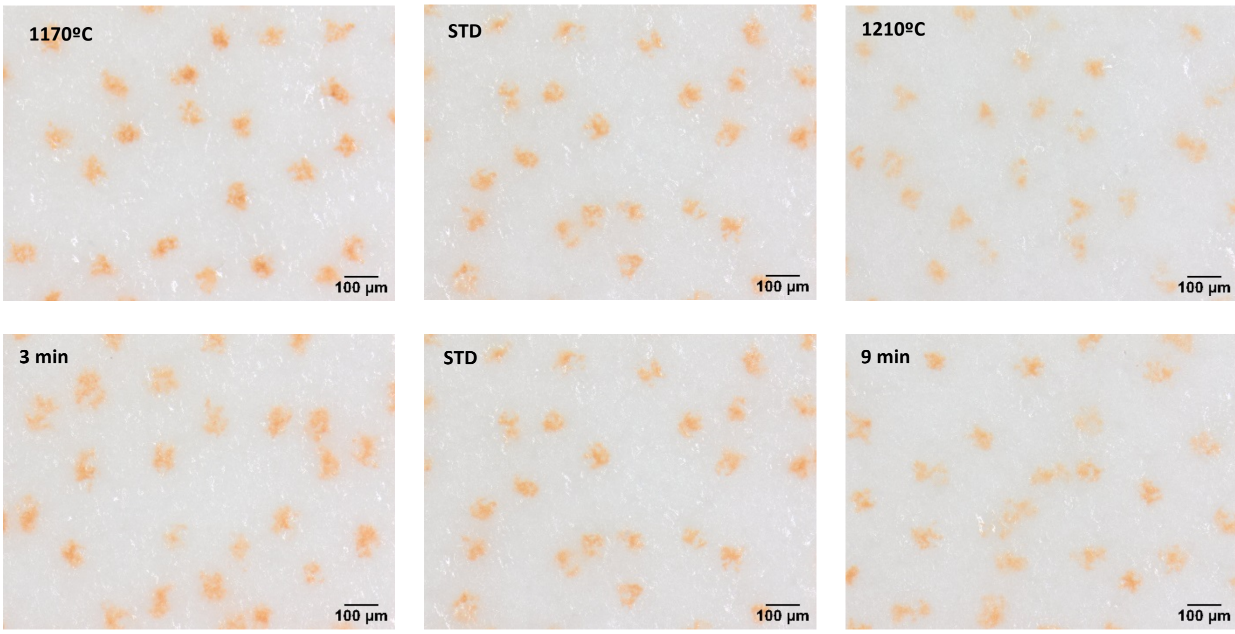


Figure 11. *Influence of Tmax (top) and tp (bottom) on dot definition.*

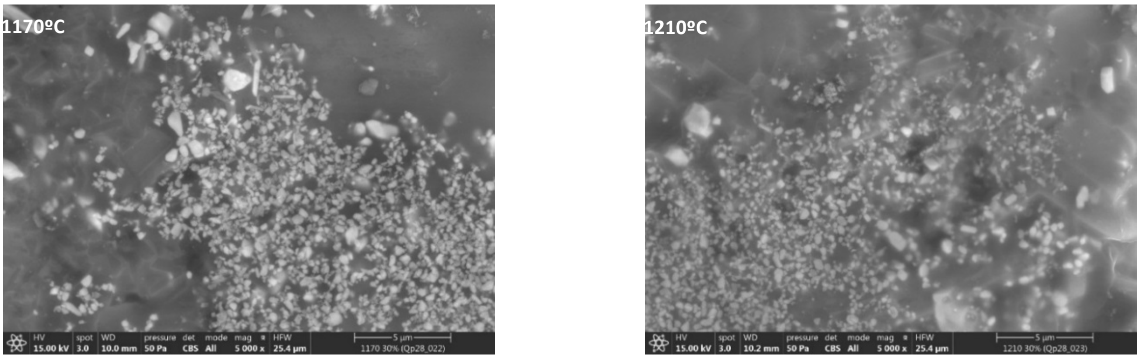


Figure 12. *Surface viewed in the SEM of the patches printed with 30% ink. 1170ºC (left) and 1210ºC (right).*

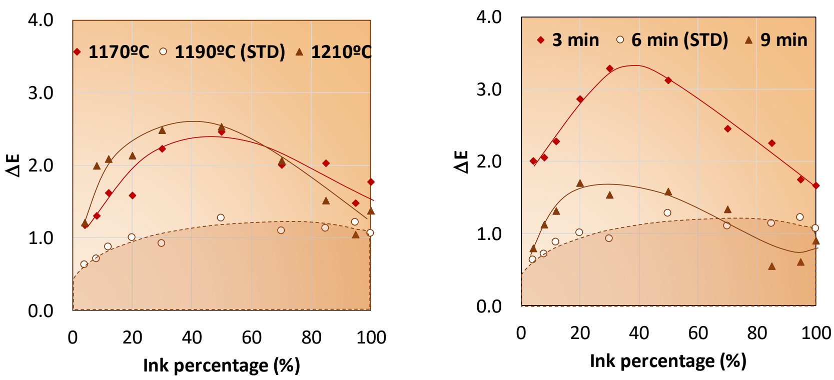


Figure 13. *Influence of Tmax (left) and tp (right) on colour variation.*

4. CONCLUSIONS

The influence that some substrate and process variables had on the appearance of shades in glazed porcelain tiles was studied on a laboratory scale, reproducing as far as possible industrial inkjet application conditions. The results indicate that, of the studied variables, moisture content of the substrate onto which the inks were applied, bentonite content, and particularly the degree of firing of the pieces had the greatest influence.

Substrate moisture content may change, for different reasons, during tile manufacture: changes in glaze characteristics (density, rheological properties, applied amount, etc.) and production line stoppages. In this case, changes in substrate moisture content can alter ink suction rate, modifying printed dot spread.

The plate-like particles in bentonite can orient themselves superficially, forming a more impermeable layer, which modifies ink suction and facilitates drop spread. In addition, this material's high water-capturing ability could also influence the drop suction process.

Variations in firing, whether in peak temperature or residence time at peak temperature, influenced pigment particle interaction with the glaze, modifying particle degree of dissolution/degradation and, therefore, the chromatic coordinates of the fired pieces.

5. ACKNOWLEDGEMENTS

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