# ENHANCEMENT OF PORCELAIN TILE SURFACE PROPERTIES

**C. Ferrer(*); V. Bagán(*)**
**A. Escardino(**); A. Barba(**); C. Felíu(**); M. J. Ibáñez(**)**

(*)ITACA S.A.
(**)Instituto de Tecnología Cerámica.
Asociación de Investigación de las Industrias Cerámicas.
Universitat Jaume I. Castellón. Spain.

## ABSTRACT

*The influence was studied of pressing conditions (moisture content and pressure) and firing cycle peak temperature on the topography and apparent porosity of fired porcelain tile surfaces.*

*A study was also undertaken of how the application of an aqueous solution containing different inorganic constituents to the fair face of green porcelain tile specimens affected the technical surface properties of fired porcelain tile.*

## 1. INTRODUCTION

Part of the porcelain tile that is currently manufactured is marketed without polishing owing to the high added costs involved, in terms of investments (machinery) and production costs (consumption of grinding wheels) in the polishing operation. The unpolished fair face of porcelain tile is matt, as it is quite rough, and tends to retain both reversible as well as irreversible staining[1].

It has recently been proposed to treat green porcelain tile surfaces with suspensions

---

[1]. ESCARDINO, A.; IBÁÑEZ, M.J.; AMORÓS, J.L.; MONZÓ, M. *Reversible dirt retention in glazed tile surfaces*. In: QUALICER 96. Castellón (Spain), 1996, p. 725-726.

bearing constituents of an organometallic nature (obtained by the sol-gel technique), with a view to heightening gloss and reducing stain retention in the unpolished porcelain tile fair face[2]. This methodology involves the formation on the surface of the tile of a fine coating of a different material, with properties that differ from those of the rest of the piece.

This study proposes an alternative solution, which entails impregnating the green porcelain tile fair face with a solution containing one or more constituents, which must penetrate 1 or 2 mm into the body. The absorbed components need to interact in firing with the body's original constituents to form a shell or layer (from the surface inwards), exhibiting properties that differ from those of the rest of the body.

These additives serve to smoothen the fair face of the fired tile (lowering its reversible stain retention capacity), and seal the surface, so as to reduce or eliminate the open pores that produce irreversible staining on soiling.

## 2. MATERIALS

The test specimens used were formed from a standard pressing powder employed for producing porcelain tile, supplied by a Spanish porcelain tile manufacturer.

### 2.1. PARTICLE-SIZE ANALYSIS OF THE SPRAY-DRIED POWDER

### 2.1.1. SPRAY-DRIED GRANULES

Particle-size analysis of the spray-dried pressing powder was performed by running 500 g of the powder after oven drying at 110°C through a vibrating screen with a screen column having mesh apertures: 1000, 750, 500, 300, 200 and 125 $\mu$m. No reject was found on the 1000 $\mu$m screen.

Fig. 1 depicts in cumulative form the quantity found on each screen (by weight) versus mesh aperture.

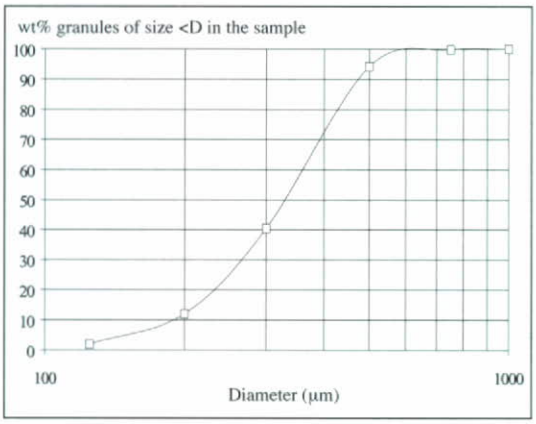

*Figure 1. Size distribution of the spray-dried granules.*

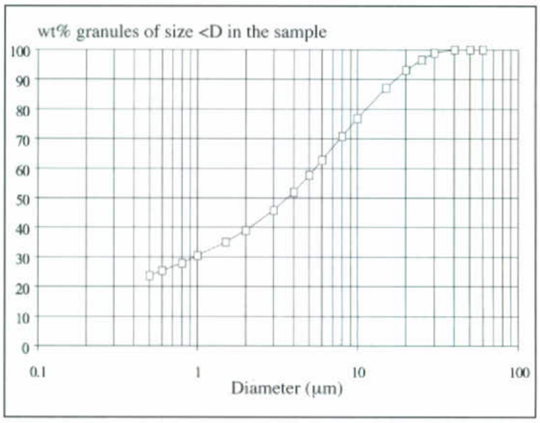

*Figure 2. Size distribution of the particles forming the granules.*

---

[2]. TAULELL S.A. (Castellón). *Proyecto OMECO: Gres porcelánico natural con aplicaciones decorativas de naturaleza organometálica de elevadas prestaciones tecnológicas.* ALFA DE ORO in CEVISAMA 97 (Valencia). Unpublished.

### 2.1.2. PARTICLES FORMING THE SPRAY-DRIED GRANULES

The spray-dried granules were broken up in an aqueous solution containing 1.8 g sodium hexametaphosphate and 0.4 g anhydrous sodium carbonate in 1 litre water. The resulting suspension was subjected to ultrasonics for 5 min and left to stand for 24 hours to achieve good particle dispersion. The suspension subsequently underwent ultrasonics treatment again for another 5 min followed immediately by magnetic stirring for 5 min, taking the fraction that passed through a screen with a mesh aperture of 60 micrometers.

Size distribution was determined on this solids fraction by controlled sedimentation using X-ray absorption. The instrument employed was a MICROMERITICS SEDIGRAPH 5100.

Fig. 2 plots the data obtained in this determination. The part of the particle-size distribution curve corresponding to sizes below 0.5 $\mu$m (24% of the mass treated) was not plotted as this fell outside the method's and the instrument's detection bounds.

### 2.2. ADDITIVE USED

Various aqueous solutions bearing different constituents were used to impregnate the green test specimen surfaces in the second part of the study.

## 3. EXPERIMENTAL TECHNIQUE

### 3.1. TEST SPECIMEN FORMING

Using the pressing powder supplied, 8 mm high cylindrical test specimens with a 50 mm diameter were formed in a laboratory press by uniaxial dry pressing.

### 3.2. ADDITIVE APPLICATION

The green test specimens were oven dried, followed by cooling to room temperature. The additive-bearing solution was then applied to one of each specimen's surfaces. Several application methods were tested:

a) Bench-scale airbrushing.
b) Industrial airbrushing.
c) Gunning in a glazing booth.
d) Foam rubber roller application.
e) Screen-printing.

Two different drying procedures were tested on the specimens to compare the outcomes:

i) Immediate drying after applying the aqueous additive solution.
ii) Drying 30 min after application of the aqueous additive solution.

In the spraying applications, the effect was studied of adding certain constituents to the additive solution, with a view to modifying solution surface tension and enhancing the finished appearance of the treated surface.

In the screen-printing applications, the influence was studied of the binder proportion that was added to the solution.

### 3.3. FIRING OF TEST SPECIMENS

On drawing the test specimens from the drying oven, they were fired in an electric laboratory kiln, using heat-treatment cycles peaking at temperatures of 1170, 1180, 1190 and 1200°C. These cycles were kept as close as possible to the industrial preheating and cooling stages used in firing porcelain tile produced from the spray-dried powder employed in this study. Fig. 3 provides an example of such a schedule, corresponding in this case to the cycle that peaked at 1200°C. The heating and cooling stages were run at the following rates:

- Stretch I (from room temperature to 500°C) free rise of temperature at maximum kiln power ($a_I \cong 80$°C/min).
- Stretch II (from 500°C to set peak temperature for each cycle), $a_{II} = 25$°C/min.
- Stretch IV (from $T_{max}$ to room temperature), $a_{IV} \approx 17$°C/min.

Stretch III involved constant heat treatment with a 20-min dwell at peak temperature.

Each test was performed with three specimens, subsequently averaging the results.

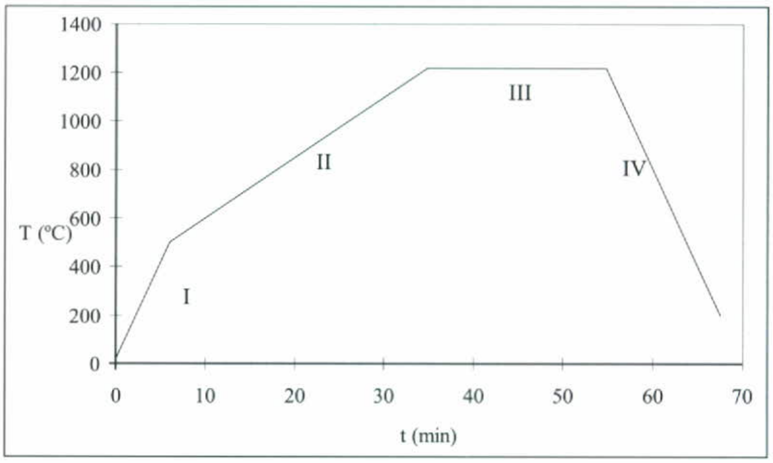

*Figure 3. Firing cycle used.*

### 3.4. DETERMINATION OF BULK DENSITY

Bulk density was determined by the mercury immersion method.

### 3.5. MEASUREMENT OF FIRED SPECIMEN PROPERTIES

### 3.5.1. DETERMINATION OF SURFACE ROUGHNESS

Surface roughness of the specimen fair face was measured with a

HOMMELWERKE, Model T4000, roughness meter. The roughness profiles were obtained using a conical, diamond pick-up stylus, with a 3 $\mu$m spherical tip, and a 90° cone opening angle

Based on previous studies[3, 4, 5] the following parameters were chosen as being the ones that were in principle considered to supply the most useful information for comparing the surface roughness of the various fired specimens:

- $R_a$: arithmetic mean roughness ($\mu$m).
- $\ell_0$ : parameter representing the quotient of the profile length scan to the traverse length scan of the pick-up in a straight line. In the ideal case involving a completely smooth surface, the two lines will coincide and the value of the parameter will be equal to unity. In practice the less smooth a surface, the further removed will the value $\ell_0$ be from unity. This parameter, as its definition indicates, is dimensionless.

### 3.5.2. DETERMINATION OF WATER ABSORPTION

The fired test specimens were submerged after determining their dry mass in a receptacle containing distilled water, which was kept boiling for 2 hours and then allowed to cool for 30 min, after which the specimens were put into a receptacle with cold water. The specimens were then wiped dry with a wrung-out damp cloth and reweighed.

### 3.5.3. STAIN TESTS

To determine irreversible stain retention in the specimen surfaces as a result of apparent porosity, a staining test was run using an EDDING 3000 indelible black glass marker. This was applied by hand, exerting a certain pressure to facilitate stain penetration into any eventual open pores in the surface. The surface was then wiped clean with a cloth moistened in ethanol and carefully dried with another cloth until only the staining retained in open pores and cracks was left on the surface (irreversible staining). This circumstance was verified with a colorimeter on achieving constant values for the chromatic coordinates.

In order to quantitatively assess the intensity of the arising irreversible staining, chromatic coordinate $L^*$ was used since the pores were stained black, measuring this value before and after the above treatment. The value $\Delta L^* = L^* - L^*_s$ was then determined, where:

$L^*$ = Value of coordinate $L^*$ prior to surface staining.

$L^*_s$= Value of coordinate $L^*$ after cleaning the black-stained surface.

A MACBETH COLOR-EYE 7000 spectrocolorimeter, fitted with a 0/8° geometry (integrating sphere) was used to measure the chromatic coordinates, under the following conditions:

---

[3]. ESCARDINO, A.; IBÁÑEZ, MªJ.; BLASCO, A.; AMORÓS, J.L. *Using the roughnessmeter for the quantitative study of ceramic glaze degradation by abrasion*. In: QUALICER 92. Castellón (Spain).

[4]. IBÁÑEZ, MªJ.; AGRAMUNT, J.V.; FELÍU, C.; ESCARDINO, A. *Using a roughnessmeter to measure the asperity of a ceramic glaze*. 8th International Symposium on Ceramics (SIMCER-92). Rimini (Italy). November, 1992.

[5]. ESCARDINO, A.; IBÁÑEZ, MªJ.; DE LEMUS, R.; MESTRE. S. *Variation of roughness and gloss in glazed tile with the intensity of the wear produced with a standard abrasion tester*. In: QUALICER 96. Castellón (Spain), 1996, p. 727-729.

- Standard CIE 10°observer.
- Standard CIE D65 lighting.
- Excluded specular component.

Five measurements were run on each surface, calculating the arithmetic mean of the values obtained for coordinate L*, which represents the white-black axis (100 ≡ white; 0 ≡ black).

### 3.5.4. GLOSS MEASUREMENT

The gloss measurements were performed with a reflectometer at a 60° angle of incidence. A minimum of five measurements was obtained randomly at different points on the same surface, subsequently computing the arithmetic mean.

## 4. RESULTS

### 4.1. RELATION BETWEEN $T_{max}$ MEASURED IN THE ELECTRIC KILN USED AND $T_{max}$ MEASURED IN INDUSTRIAL KILNS

The bulk densities were compared of industrially fired tiles and test specimens made from the same pressing powder, formed under the same pressing conditions as those used in industry, and fired at different peak temperatures in an electric kiln. To obtain identical bulk density in the fired pieces, it was observed that the peak temperatures in the electric kiln used in the study needed to be approximately 15 to 20°C lower than $T_{max}$ of the industrial kilns. This finding allowed relating firing conditions in an electric laboratory kiln to the firing conditions used in an industrial single-layer roller kiln.

### 4.2. EFFECT OF PRESSING CONDITIONS (POWDER MOISTURE CONTENT AND PRESSING PRESSURE) AND PEAK FIRING TEMPERATURE ON FIRED SPECIMEN FAIR FACE CHARACTERISTICS

Test specimens were formed from spray-dried pressing powder with three different moisture contents ($X_1$=0.045 kg water/kg dry solid; $X_2$=0.062 kg water/kg dry solid; $X_3$=0.075 kg water/kg dry solid), using the same pressing pressure, $P_1$=400 kg/cm$^2$. With spray-dried powder at moisture content $X_2$, a further two pressing pressures were tested ($P_2$=300 kg/cm$^2$ and $P_3$=450 kg/cm$^2$). Thus, five different types of test specimens were prepared, whose mean green bulk densities have been detailed in Table 1, together with their respective pressing conditions.

| Specimen type | X (kg water/kg d.s.) | P (kg/cm$^2$) | $d_{ap}$ (g/cm$^3$) |
|---|---|---|---|
| 1 | 0.062 | 300 | 1.828 |
| 2 | 0.062 | 400 | 1.871 |
| 3 | 0.062 | 450 | 1.892 |
| 4 | 0.045 | 400 | 1.843 |
| 5 | 0.075 | 400 | 1.884 |

***Table 1.*** *Pressing conditions and bulk density of the green specimens*

Each type of specimen was fired in an electric kiln at four different peak temperatures (1170, 1180, 1190 and 1200°C) using the firing cycles set out above.

Table 2 lists the mean values of the fired specimen properties that were considered most representative for this study. The table indicates the type of green starting specimen and peak firing temperature together with the corresponding properties of the fired piece. The selected properties were as follows: bulk density, water absorption (according to the DIN standard), four parameters representing specimen surface topography ($\ell_0$ , $R_a$, $R_t$ and $v_s$) (see Section 3), chromatic coordinate L* of the fired specimen surface (before and after staining and cleaning as described in Section 3), surface gloss and visual appearance. This last organoleptic appraisal is not given in Table 2.

An examination of the values found for the surface properties detailed in Table 2 allows highlighting the following points:

i) For the five types of studied test specimens, fired bulk density peaked at 1190°C. These data indicate that at 1200°C the piece already exhibited slight bloating, which is not recommendable for industrial tile manufacture.

ii) For specimens types 2 to 5, water absorption was zero in the pieces fired at $T_{max}$=1190°C.

iii) The minor variations in $R_a$ values did not evolve consistently with peak firing temperature for any of the five studied specimen types, but exhibited alternating values. To be highlighted is the fact that the lowest values for this roughness parameter corresponded to specimen types 2 and 3.

iv) For each specimen type, parameter $\ell_0$ representing surface smoothness tended to decrease on raising firing cycle $T_{max}$. Specimens types 2, 3 and 5 exhibited the lowest values, although the differences with the other specimen types were practically insignificant.

v) Gloss (β) tended to rise with peak firing temperature for each type of specimen. The highest values were found for specimen type 5.

vi) ΔL* decreased on raising peak firing cycle temperature for each studied specimen type. The lowest values of ΔL* corresponded to specimen types 2, 3 and 5.

Taking into consideration the above remarks, if the values of $\ell_0$ and ΔL* (closely related to reversible and irreversible staining) are used as references, it can be inferred that under the operating conditions studied, the optimum $T_{max}$ range for the studied pressing powder lay between 1180 and 1190°C, if $T_{max}$=1200°C is excluded. As all the specimens fired at this last temperature, as indicated above, presented a slightly lower bulk density than the specimens fired at $T_{max}$=1190°C, it was considered advisable to discard these as they exhibited slight bloating. The most appropriate pressing conditions were therefore those corresponding to specimen type 2 (X=0.062 kg water/kg dry solid; P=400 kg/cm$^2$), and type 3 (X=0.062 kg water/kg dry solid; P=450 kg/cm$^2$), fired at $T_{max}$ 1190°C (if the data obtained at 1200°C are disregarded). Under these conditions, the $\ell_0$ values closest to unity (1.017 to 1.022) were obtained, corresponding to the smoothest surfaces with the lowest ΔL* (<1.0) which involves least irreversible staining, while yielding the highest fired bulk density values.

These conclusions have been graphically represented in Figs. 4 and 5, in which the variation has been plotted of parameters $\ell_0$ and ΔL* (respectively representing planarity and apparent porosity of the specimen fair face surface), and fired bulk density for the five studied specimen types versus firing cycle $T_{max}$.

| Test series no. | Specimen type | Tmax (°C) | dap (g/cm$^3$) | AA (%) | $R_a$ (µm) | $\ell_0$ (mm/mm) | β | $\Delta L^*$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1170 | 2.364 | 0.05 | 2.27 | 1.025 | 4.5 | 4.64 |
| 2 | 1 | 1180 | 2.376 | 0.03 | 2.50 | 1.026 | 4.1 | 2.99 |
| 3 | 1 | 1190 | 2.382 | 0.03 | 2.48 | 1.023 | 5.0 | 1.60 |
| 4 | 1 | 1200 | 2.376 | 0.03 | 2.44 | 1.019 | 5.0 | 1.28 |
| 5 | 2 | 1170 | 2.369 | 0.06 | 2.01 | 1.022 | 4.8 | 3.49 |
| 6 | 2 | 1180 | 2.383 | 0.00 | 2.11 | 1.019 | 5.2 | 0.98 |
| 7 | 2 | 1190 | 2.386 | 0.00 | 2.14 | 1.018 | 5.5 | 0.75 |
| 8 | 2 | 1200 | 2.383 | 0.00 | 2.20 | 1.017 | 5.7 | 0.41 |
| 9 | 3 | 1170 | 2.377 | 0.03 | 2.14 | 1.027 | 4.7 | 2.74 |
| 10 | 3 | 1180 | 2.387 | 0.00 | 2.12 | 1.022 | 4.6 | 0.90 |
| 11 | 3 | 1190 | 2.388 | 0.00 | 2.15 | 1.019 | 5.2 | 0.72 |
| 12 | 3 | 1200 | 2.381 | 0.00 | 2.16 | 1.017 | 5.7 | 0.32 |
| 13 | 4 | 1170 | 2.371 | 0.06 | 2.12 | 1.022 | 3.9 | 3.79 |
| 14 | 4 | 1180 | 2.384 | 0.03 | 2.34 | 1.022 | 4.6 | 1.41 |
| 15 | 4 | 1190 | 2.388 | 0.00 | 2.32 | 1.022 | 4.5 | 1.34 |
| 16 | 4 | 1200 | 2.383 | 0.00 | 2.20 | 1.019 | 4.9 | 1.02 |
| 17 | 5 | 1170 | 2.374 | 0.00 | 2.33 | 1.025 | 6.2 | 1.97 |
| 18 | 5 | 1180 | 2.381 | 0.00 | 2.22 | 1.020 | 7.3 | 1.24 |
| 19 | 5 | 1190 | 2.386 | 0.00 | 2.18 | 1.018 | 7.0 | 0.79 |
| 20 | 5 | 1200 | 2.379 | 0.00 | 2.25 | 1.017 | 7.8 | 0.11 |

***Table 2.*** *Fired specimen properties at different peak temperatures*

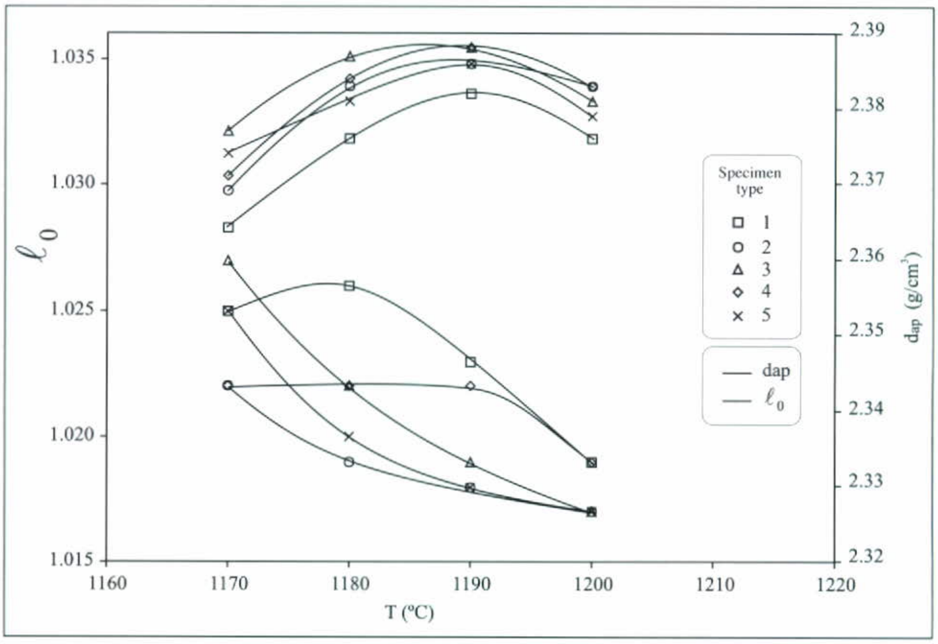

***Figure 4.*** *Variation of* $\ell_0$ *and* $d_{ap}$ *of the fired specimens with firing cycle* $T_{max}$.

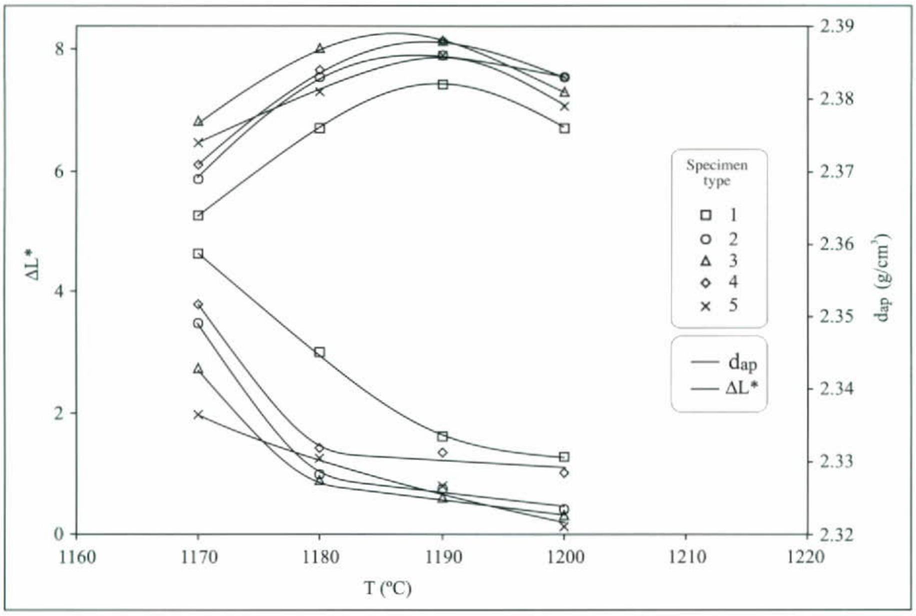

*Figure 5. Variation of ΔL* and $d_{ap}$ of the fired specimens with firing cycle $T_{max}$.*

## 4.3. ENHANCEMENT OF PORCELAIN TILE SURFACE PROPERTIES BY TREATING THE GREEN BODIES WITH ADDITIVES DISSOLVED IN WATER

With a view to enhancing surface smoothness and raising fair face sealing of the fired specimens, the influence was studied of treating the green test specimen surfaces with solutions containing different additives. The test specimens used were formed at pressing conditions that lay within the optimum range selected in the foregoing section (X=0.062 kg water/kg dry solid; P=450 kg/cm$^2$) for firing with heat-treatment cycles of $T_{max}$= 1180 and 1190°C. Certain test specimens were fired at $T_{max}$=1200°C for comparative purposes.

Surface treatment involved applying aqueous solutions of different composition, which were to be wholly or partially absorbed by the solid material. The nature of the dissolved constituents was chosen so that they would interact during firing with the specimen outer layer next to the fair face surface to form a thin shell that would exhibit enhanced properties compared to the rest of the specimen. The most suitable aqueous solution was finally selected out of the studied aqueous solutions. The various application methods described in Section 3.2 were then tested with the selected dissolved additive.

### 4.3.1. SPRAYING APPLICATIONS

In spraying on the solution containing the additive with a laboratory airbrush, the following variables were studied: dissolved additive concentration, mass (g) of the applied solution (relative to a square surface area of 30 cm x 30 cm), elapsed time between solution application and specimen drying.

### 4.3.1.1. SPECIMEN DRYING IMMEDIATELY AFTER SOLUTION APPLICATION

The effect was studied of applying a solution containing 0.25 g/cm$^3$ additive, testing different applied solution masses. The test specimens were oven dried at 110°C immediately after applying the solution bearing the additive, subsequently firing the specimens with heat-treatment cycles of $T_{max}$1180 and 1190°C.

Table 3 details the resulting values of the fair face properties of the fired specimens obtained on treatment with different applied solution concentrations and masses, as well as those corresponding to type 3 specimens fired under the same conditions, without any kind of surface application (see Table 2). For comparative purposes the results are also listed of a test run using a firing schedule with $T_{max}$=1200°C.

| Test series no. | Additive concentration (g/cm$^3$) | Firing cycle $T_{max}$ (°C) | Applied solution mass (g) | Gloss | $\Delta L^*$ | $R_a$ (μm) | $\ell_0$ |
|---|---|---|---|---|---|---|---|
| 10 | 0.0 | 1180 | -- | 4.6 | 0.90 | 2.12 | 1.022 |
| 21 | 0.25 | 1180 | 15 | 7.3 | 0.59 | 2.24 | 1.013 |
| 22 | 0.25 | 1180 | 25 | 7.4 | 0.47 | 2.24 | 1.013 |
| 23 | 0.25 | 1180 | 40 | 9.5 | 0.44 | 2.31 | 1.010 |
| 24 | 0.25 | 1180 | 50 | 13.5 | 0.29 | 2.35 | 1.008 |
| 11 | 0.0 | 1190 | -- | 5.2 | 0.72 | 2.15 | 1.019 |
| 25 | 0.25 | 1190 | 15 | 7.4 | 0.54 | 2.26 | 1.013 |
| 26 | 0.25 | 1190 | 25 | 8.1 | 0.47 | 2.29 | 1.011 |
| 27 | 0.25 | 1190 | 40 | 12.7 | 0.44 | 2.44 | 1.008 |
| 28 | 0.25 | 1190 | 50 | 15.4 | 0.41 | 2.44 | 1.006 |
| 12 | 0.0 | 1200 | -- | 5.7 | 0.32 | 2.16 | 1.017 |
| 29 | 0.25 | 1200 | 50 | 17.3 | 0.07 | 2.93 | 1.004 |

***Table 3.*** *Fired specimen fair face properties.*

It can be observed that at the two studied $T_{max}$, on raising applied solution mass, surface gloss of the fired treated specimen surface increased, $\Delta L^*$ decreased (less irreversible staining was retained), and the value of $\ell_0$ approached unity more closely (smoother surface). Important differences were not observed between the $\Delta L^*$ and $\ell_0$ values corresponding to the same applied solution mass at the two tested peak temperatures. However, gloss was slightly higher in the specimens fired at $T_{max}$=1190°C than in those corresponding to $T_{max}$=1180°C.

Parameter $R_a$, indicative of mean roughness, rose with applied solution mass, which matched the visual appearance of the fired pieces. Thus, the fired specimens exhibited a slightly wavy surface, as if some of the applied solution droplets had dried on the specimen surface without being wholly absorbed. This slight waviness (Fig. 6, specimen b), exhibited a minor increase with applied solution mass. The lowest $\ell_0$ values and the highest gloss were found for $T_{max}$=1190°C and an applied solution mass of 50 g, with no large variations being observed in the values of $\Delta L^*$ obtained for the specimens to which a solution mass was applied of 25-50 g (relative to the 30 cm x 30 cm specimens). In the piece fired at $T_{max}$=1200°C, a considerable improvement was observed in the values for gloss, $\Delta L^*$ and $\ell_0$ , compared to those found for the non-treated specimen (test series no. 12). A much higher value for $R_a$ was however obtained than in the test no. 12 specimen.

### 4.3.1.2. SPECIMEN DRYING 30 MIN AFTER SOLUTION APPLICATION

Table 4 details the resulting data for solution additive concentrations of 0.25 g/cm$^3$, on applying different solution masses, drying 30 min after the application, and firing at heat-treatment cycles with peak temperatures of 1180°C and 1190°C. It can be observed that a noticeable improvement was obtained in the surface properties ($\Delta L^*$; $\beta$ and $\ell_0$ )

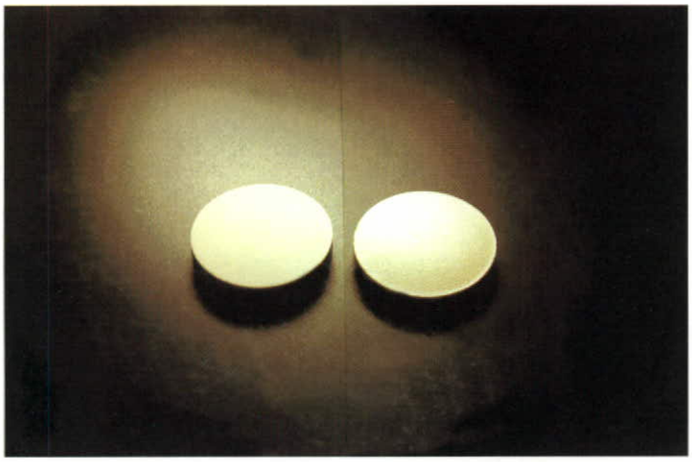

***Figure 6.*** *Appearance of fired specimen fair faces: a) Non-treated specimen; b) Treated specimen with immediate drying*

of the treated specimens compared to the non-treated ones, at the three tested $T_{max}$ values.

Comparing the data in Table 4 with those of Table 3 shows that on allowing the piece to stand for 30 min after applying the solution, followed by drying, gloss decreased while ΔL* rose slightly, and $\ell_0$ generally also increased a little in the fired specimen fair face. On the other hand, visual appraisal revealed that the surface waviness mentioned in the foregoing section had virtually disappeared, i. e. specimen fair face appearance had improved. This last result was confirmed by the $R_a$ values detailed in Table 4, which were generally lower than those in Table 3. The change was probably due to better absorption of the applied solution. Thus, a slight variation in colour was observed in a 1.5 to 2 mm thick layer at the specimen edge, apparently due to solution penetration and subsequent interaction with the specimen. The layer's thickness depended on applied solution mass.

| Test series no. | Additive concentration (g/cm³) | Firing cycle $T_{max}$ (°C) | Applied solution mass (g) | Gloss | $\Delta L^*$ | $R_a$ (µm) | $\ell_0$ |
|---|---|---|---|---|---|---|---|
| 10 | 0.0 | 1180 | -- | 4.6 | 0.90 | 2.12 | 1.022 |
| 30 | 0.25 | 1180 | 15 | 5.3 | 0.84 | 2.05 | 1.017 |
| 31 | 0.25 | 1180 | 25 | 5.4 | 0.72 | 2.09 | 1.017 |
| 32 | 0.25 | 1180 | 40 | 6.0 | 0.64 | 2.15 | 1.016 |
| 33 | 0.25 | 1180 | 50 | 6.2 | 0.52 | 2.24 | 1.015 |
| 11 | 0.0 | 1190 | -- | 5.2 | 0.72 | 2.15 | 1.019 |
| 34 | 0.25 | 1190 | 15 | 5.5 | 0.68 | 2.19 | 1.018 |
| 35 | 0.25 | 1190 | 25 | 5.9 | 0.57 | 2.20 | 1.016 |
| 36 | 0.25 | 1190 | 40 | 6.6 | 0.49 | 2.30 | 1.015 |
| 37 | 0.25 | 1190 | 50 | 8.0 | 0.47 | 2.46 | 1.012 |
| 12 | 0.0 | 1200 | -- | 5.7 | 0.32 | 2.16 | 1.017 |
| 38 | 0.25 | 1200 | 40 | 7.9 | 0.32 | 2.52 | 1.013 |

***Table 4.*** *Fired specimen fair face properties.*

### 4.3.1.3. STUDY OF ADDITIVE EFFECTIVENESS ON APPLYING SOLUTIONS WITH A 0.35 G/CM³ CONCENTRATION

Several series of tests were conducted with a view to studying the effect of the additive concentration on the applied aqueous solution. Table 5 sets out the operating conditions used in each case, together with the values of the corresponding fair face properties of the fired specimens.

On comparing the values of $\ell_0$ and ΔL* detailed in Table 5 with those in Tables 3 and 4, no noticeable differences are found, so that the rise in additive concentration in the applied solution from 0.25 to 0.35 g/cm³ was not considered to enhance the values of the properties obtained at a concentration of 0.25 g/cm³. To be highlighted is only the rise in gloss of the specimens in which the applied solution was dried immediately after application.

| Test series no. | Additive concentration (g/cm³) | Firing cycle $T_{max}$ (°C) | Drying | Applied solution mass (g) | Gloss | $\Delta L^*$ | $R_a$ (μm) | $\ell_0$ |
|---|---|---|---|---|---|---|---|---|
| 39 | 0.35 | 1180 | 30 min | 15 | 5.4 | 0.85 | 2.17 | 1.018 |
| 40 | 0.35 | 1180 | 30 min | 25 | 5.6 | 0.84 | 2.26 | 1.017 |
| 41 | 0.35 | 1180 | 30 min | 40 | 6.0 | 0.80 | 2.25 | 1.016 |
| 42 | 0.35 | 1180 | 30 min | 50 | 6.3 | 0.50 | 2.35 | 1.015 |
| 43 | 0.35 | 1190 | 30 min | 15 | 5.6 | 0.72 | 2.47 | 1.020 |
| 44 | 0.35 | 1190 | 30 min | 25 | 5.9 | 0.65 | 2.36 | 1.017 |
| 45 | 0.35 | 1190 | 30 min | 40 | 6.5 | 0.44 | 2.29 | 1.016 |
| 46 | 0.35 | 1190 | 30 min | 50 | 6.7 | 0.49 | 2.36 | 1.014 |
| 47 | 0.35 | 1190 | Inmediate | 40 | 28.4 | 0.45 | 2.54 | 1.002 |
| 48 | 0.35 | 1190 | Inmediate | 50 | 28.4 | 0.43 | 2.63 | 1.001 |

***Table 5.*** *Fired specimen fair face properties.*

### 4.3.1.4.. INDUSTRIAL AIRBRUSHING

Several tests were run to establish whether an industrial airbrush application of the solution containing the additive yielded important differences in the fired specimens' fair face characteristics compared to the results obtained by bench-scale airbrushing. The results have been reported in Table 6.

| Test series no. | Application method | Drying | Applied solution mass (g) | Firing cycle $T_{max}$ (°C) | Gloss | $\Delta L^*$ | $R_a$ (μm) | $\ell_0$ |
|---|---|---|---|---|---|---|---|---|
| 49 | Airbrush | Immed. | 40 | 1170 | 12.5 | 0.45 | 2.35 | 1.009 |
| 50 | " | " | 40 | 1180 | 14.7 | 0.41 | 2.36 | 1.007 |
| 51 | " | " | 40 | 1190 | 16.9 | 0.35 | 2.85 | 1.005 |
| 52 | Airbrush | 30 min | 40 | 1170 | 5.3 | 1.17 | 2.14 | 1.018 |
| 53 | " | " | 40 | 1180 | 6.5 | 0.62 | 2.24 | 1.015 |
| 54 | " | " | 40 | 1190 | 7.1 | 0.59 | 2.25 | 1.013 |

***Table 6.*** *Fired specimen fair face properties at different $T_{max}$. Dissolved additive solution: 0.25 g/cm³*

It can be observed that there were no significant differences between the ΔL* and $\ell_0$ values obtained in the tests run between 1180 and 1190°C and the respective values of these properties found for applied solution masses of 40 g in Tables 3 and 4. The gloss values (β) for the specimens that were dried immediately were a little higher than the corresponding ones in Table 3, and a slightly wavier surface was also found. It may therefore be concluded that industrial airbrushing did not entail any significant change with regard to the bench-scale airbrush application, except a slight improvement.

### 4.3.1.5. BENCH-SCALE AIRBRUSHING ADDING TENSOACTIVE CONSTITUENTS TO THE SOLUTION

Even though the visual appearance of the fired specimen fair face had already improved considerably in the tests run with specimens dried 30 min after additive application compared to those listed in Section 4.3.1.1, the effect was studied of adding certain tensoactive constituents to the solution to reduce surface tension, and encourage absorption by the body. The outcomes did not improve the results obtained with the tensoactive-free solution.

### 4.3.2. FOAM RUBBER ROLLER APPLICATIONS

To see whether the foregoing results could be improved, a roller application was run of a solution containing 0.25 g/cm$^3$ additive, with immediate specimen drying and drying after 30 min. The specimens were subsequently subjected to heat-treatment cycles of $T_{max}$ 1180 and 1190°C. The mean values of the resulting data are detailed in Table 8. The applied solution mass was the amount deposited by the soaked roller, which was not determined.

| Test series no. | Firing cycle $T_{max}$ (°C) | Drying | Gloss | $\Delta L^*$ | $R_a$ (μm) | $\ell_0$ |
|---|---|---|---|---|---|---|
| 55 | 1180 | Immediate | 6.0 | 0.81 | 2.16 | 1.017 |
| 56 | 1190 | " | 6.6 | 0.73 | 2.35 | 1.016 |
| 57 | 1180 | 30 min | 4.7 | 0.91 | 2.06 | 1.017 |
| 58 | 1190 | " | 5.4 | 0.58 | 2.35 | 1.019 |

***Table 7.*** *Fired specimen fair face properties. Dissolved additive concentration = 0.25 g/cm$^3$. Application method: roller.*

It can be observed that the values obtained for $\Delta L^*$ and $\ell_0$ were a little higher, though of the same order as those found in the spraying application, while a slight improvement of the surface appearance was found in the fired specimen with regard to the slight waviness mentioned in Section 4.3.1.1. The reason why the $\ell_0$ and $\Delta L$ values were a little higher than those corresponding to the applied mass of 15 g at the same temperatures in Tables 3 and 4 could have been due to the roller applying a mass of less than 15 g (per 30 cm x 30 cm specimen).

### 4.3.3. APPLICATION WITH A PRINTING SCREEN SIMILAR TO THE ONE USED FOR APPLYING SOLUBLE PIGMENTS TO GREEN PORCELAIN TILE

With a view to attempting to improve the visual appearance of the fired specimen treated surface, the application was tested of solutions containing 0.25 g/cm$^3$ additive via printing screens of the type indicated. Different proportions (4% and 3.2%) of a thickener supplied by ITACA S.A. were added. The resulting specimens were fired using heat-treatment cycles of $T_{max}$ 1180 and 1190°C. The findings are detailed in Table 8.

It can be observed that the values of $\Delta L^*$, $\ell_0$ and $\beta$, corresponding to a solution containing a 4% thickener addition were slightly better than those of the solution bearing 3.2% thickener, in the test pieces dried 30 min after application. However, the best results obtained for these properties (at 4% thickener) were of the same order as the best values found, under the same drying conditions, on using the other tested application methods (Tables 4, 5 and 6) on applying 40 g solution.

The specimens dried immediately after application exhibited slightly lower $\Delta L^*$ (better) values than the corresponding ones in Table 3.

| Test series no. | % Thickener addition | Drying | Firing cycle $T_{max}$ (°C) | Gloss | $\Delta L^*$ | $R_a$ (μm) | $\ell_0$ |
|---|---|---|---|---|---|---|---|
| 59 | 3.2 | 30 min | 1180 | 6.1 | 0.88 | 2.19 | 1.017 |
| 60 | 3.2 | " | 1190 | 6.9 | 0.48 | 2.17 | 1.015 |
| 61 | 4.0 | " | 1180 | 7.2 | 0.70 | 2.18 | 1.015 |
| 62 | 4.0 | " | 1190 | 7.4 | 0.34 | 2.18 | 1.013 |
| 63 | 3.2 | Immed. | 1190 | 12.1 | 0.25 | 2.23 | 1.008 |
| 64 | 4.0 | " | 1190 | 13.6 | 0.27 | 2.25 | 1.007 |

***Table 8.*** *Fired specimen fair face properties.*

## 4.3.4. EFFECT OF THE ADDITIVE APPLICATION ON FIRED SPECIMEN SURFACE PROPERTIES

Table 9 compares certain technical properties of the resulting fired specimen fair faces obtained on either previously treating or non-treating the green specimens with the additive solution, followed by firing at peak temperatures of 1180 and 1190°C. The chosen properties were Mohs hardness (according to the standard, examining for the appearance of the scratch in an optical microscope); width of the scratch produced in a Scratch-Tester under constant loading (40 N); force needed to produce scratching using this apparatus; wear resistance measured with a Pin-on-Disk tribometer[6], determined by mass loss.

| Application method | Additive concentration (g/cm³) | Applied solution mass (g) | Firing cycle $T_{max}$ (°C) | Mohs hardness (*) | Mohs hardness (**) (microsc.) | Scratch sidth (***) (μm) | Force (****) required for scratching (N) | Wear resistance (n.r./mg) |
|---|---|---|---|---|---|---|---|---|
| -- (Reference material) | -- | -- | 1190 | 6 | 5 | 161 | 3 | 820 |
| Spraying (immediate drying) | 0.25 | 50 | 1190 | 5 | 5 | 162 | 7 | 1800 |
| | 0.25 | 50 | 1180 | 6 | 5 | 153 | 6 | -- |
| Spraying (dryng after 30 min.) | 0.25 | 50 | 1180 | 6 | 5 | 146 | 5 | -- |
| | 0.25 | 40 | 1180 | 6 | 6 | 123 | 5 | -- |
| | 0.25 | 25 | 1180 | 6 | 5 | 144 | 5 | -- |
| | 0.25 | 50 | 1190 | 5 | 5 | 151 | 5 | -- |
| | 0.25 | 40 | 1190 | 6 | 6 | 140 | 6 | -- |
| | 0.25 | 25 | 1190 | 6 | 5 | 139 | 5 | 970 |
| | 0.35 | 50 | 1190 | 6 | 5 | 136 | 6 | -- |
| | 0.35 | 40 | 1190 | 6 | 5 | 128 | 6 | 1200 |

(*) Measured according to standard EN-101
(**) Determined by examining the scratch in an optical microscope.
(***) Determined in the SCRATCH-TESTER applying a load of 40 N.
(****) Determined in the SCRATCH-TESTER with rising loading.

***Table 9.*** *Comparison between certain fired specimen technical properties on treating or non-treating the green specimens with the additive solution.*

---

[6]. IBÁÑEZ, Mª J. *Estudio de las propiedades mecánicas y superficiales de recubrimientos vidriados de piezas cerámicas. Puesta a punto de nuevas técnicas de medida.* Doctoral dissertation. Universitat Jaume I. Castellón. Spain. 1997.

On comparing the values obtained for the above properties, the following may be highlighted:

i) Mohs hardness of the treated test pieces, whether determined according to standard EN-101 or measured in an optical microscope, exhibited no variation in respect of the reference material on which no additive solution was applied.

ii) The width of the scratch produced in the Scratch-Tester, loading at 40 N, dropped slightly (compared to that of the reference material) in the treated specimens that were dried 30 min after applying the additive solution. The result suggests that scratch resistance improved slightly.

iii) The load required in the Scratch-Tester to produce a scratch on the fair face specimen surface was greater in the treated specimens (dried immediately as well as after 30 min) than in the (non-treated) reference material, which supports the conclusion set out in the foregoing sub-section.

iv) The wear resistance measured with the Pin-on-Disk tribometer was a little greater than that of the reference material in the specimens dried 30 min after the application, and twice as high as that of the specimens dried immediately after the application. This finding could be due to the applied solution being only partially absorbed by the test specimen on undergoing immediate drying. Consequently, a fine coating of additive could have been formed on the surface, which after firing provided the specimen fair face with greater abrasion resistance.

## 5. CONCLUSIONS

The results obtained in the tested range of operating conditions with the raw materials mixture studied allow drawing the following conclusions:

5.1. The optimum conditions for the greatest smoothness ($\ell_0 \cong 1.0$), highest gloss ($\beta$) and lowest apparent porosity in the studied specimen fair faces ($\Delta L^*$) were: Pressing pressure: 400-450 $kg/cm^2$; Pressing moisture content: 0.062-0.075 kg water/kg dry solid; firing cycle $T_{max}$ 1190-1200°C (at this last temperature there was a slight decrease in fired bulk density).

5.2 Application of an aqueous solution containing an additive to the green test specimens appreciably enhanced the above three properties ($\Delta L^*$; $\ell_0$ and $\beta$) of the fired specimen fair face compared to those of the fired specimens that were not treated with the additive. This improvement was detected both when the specimens were immediately dried after the application, or on drying after allowing the specimens to stand for 30 min. In the former case, these properties were slightly better than in the latter case. The surface appearance of the specimens was however better in the latter case (on drying after 30 min).

5.3 Application of an additive solution to the green test specimens did not appear to impair other fair face surface properties such as: Mohs hardness, scratch resistance (width of the scratch produced in a Scratch-Tester under constant loading, and load required to produce scratching), as well as wear resistance (measured with a Pin-on-Disk tribometer). Instead, the application appeared to enhance these properties slightly.