

ENHANCEMENT OF PORCELAIN TILE SURFACE PROPERTIES

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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 μm . No reject was found on the 1000 μm screen.

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

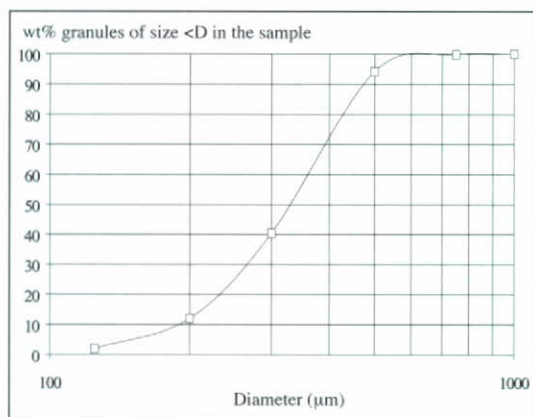


Figure 1. Size distribution of the spray-dried granules.

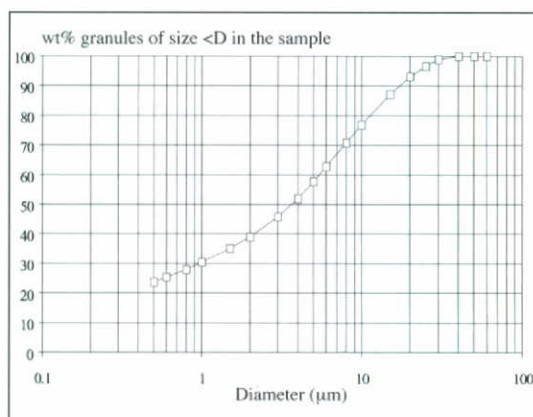


Figure 2. Size distribution of the particles forming the granules.

[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 $0.5\ \mu\text{m}$ (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 ($a_I \approx 80^\circ\text{C}/\text{min}$).
- Stretch II (from 500°C to set peak temperature for each cycle), $a_{II} = 25^\circ\text{C}/\text{min}$.
- Stretch IV (from T_{max} to room temperature), $a_{IV} \approx 17^\circ\text{C}/\text{min}$.

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.

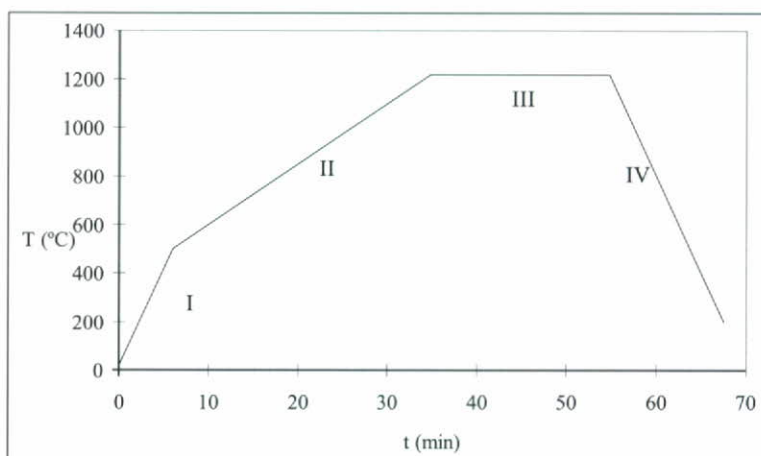


Figure 3. Firing cycle used.

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 $3\text{ }\mu\text{m}$ 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 (μm).
- ℓ_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 ℓ_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 spectrophotometer, fitted with a $0/8^\circ$ geometry (integrating sphere) was used to measure the chromatic coordinates, under the following conditions:

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- [3]. ESCARDINO, A.; IBÁÑEZ, M^J.; 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, M^J.; AGRAMUNT, J.V.; FELIÚ, 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, M^J.; 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/cm². With spray-dried powder at moisture content X_2 , a further two pressing pressures were tested ($P_2=300$ kg/cm² and $P_3=450$ kg/cm²). 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 (ℓ_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 $T_{\max}=1190^\circ\text{C}$.
- 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 ℓ_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 ℓ_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 $T_{\max}=1200^\circ\text{C}$ 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 $T_{\max}=1190^\circ\text{C}$, 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/cm²), and type 3 ($X=0.062$ kg water/kg dry solid; $P=450$ kg/cm²), fired at $T_{\max}$ 1190°C (if the data obtained at 1200°C are disregarded). Under these conditions, the ℓ_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 ℓ_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	T _{max} (°C)	d _{ap} (g/cm ³)	AA (%)	R _a (μm)	ℓ ₀ (mm/mm)	β	ΔL*
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

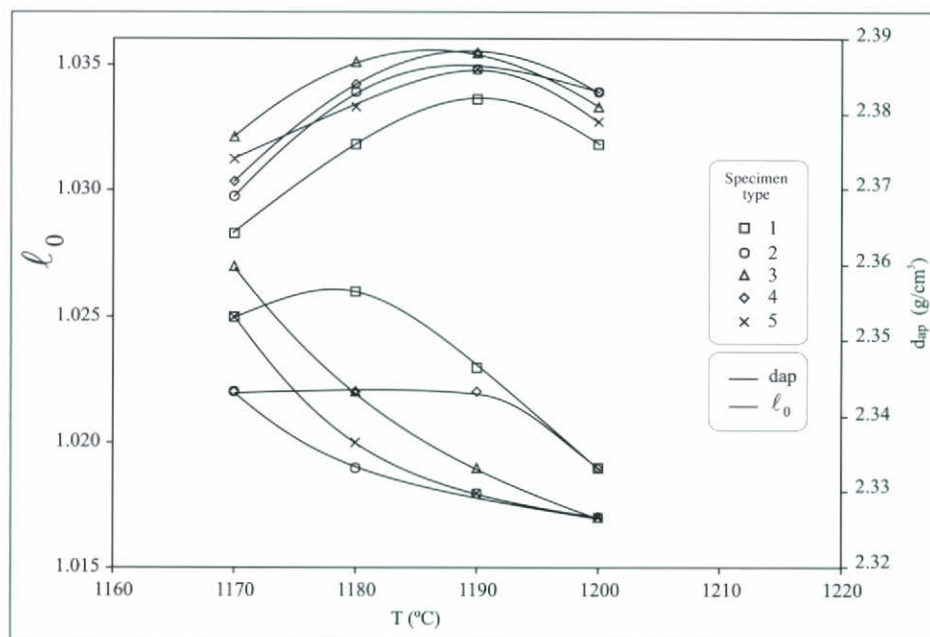


Figure 4. Variation of ℓ_0 and d_{ap} of the fired specimens with firing cycle T_{max} .

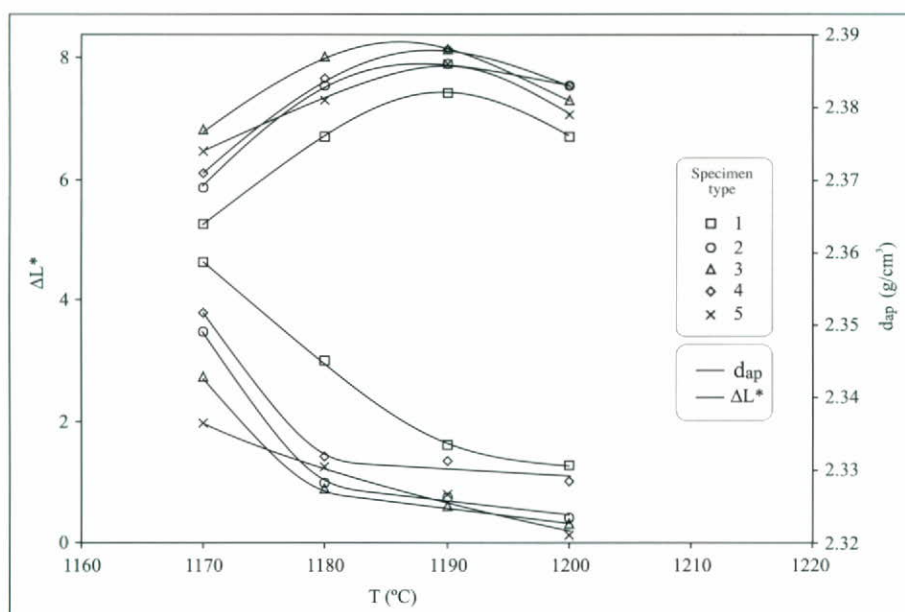


Figure 5. Variation of ΔL^* and d_{ap} of the fired specimens with firing cycle T_{max} .

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/cm²) for firing with heat-treatment cycles of $T_{max}=1180$ and 1190°C . Certain test specimens were fired at $T_{max}=1200^\circ\text{C}$ 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/cm³ 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	ΔL^*	R_a (μm)	ℓ_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, ΔL^* decreased (less irreversible staining was retained), and the value of ℓ_0 approached unity more closely (smoother surface). Important differences were not observed between the ΔL^* and ℓ_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 ℓ_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 ΔL^* 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, ΔL^* and ℓ_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/cm³, 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 (ΔL^* ; β and ℓ_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 ℓ_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/cm ³)	Firing cycle T_{max} (°C)	Applied solution mass (g)	Gloss	ΔL^*	R_a (µm)	ℓ_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 ℓ_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/cm ³)	Firing cycle T _{max} (°C)	Drying	Applied solution mass (g)	Gloss	ΔL^*	R _a (μm)	ℓ_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	Immediate	40	28.4	0.45	2.54	1.002
48	0.35	1190	Immediate	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	ΔL^*	R _a (μm)	ℓ_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 ℓ_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/cm³ 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	ΔL*	R _s (μm)	ℓ 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/cm³. Application method: roller.

It can be observed that the values obtained for ΔL* and ℓ₀ 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 ℓ₀ and ΔL 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/cm³ 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 ΔL*, ℓ₀ and β, 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 ΔL^* (better) values than the corresponding ones in Table 3.

Test series no.	% Thickener addition	Drying	Firing cycle T_{max} (°C)	Gloss	ΔL^*	R_a (μm)	ℓ_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/cm ³)	Applied solution mass (g)	Firing cycle T_{max} (°C)	Mohs hardness (*)	Mohs hardness (**) (microsc.)	Scratch width (***) (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 (drying 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, M^a 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 ($\ell_0 \approx 1.0$), highest gloss (β) and lowest apparent porosity in the studied specimen fair faces (ΔL^*) were: Pressing pressure: 400-450 kg/cm²; 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 (ΔL^* ; ℓ_0 and β) 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.