Published on the *Journal of the European Ceramic Society*, 25 (2005) 357-365.
 DOI: 10.1016/j.jeurceramsoc.2004.01.017

The role of surface microstructure on the resistance to stains of porcelain stoneware tiles

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Abstract

Porcelain stoneware tiles frequently undergo a polishing process, aimed at improving their aesthetical appearence, that brings about a consistent material removal, with formation of superficial defects and opening of closed pores. The consequent degradation of surface characteristics – and especially the increased sensitivity to stains – represent the main limit to the use of polished tiles in many indoor and outdoor applications. In order to better understand the role of microstructure on the resistance to stains, a phenomenological study of staining/cleaning operations (ISO 10545 parts 14 and 16) and a thoroughful physico-microstructural characterisation of tile working surfaces (SEM, open and closed porosity, rugosimetry, MIP) were carried out on twelve industrially manufactured and polished products. Diverse staining behaviours proved to be connected with different tile microstructures, being the surface roughness as well as the amount and shape of coarser pores the most influent variables. Through a statistical approach, an empirical predictional model of the amount of stain retained by the tile surface after mild washing with warm water was set up. It is based on roughness measurements (both R_a and R_t), estimation of macropores (i.e. 1-50 µm by MIP) and pore roundness (by image analysis of SEM photomicrographs).

Keywords: Microstructure-final, Porcelain stoneware, Porosity, Stain resistance, Traditional ceramics.

1. Introduction

Porcelain stoneware tile – a low porosity, glass-bonded material with excellent technical characteristics – is widely used in the building industry. For this reason, these products are required to have ever improved service performances in terms of mechanical, tribological and functional properties.[1-4]

Nowadays, the widespread industrial process of polishing – aimed at enhancing the aesthetical appearence of products – brings about a relevant material removal from the tile surface, commonly ranging from 0.4 to 0.8 mm.[5-6] These grinding/polishing operations induce a significant degradation of the superficial characteristics, due to both the formation of cracks and flaws produced by the machining procedure and to the opening of closed pores occurring into the ceramic body.[3-6] Overall, the polished tiles exhibit a worsening of functional performances, particularly an increased sensitivity to staining agents, that is currently the main limitation to their use in many outdoor and indoor applications.[7-10]

The resistance to stains is to a large extent related to the "microstructural quality" of the tile surface, thus amount, size and morphology of defects (e.g. pores, cracks, grooves). The previous studies on this subject found a generic dependence of the stain resistance on the superficial concentration of pores and defects, but without any univocal correspondence with the amount of stain retained by the tile surface.[7-12]

A better understanding of the role of surface microstructure is fundamental to achieve a phenomenological model of the staining behaviour, in order to improve the tile performance. The rationale of the present study is to characterize different typologies of industrially polished porcelain stoneware tiles, trying to point out the relative influence of surface morphology and ceramic body microstructure on the resistance to stains.

2. Materials and Methods

Twelve different types of industrially manufactured porcelain stoneware tiles were selected, in order to represent the wide range of technical performances, and decoration techniques of the products currently on the market (Table 1). All samples underwent the same grinding/polishing process carried out in an industrial plant, but the glazed tile (sample P11) which required different operating conditions. Every product was characterized determining its resistance to stains as well as surface and bulk properties.
The stain resistance and the cleanability of the tile working surface were appraised following the ISO 10545-14 standard, using the red staining agent (i.e. a 50% w/w of ferric oxide in light oil). The amount of staining was quantified after each cleaning step:

1. mild washing with warm water;
2. washing with warm water plus a neutral detergent;
3. vigorous brushing with a rotary equipment plus an alkaline detergent.

Five fragments of about 20 cm^2 each were utilised for every sample. The colour difference before and after the staining and cleaning operations was measured by means of a spectrophotometer (Hunterlab, MSXP 4000S, illuminant D65 and visual angle 10°) and expressed as ΔE^* (= $\sqrt{(\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})}$), where ΔL^*, Δa^* and Δb^* are the variations of the respective CieLab parameters, taking the as-received polished surface as a reference (standard ISO 10545-16). As the results of the three cleaning steps are strictly correlated each other (Fig. 1), just the ΔE^* values after the warm water cleaning step will be presented hereafter.
The following physical and microstructural characteristics were determined:

- bulk density (D_b) and open porosity (P_o) by water saturation under vacuum and Archimedes' principle (ISO 10545-3);
- total porosity (P_t) by the relation $P_t = 1 - (D_b / D_s)$ where D_s is the specific weight of the ceramic material measured by Helium pycnometry (Micromeritics MVP 1305);
- closed porosity (P_c) as difference: $P_c = P_t - P_o$;
- surface roughness with a Talisurf Plus equipment (Rank Taylor Hobson) calculating on five 80 mm runs (standard CEN 85): the average roughness (R_a) and the total height of profile (R_t) i.e. the sum of the maximum peak height and the maximum valley depth within the evaluation length;
- pore size distribution by mercury intrusion porosimetry (ThermoFinnigan Pascal 140 and 240) on tile fragments with an apparent area around 3 cm^2.

Cumulative curves and frequency histograms of mercury intruded in function of pore size – though affected by a limited significance due to the low porosity of porcelain stoneware – exhibit a clear bimodality, with two populations approximately in the 0.01-0.1 µm range (hereafter referred to as *micropores* P_{mi}) and the 1-50 µm range (called *macropores* P_{ma}) respectively.
The microstructure was investigated by SEM (Leica Cambridge Stereoscan 360) on the working surface of tiles, preliminarily washed, dried and gold-coated. An image analysis

was performed, using the Image Pro Plus 4.0 software, on SEM photomicrographs previously interpreted in order to highlight the textural elements. The following parameters were measured: pore volume P_{ia}, mean size of macropores P_{av}, pore aspect ratio (P_{ar}) and pore roundness (P_{ro}). These latter variables were calculated as the ratio between the major axis and the minor axis of the ellipse equivalent to the pore (P_{ar}) or according to the equation perimeter^2 / (4·π·area) for P_{ro}; in both cases, a round pore has a value = 1, while other shapes have values >1.

3. Results and Discussion

3.1. Physical and microstructural characteristics

The total porosity amounts to about 3 to 7%, being mostly represented by closed pores with a negligible fraction of open pores (at maximum 0.2%) while the bulk density fluctuates in the 2.37-2.44 g cm^{-3} interval. The porosity calculated by image analysis (P_{ia}) range from 3 to 10%, in acceptable agreement with P_t values. The average roughness values vary from 0.14 to 0.55 µm (R_a) and the total height of profile (R_t) was found to be from 6 to 15 µm (Tab. 2).

Porcelain stoneware microstructure is characterised by a fair variability of pore size distribution and pore shape (Table 3). Mercury porosimetry revealed that either micropores (<0.1 µm) or macropores (>1 µm) can predominate depending on the sample; however, the mean size of macropores – though affected by a remarkable standard deviation – varies in a rather narrow range (9-12 µm) with the exception of the glazed surface (Sample P11, P_{av} 18 µm). The pore morphology is characterised by moderate variations of pore aspect ratio and pore roundness (both in the 1.37-1.53 range and exhibiting a considerable standard deviation of data).

The surface of polished porcelain stoneware tiles presents diverse microstructural elements, either intrinsic features of the ceramic body (e.g. residual pores) or superficial defects created during the grinding/polishing process (Fig. 2). In particular, different kinds of residual pores are usually found:

a) small-sized (commonly <10 µm), spherical pores, that were probably gas-filled, so resulting insinterable during the industrial firing;
b) coarse-sized (often >20 µm), irregularly shaped pores, presumably originated from coalescence of smaller pores during sintering or inherited by large defects of the green compact;
c) discontinuities around bigger particles, partly deriving from residual stresses (e.g. polymorph transition of quartz).

Other textural features may be to a large extent attributable to the machining operations, such as:

d) scratches and thin grooves (several millimetres long and few micrometres wide);
e) larger grooves and chips (generally 10-20 µm);
f) abrasion of the edge of coarser pores.

3.2. Resistance to stains

The amount of red stain retained on the tile surface is summarised in terms of CIELab coordinates (Table 1). The surface is considered completely clean when the colourimetric variation after staining/cleaning operations drops below 1.0 ΔE*, that is a value approximately corresponding to the detection limit of human eye.

Overall, the samples taken into account exhibit four different trends of the intensity of staining in function of the cleaning steps (Fig. 3):

a) surfaces easily cleanable by washing with the neutral detergent used in the step 2 (samples P1, P2, P7 and P11);
b) surfaces that are completely clean only after brushing with an alkaline detergent as in step 3 (samples P3, P4, P8 and P10);
c) surfaces that remain moderately stained even after the cleaning step 3 (samples P5 and P9);
d) surfaces heavily stained that cannot be cleaned with the standard procedure (samples P6 and P12).

3.3. Stain resistance and microstructure

The above described behaviour of tiles during the staining/cleaning operations may be related to different surface microstructures, whose examples are represented in SEM photomicrographs (Fig. 4).

a) Easily cleanable products present a very compact texture, with low porosity and some coarse pores (up to 50 µm). In the case of sample P1 (ΔE* 1.7 after cleaning by mild washing with warm water) the occurrence of small grooves – about 5 µm, presumably produced by the polishing treatment – is not influent on the resistance to stains.
b) Another class of tiles relatively easy to clean – at least when the stain is a liquid or a viscous paste – is characterised by coarse spherical pores, originated by gas entrapment in the glaze layer, spread over a rather smooth surface with almost no other microstructural element (example P11, ΔE* 2.7).
c) Tile surfaces that are moderately stained after the cleaning step 3 seem to be less compact than those of previous categories, having a frequent occurrence of pore clusters with an irregular morphology (example P10, ΔE* 3.4).
d) The surface with the worst performance – being heavily stained after cleaning step 3 – is characterised by a wide range of pore sizes and particularly the presence of coarse, spherical pores with a peculiar internal microstructure, consisting of an apparently granular, sometimes fractured filling that offers a vast area for the stain attachment (example P6, ΔE* 7.7).

The intensity of staining is contrasted with the most significant parameters describing amount, size and shape of porosity (Fig. 5). Overall, every binary relationship has a poor statistical significance, suggesting that the resistance to stains has a complex dependence on several microstructural variables.

However, a noteworthy positive trend may be seen between stain intensity on one side and average roughness, amount of macropores and pore roundness on the other side. In contrast, an inverse correlation seems to exist between ΔE* and mean size of macropores, while the influence of total porosity on the stain intensity is weak, since data suffer of a considerable scattering.

On the other hand, the relationship with the total height of profile is doubtful; as a matter of fact, the positive trends between ΔE* and R_t or R_a exclude four outliers (i.e. P1, P2, P4 and P7) that are less stained than expected on the basis of roughness measurements. These easily cleanable products are characterised by the lowest values of P_{ma} and P_{ro}.

These observations are to a large extent confirmed by a statistical analysis with extraction of principal components (Fig. 6): the intensity of staining appears to be directly related with the values of R_a, P_{ro} or P_{ma}. In this standview, the stronger the stain resistance:

- the smoother the surface;
- the rounder the pores (i.e. P_{ro} closer to 1);
- the lower the amount of coarse pores (i.e. 1-50 µm).

The dependence of the stain intensity on other variables, such as R_t, P_{ar}, P_{av} or P_t, is much less significant.

These results provide a new insight into the design of stain-resistant tiles: in contrast with previous studies,[7,8,10] the role of total porosity is completely denied and even the emphasis on a specific critical range of pore size (e.g. 1-10 µm)[8] is debated. Hence, the attention of tilemakers should be paid to both the polishing treatment and the final stage of sintering. A proper compromise between grinding and polishing operations, in fact, should ensure a minimum surface roughness, while a suitable firing cycle is required to avoid a microstructural coarsening, with consequent pore growth.[13]

3.4. Prediction of the stain resistance

A further statistical elaboration of data was performed, through a multiple linear regression analysis, taking ΔE^* as the dependent variable and the main microstructural and physical parameters as independent variables, in order to quantify their influence on the resistance to stains. This procedure provided a simple predictional model with a good reliability (multiple correlation factor R^2 = 0.92, p-level <0.002) based on four variables selected through forward stepwise analysis (Fig. 7). The average roughness (R_a) and the total height of profile (R_t) are the most influent variables according to their standardised correlation factors, while minor effects are attributed to the amount (P_{ma}) and the mean size (P_{av}) of macropores. Taking into account the sign of the correlation factors, it appears that:

- the rougher is the surface, the stronger is its sensitivity to stains;
- a greater height of profile is not detrimental to the stain resistance, probably because coarser pores are easier to clean.[8,12]

In reality, this latter statement is in contrast with the other two variables selected: an increase of both the amount and the mean size of macropores contributes to decrease the resistance to stains of polished surfaces.

To improve this empirical model, it seems necessary to evaluate better the 'microstructural quality' of the tile surface, particularly some factors playing a determinant role, but very difficult to quantify, such as the irregular microstructure of the interior of macropores in the tile with the worst resistance to stains (sample P6).

4. Conclusions

The resistance to stains of polished porcelain stoneware tiles depends to a large extent on the surface microstructure. The amount of stain retained by the tile surface is somehow proportional to the concentration of superficial defects, either inherited by the ceramic body (i.e. pores) or originated during polishing (e.g. grooves, scratches).

This investigation has succeeded – coupling a phenomenological study of cleaning behaviour with a thoroughful microstructural characterisation of the polished surface – in highlighting the primary role of the surface roughness, together with the important effects due to the amount, size and morphology of pores. A significant contribution has been brought toward a quantitative evaluation of stain resistance and its prediction.

A statistical approach allowed to develop an empirical model able to predict the intensity of staining after mild washing with warm water, which is based on measurements of surface roughness (both R_a and R_t) pore roundness (by image analysis of SEM photomicrographs) and amount of macropores (by mercury intrusion porosimetry).

Acknowledgements

Authors are grateful to Penta Group, Castellarano (Italy) which provided the samples and carried out the polishing treatments.

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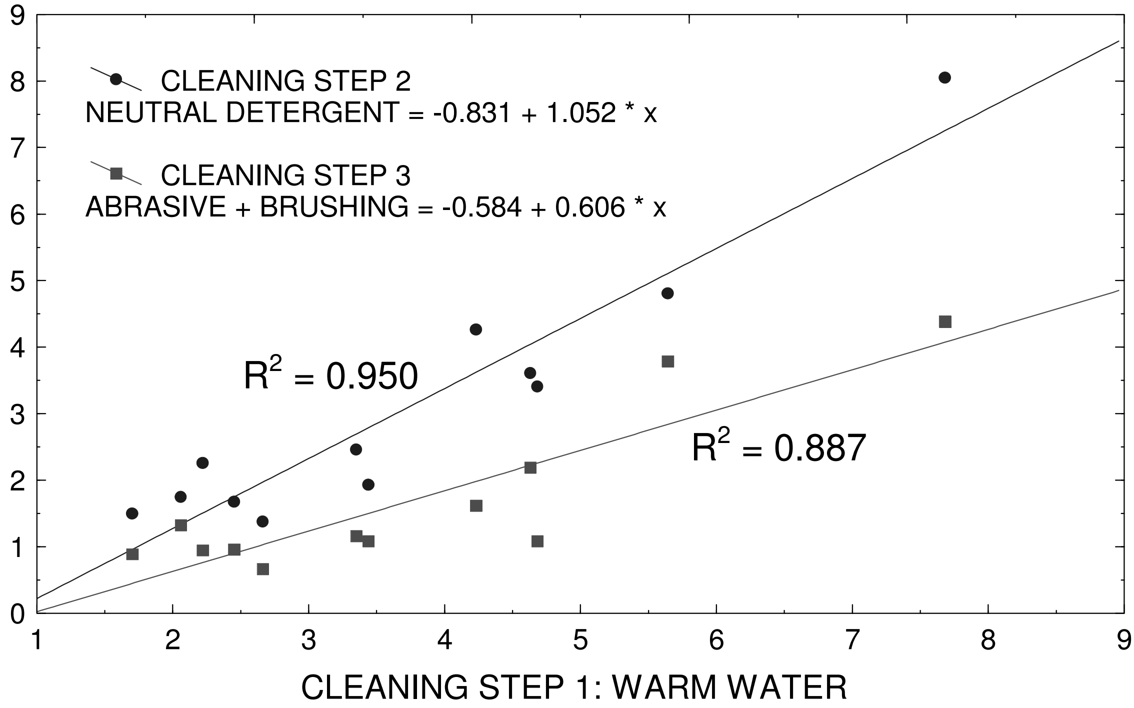


Fig. 1. Comparison of the intensity of staining (ΔE*) measured after the three cleaning steps of standard ISO 10545-14: mild washing with warm water (step 1) versus washing with warm water plus neutral detergent (step 2) and brushing with alkaline detergent (step 3).

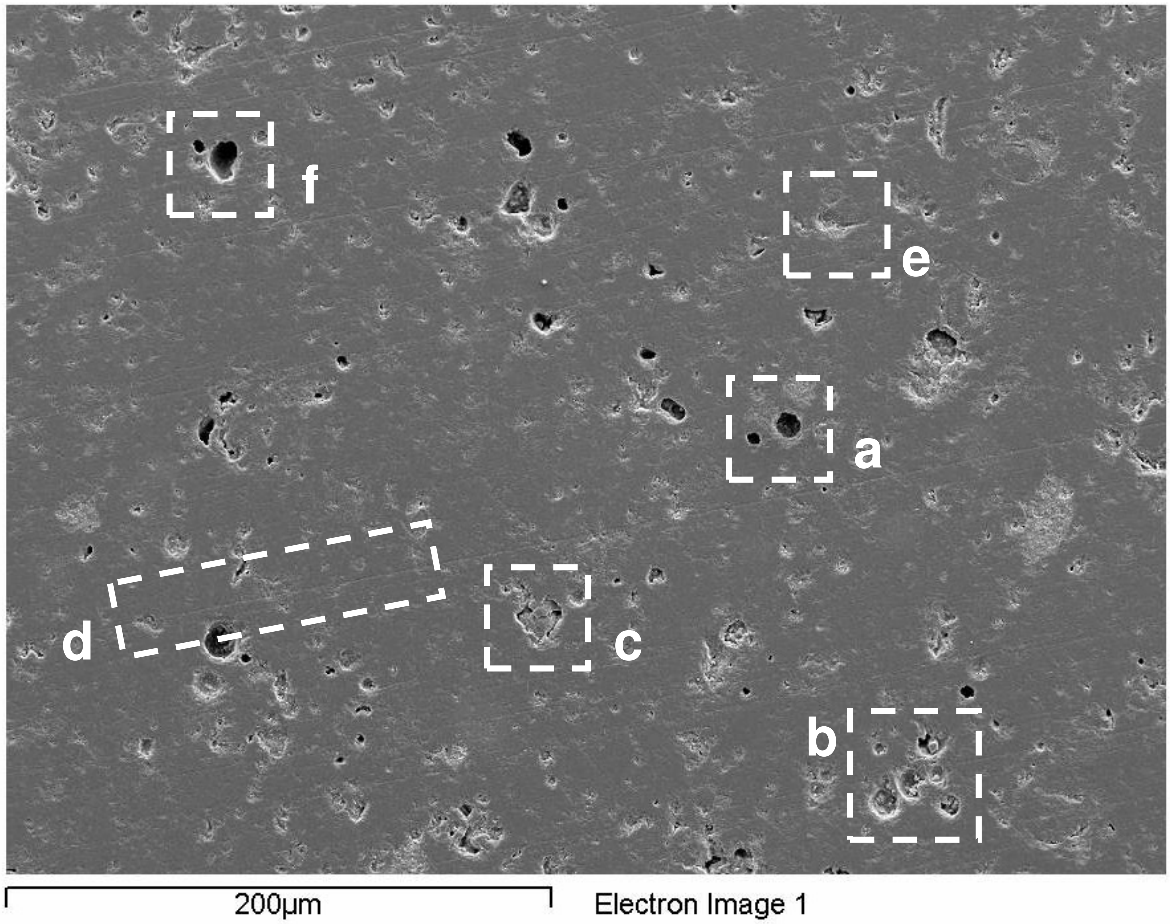
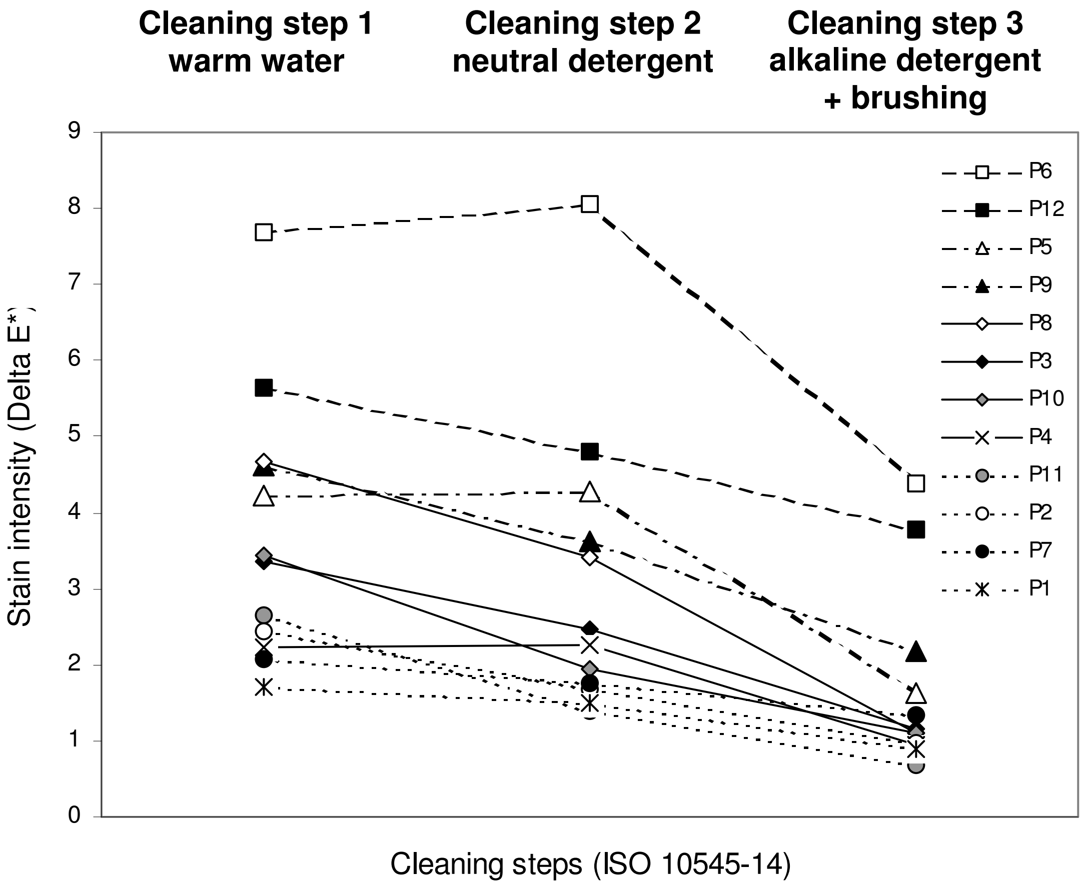


Fig. 2. Example of typical microstructural elements on the working surface of polished porcelain stoneware tiles. Description of single elements in the text.

Fig. 3.



Cleaning behaviour of the porcelain stoneware tiles.

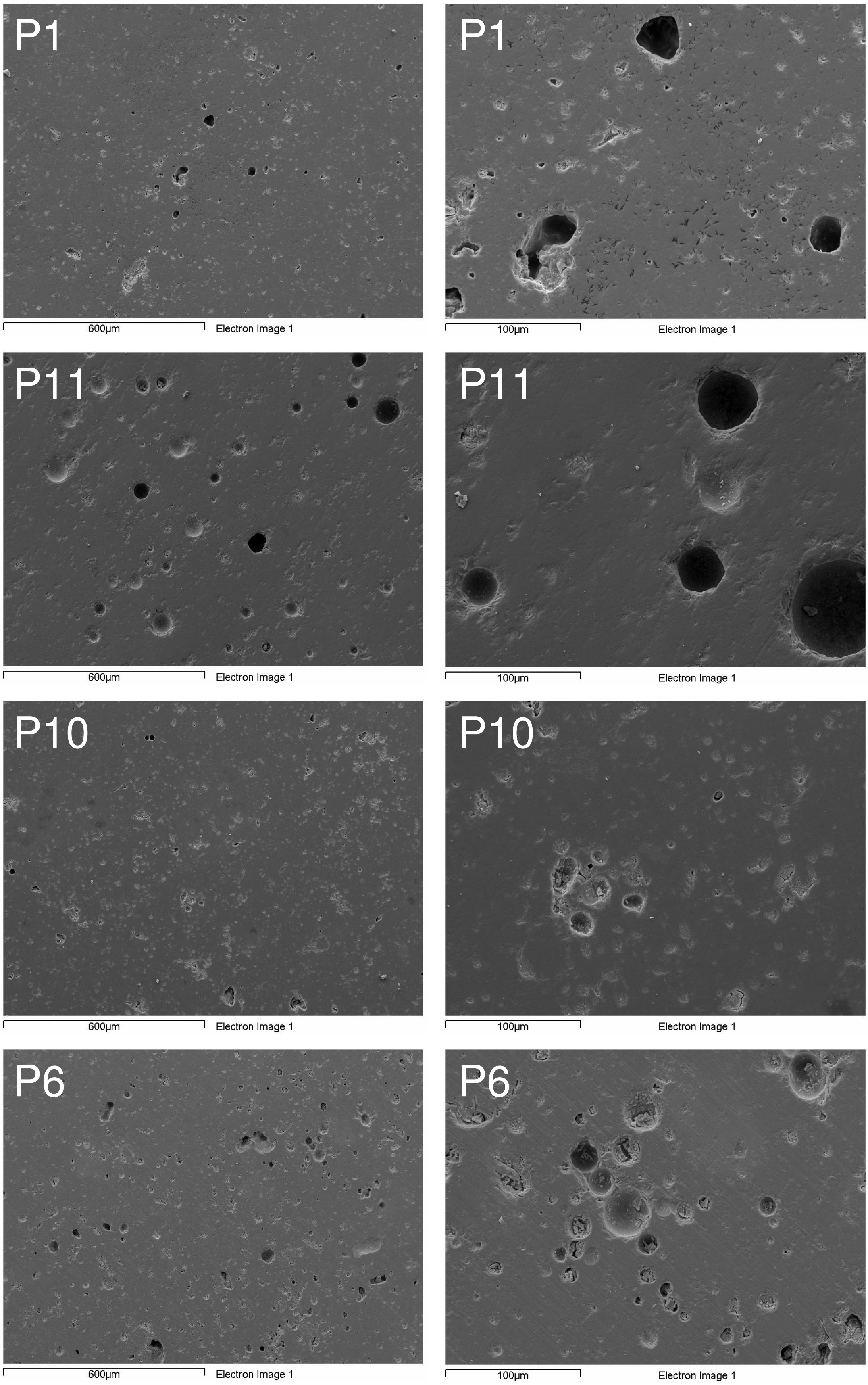


Fig. 4. SEM photomicrographs with examples of easily cleanable (samples P1 and P11), moderately stained (P10) and heavily stained surface (P6).

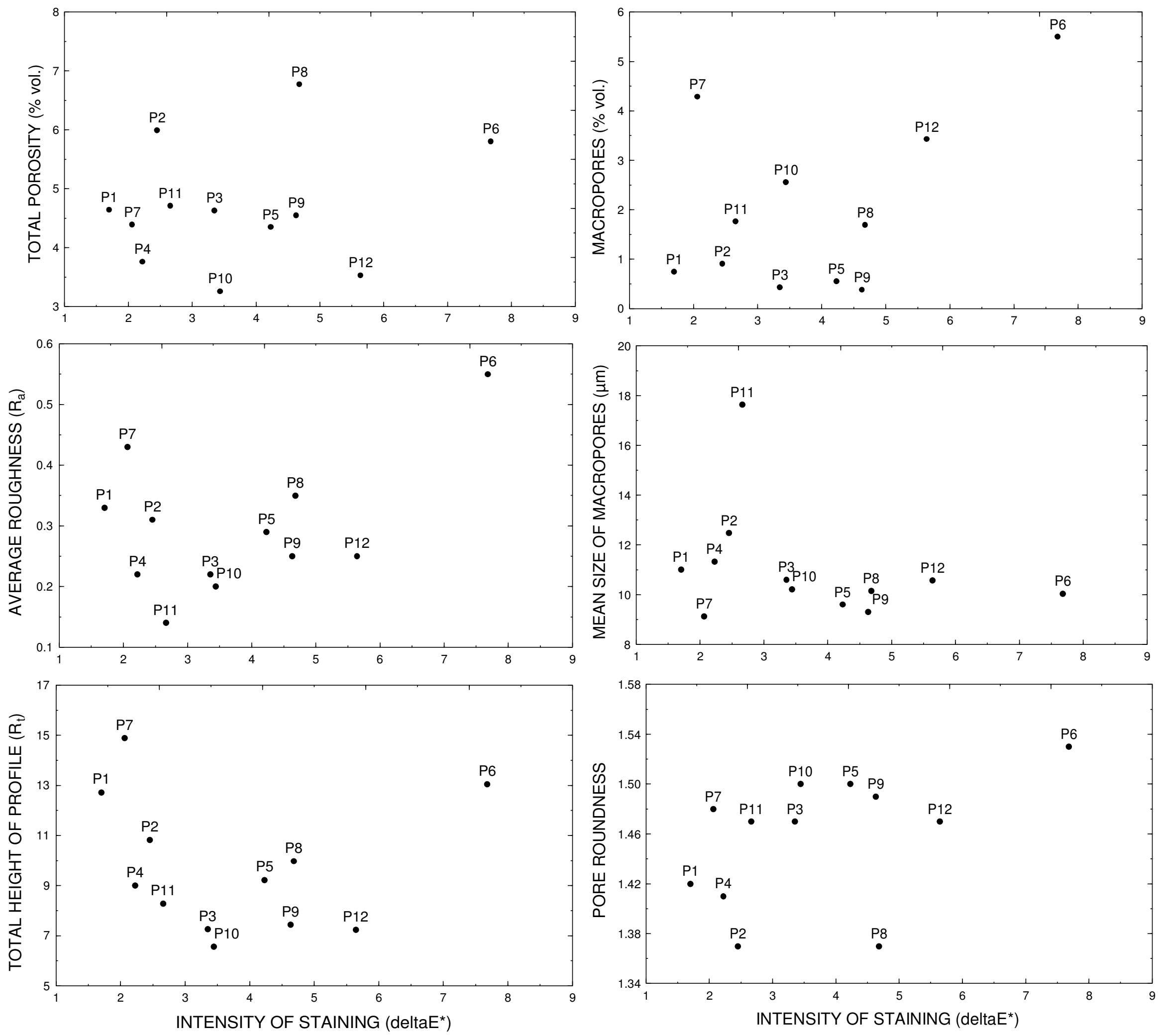


Fig. 5. Binary correlations of the intensity of staining (ΔE^* after cleaning step 1 of ISO 10545-14) with total porosity (P_t), average roughness (R_a), total height of profile (R_t), amount of macropores (P_{ma}), mean size of macropores (P_{av}) and pore roundness (P_{ro}).

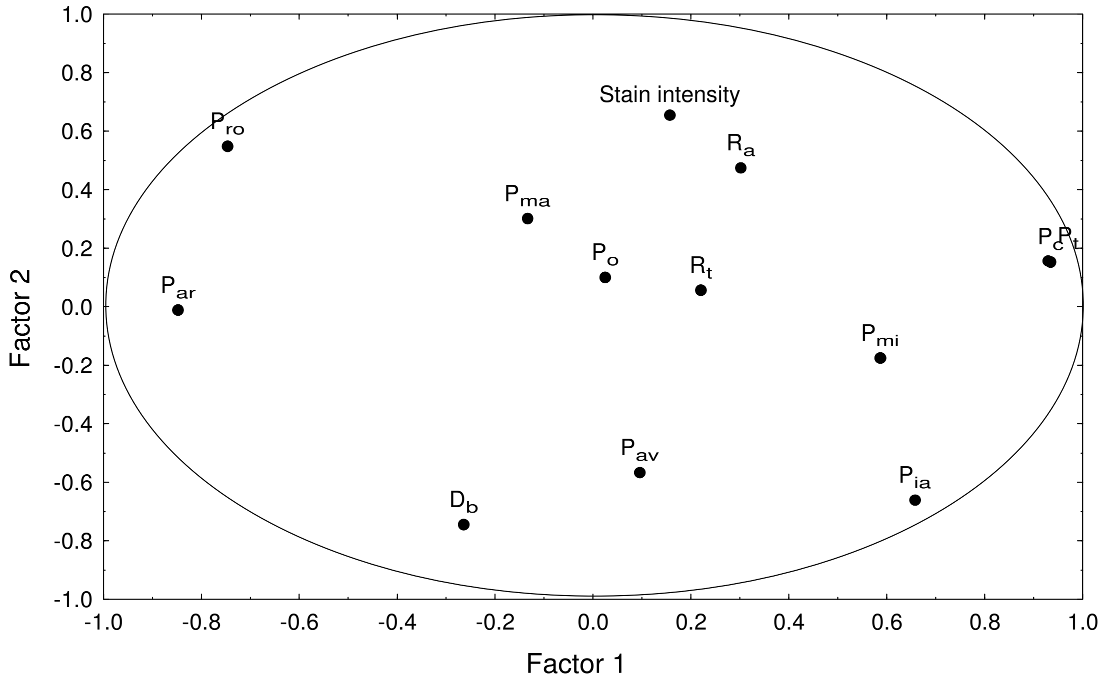
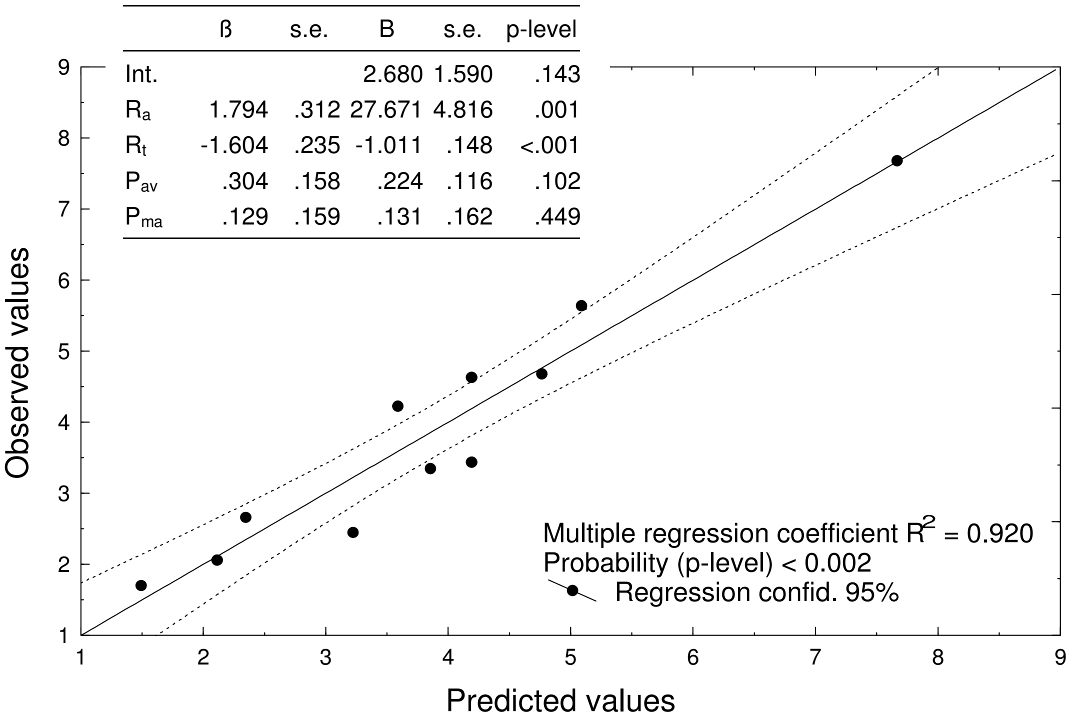


Fig. 6. Plot of factors 1 and 2 extracted by the principal components analysis. ∆E* intensity of staining after the warm water cleaning step, D_b bulk density, P_o open porosity, P_t total porosity, P_c closed porosity, R_a average roughness, R_t total height of profile, P_{mi} micropores, P_{ma} macropores, P_{ia} pore volume by image analysis, P_{av} mean size of macropores, P_{ar} pore aspect ratio, P_{ro} pore roundness.



	ß	s.e.	B	s.e.	p-level
Int.			2.680	1.590	.143
R_a	1.794	.312	27.671	4.816	.001
R_t	-1.604	.235	-1.011	.148	<.001
P_{av}	.304	.158	.224	.116	.102
P_{ma}	.129	.159	.131	.162	.449

Fig. 7. Observed versus predicted values of intensity of staining after mild washing with warm water (ΔE^*) obtained by multiple regression analysis. Both standardised (β) and non-standardised (B) correlation coefficients as well as respective standard errors and probability levels are listed for each variable selected by the statistical procedure. R_a=average roughness, R_t=total height of profile, P_{ma}=amount of macropores, P_{ro}=pore roundness.

Table 1
Resistance to stains of porcelain stoneware tiles expressed as CIELab colourimetric parameters before (reference) and after staining and cleaning with warm water (step 1 of ISO 10545-14) in absolute (L*, a*, b*) and relative terms (ΔL*, Δa*, Δb*, ΔE*).

Sample	Typology	Reference			ΔL*		Δa*		Δb*		ΔE*	
		L*	a*	b*	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.
P1	single colour	79.3	1.4	9.9	-1.2	0.1	1.2	0.1	0.4	0.0	1.7	0.2
P2	double loading	85.3	-0.4	6.3	-1.8	0.2	1.7	0.2	0.3	0.0	2.5	0.2
P3	double loading	82.4	0.6	8.0	-2.7	0.3	1.5	0.1	1.2	0.1	3.3	0.3
P4	soluble salts	76.7	-0.4	7.9	-1.1	0.1	1.7	0.2	0.8	0.1	2.2	0.2
P5	salt and pepper	62.2	-1.3	2.6	-3.8	0.4	1.8	0.2	0.7	0.1	4.2	0.4
P6	de-mixed	78.6	1.2	8.1	-6.2	0.6	3.9	0.4	2.4	0.2	7.7	0.8
P7	de-mixed + granulated	68.7	1.1	9.2	-1.3	0.1	1.6	0.2	0.3	0.0	2.1	0.2
P8	soluble salts	88.5	-0.2	4.8	-3.7	0.4	2.7	0.3	1.0	0.1	4.7	0.5
P9	micronized	77.1	4.1	13.0	-3.7	0.4	2.5	0.3	1.3	0.1	4.6	0.5
P10	de-mixed + granulated	77.5	2.1	11.3	-2.6	0.3	2.2	0.2	0.5	0.0	3.4	0.3
P11	polished glaze	87.3	-0.7	4.6	-2.1	0.2	1.6	0.2	0.4	0.0	2.7	0.3
P12	de-mixed + micronized	80.9	2.6	10.6	-4.6	0.5	2.6	0.3	1.8	0.2	5.6	0.6

Table 2
Physical properties of porcelain stoneware tiles

Sample	Open porosity (P_o, % vol.)		Closed porosity (P_c, % vol.)		Total porosity (P_t, % vol.)		Bulk density (D_b, g cm^{-3})		Specific weight (D_s, g cm^{-3})		Mean roughness (R_a, µm)		Total height of profile (R_t, µm)	
	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.
P1	0.21	0.05	4.43	0.14	4.64	0.09	2.44	0.01	2.56	0.02	0.33	0.08	12.73	2.00
P2	0.15	0.06	5.84	0.18	5.99	0.12	2.42	0.01	2.57	0.02	0.31	0.09	10.82	5.50
P3	0.21	0.06	4.42	0.15	4.63	0.09	2.41	0.01	2.53	0.02	0.22	0.06	7.26	2.92
P4	0.11	0.03	3.65	0.10	3.76	0.08	2.42	0.01	2.51	0.02	0.22	0.06	9.01	4.10
P5	0.21	0.10	4.14	0.18	4.35	0.09	2.38	0.01	2.49	0.02	0.29	0.08	9.23	4.62
P6	0.15	0.10	5.65	0.21	5.80	0.12	2.37	0.01	2.52	0.02	0.55	0.11	13.05	4.56
P7	0.14	0.02	4.25	0.11	4.39	0.09	2.38	0.01	2.49	0.02	0.43	0.18	14.90	6.88
P8	0.14	0.12	6.63	0.25	6.77	0.14	2.37	0.02	2.54	0.02	0.35	0.07	9.98	3.42
P9	0.12	0.07	4.43	0.16	4.55	0.09	2.42	0.01	2.54	0.02	0.25	0.07	7.45	1.96
P10	0.12	0.04	3.13	0.10	3.26	0.07	2.40	0.01	2.48	0.02	0.20	0.03	6.57	2.57
P11	0.15	0.03	4.56	0.12	4.71	0.09	2.40	0.01	2.52	0.02	0.14	0.05	8.29	2.55
P12	0.08	0.04	3.45	0.11	3.53	0.07	2.44	0.01	2.53	0.02	0.25	0.09	7.24	3.21

s.d. = standard deviation (n-1)

Table 3
Microstructural properties of porcelain stoneware tiles

Sample	Porosity by i.a. (P_{ia}, % vol.)		Micropores (P_{mi}, % vol.)		Macropores (P_{ma}, % vol.)		Mean pore size (P_{av}, µm)		Pore aspect ratio (P_{ar}, 1)		Pore roundness (P_{ro}, 1)	
	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.	mean	s.d.
P1	8.0	0.8	3.9	0.4	0.7	0.1	11.0	5.5	1.51	0.45	1.42	0.40
P2	9.7	1.0	5.1	0.6	0.9	0.1	12.5	7.5	1.41	0.57	1.37	1.17
P3	5.3	0.5	4.2	0.5	0.4	0.1	10.6	5.4	1.54	0.52	1.47	0.39
P4	4.0	0.4	n.d.		n.d.		11.3	6.4	1.48	0.45	1.41	0.40
P5	4.8	0.5	3.8	0.4	0.6	0.1	9.6	6.3	1.46	0.46	1.50	0.89
P6	4.5	0.5	0.3	0.1	5.5	0.6	10.0	7.1	1.49	0.50	1.53	0.89
P7	3.2	0.3	0.1	0.1	4.3	0.5	9.1	5.5	1.48	0.58	1.48	0.47
P8	7.3	0.7	5.1	0.6	1.7	0.2	10.2	5.0	1.37	0.33	1.37	0.29
P9	4.4	0.4	4.2	0.5	0.4	0.1	9.3	4.7	1.53	0.55	1.49	0.43
P10	2.8	0.3	0.7	0.1	2.6	0.3	10.2	5.4	1.52	0.44	1.50	0.38
P11	6.7	0.7	2.9	0.3	1.8	0.2	17.6	14.3	1.52	0.56	1.47	0.45
P12	7.0	0.7	0.1	0.1	3.4	0.4	10.6	5.8	1.48	0.47	1.47	0.58

s.d. = standard deviation (n-1)