Key Engineering Materials *Online: 2004-05-15*
ISSN: 1662-9795, Vols. 264-268, pp 1511-1514
doi:10.4028/www.scientific.net/KEM.264-268.1511

Stain Resistance of Porcelain Stoneware Tiles: the Influence of Microstructure

M. Dondi[1], G. Guarini[1] and M. Raimondo[1],
E. R. Almendra[2], P.M. T. Cavalcante[2]

[1] CNR-Institute of Science and Technology for Ceramics, Faenza (Italy)

[2] UFRJ-COPPE, Federal University of Rio de Janeiro (Brasil)

Keywords: Porcelain stoneware tile, Stain resistance, Microstructure, Pore morphology.

Abstract. This work deals with the appraisal of the most important microstructural parameters influencing the stain resistance of polished porcelain stoneware tiles. The correlations between the stain resistance on one side and bulk or surface characteristics on the other side were evaluated through a statistical approach, which provided a previsional model of the staining behaviour of tiles, based on the surface roughness as well as the pore amount, size and morphology.

Introduction

Porcelain stoneware tiles, being widely used in outdoor and indoor applications, are required to have enhanced service performances in terms of mechanical, tribological and functional properties [1]. Nowadays, the widespread industrial process of polishing gives products an increased aesthetic quality, but, at the same time, the material removal from the surface involves a worsening of the functional performances. The degradation of the surface is due to both the presence of cracks and flaws induced by the machining procedure and to the opening of the closed pores occurring into the ceramic body, resulting in an increase of the surface sensitivity to staining agents [2].
Therefore, the stain resistance depends to a large extent on the amount of surface defects (e.g. pores and cracks), but also on the pore size and morphology. The experimental data available in the ruevant literature do not provide an univocal correspondence of the concentration of pores and defects with the functional properties [3,4]. In order to quantify the staining effect, a better understanding of the surface physico-microstructural parameters is required.
The rationale of this work is to characterize different typologies of industrially polished porcelain stoneware tiles, trying to point out the relative influence of the surface morphology and the ceramic body microstructure on the stain resistance.

Materials and Methods

Twelve different types of porcelain stoneware tiles, representing a wide range of product performances, were selected and submitted to an industrial polishing process. The products were characterized measuring: water absorption, bulk density and open porosity (ISO 10545-3), total and closed porosity (ASTM C 329), surface roughness (CEN 85), microstructure by SEM observations (Leica Cambridge Stereoscan 360), stain resistance and cleanability (ISO 10545-14). The staining after each cleaning step (warm water, neutral detergent, brushing plus abrasive detergent) was quantified by the colour difference before and after the staining and cleaning operations, expressed as $\Delta E = \sqrt{(\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})}$, where ΔL^*, Δa^* and Δb^* are the differences of the three CieLab parameters (ISO 10545-16) taking the as-received polished surface as a reference. Hereafter just the ΔE values after the warm water cleaning step are presented, as they are strictly correlated with the other two. The pore amount and morphology (mean pore size and roundness) were also evaluated through image analysis (Image Pro Plus 4.0 software) performed on SEM photomicrographs.

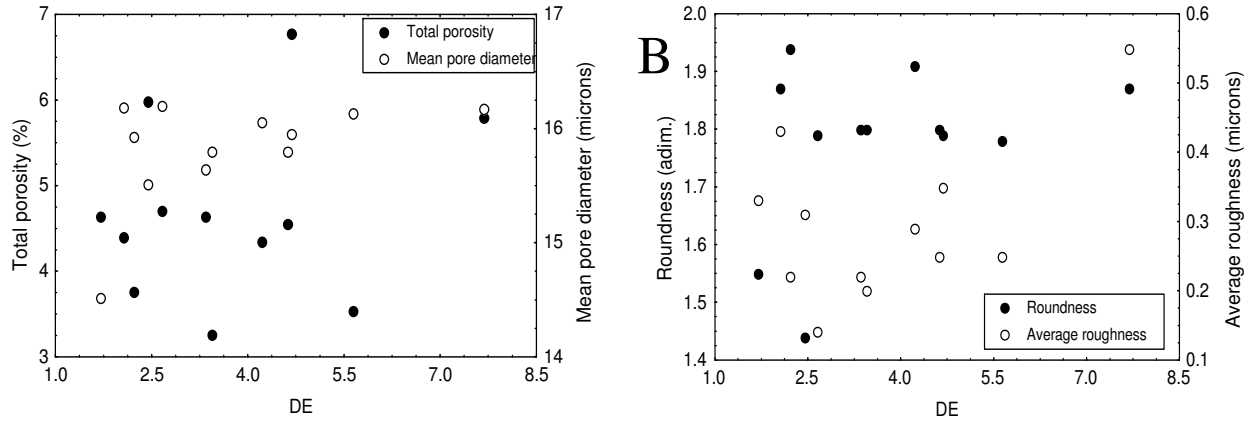
Table 1. Physico-microstructural properties and stain resistance of porcelain stoneware tiles

Property	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
Bulk density [g cm^{-3}]	2.44	2.42	2.41	2.42	2.38	2.37	2.38	2.37	2.42	2.40	2.40	2.44
Water absorption [% wt.]	0.08	0.06	0.09	0.05	0.09	0.06	0.06	0.06	0.05	0.05	0.06	0.03
Open porosity [% vol.]	0.21	0.15	0.21	0.11	0.21	0.15	0.14	0.14	0.12	0.12	0.15	0.08
Total porosity [% vol.]	4.64	5.99	4.63	3.76	4.35	5.80	4.39	6.77	4.55	3.26	4.71	3.53
Porosity by image analysis [% vol.]	8.0	9.7	5.3	4.0	4.8	4.5	3.2	7.3	4.4	2.8	6.7	7.0
Pore roundness [adim.]	1.42	1.37	1.47	1.41	1.50	1.53	1.48	1.37	1.49	1.50	1.47	1.47
Mean pore size [µm]	11.0	12.5	10.6	11.3	9.6	10.0	9.1	10.2	9.3	10.2	17.6	10.6
Average roughness R_a [µm]	0.33	0.31	0.22	0.22	0.29	0.55	0.43	0.35	0.25	0.20	0.14	0.14
Maximum roughness R_t [µm]	12.7	10.8	7.3	9.0	9.2	13.1	14.9	10.0	7.5	6.6	8.3	8.3
Stain resistance [ΔE]:												
- warm water	1.7	2.5	3.4	2.2	4.2	7.7	2.1	4.7	4.6	3.4	2.7	5.6
- neutral detergent	1.5	1.7	2.5	2.3	4.3	8.1	1.8	3.4	3.6	1.9	1.4	4.8
- alkaline detergent + brushing	0.9	1.0	1.2	1.0	1.6	4.4	1.3	1.1	2.2	1.1	0.7	3.8

Results and Discussion

The products here considered show a wide range of physical properties: total porosity ranges from about 3 to 7%, with a small fraction of open pores (up to 0.2%), while the bulk density is in the 2.37-2.44 g cm^{-3} range (Table 1). The microstructure is characterised by a certain variability of roundness (1.37-1.53) and by a rather narrow range for the mean pore size (9-13 µm, with one exception). Roughness values vary from 0.1 to 0.6 µm (R_a) and from 6 to 15 µm (R_t).

Inorder to better understand the influence of both the bulk and the surface properties on the stain resistance, colourimetric ΔE values are contrasted to both total porosity and mean pore size (Figure 1.a). The influence of the total porosity on the stain resistance is not statistically significant, since the data suffer of a considerable scattering, while a positive trend may be seen between the mean pore diameter and the staining attitude. However, higher ΔE values do not correspond always to high porosity or larger amounts of big pores.



(a) (b)

Figure 1 – Intensity of staining (DE) versus a) total porosity and mean pore diameter; b) pore roundness and average roughness.

Table 2. Results of the stepwise multiple regression analysis.

N = 12	Standardized regression coefficients		Raw regression coefficients		Probability level
	β	std error	B	std error	p
Intercept			-26.265	11.025	0.063
Average roughness	1.521	0.194	23.735	3.035	0.001
Maximum roughness	-1.236	0.198	-0.805	0.129	0.016
Porosity by image analysis	0.442	0.185	0.371	0.156	0.632
Pore roundness	0.405	0.201	10.071	5.028	0.101
Mean pore size	0.168	0.130	0.631	0.488	0.252
Multiple correlation coefficients: $R = 0.971$; $R^2 = 0.943$					

This apparently predominant influence of the surface characteristics on the tile functional properties is confirmed plotting ΔE versus pore roundness and average surface roughness (Fig. 1.b). Roundness values close to one (i.e. corresponding to almost spherical pores) are expected to involve a greater sensitivity to staining agents [3] but this is not appreciable in the samples, which are characterised by quite high values, that mean a less regular morphology and consequently a more complex relationship with the staining attitude. On the other hand, the average roughness is correlated well with ΔE values, with some exceptions concerning tiles with a high resistance to stains (ΔE <2.5).

A statistical elaboration of data was performed, through a multiple linear regression analysis, taking ΔE as dependent variable and the main microstructural and physical parameters as independent ones, in order to quantify their influence on the resistance to stains. This statistical procedure selected the average (R_a) and the maximum roughness (R_t) as the most influent variables, followed by the total porosity measured by image analysis, pore roundness and mean pore size, with a good multiple correlation factor $R^2 = 0.943$ (Table 2 and Fig. 2).

As a matter of fact, the smoother the surface, the higher the stain resistance. However, there is a different sign of the R_a and R_t β factors: this means that more rough is on average the surface, the more is its susceptibility to staining, but the maximum the roughness (that somehow express the occurrence of large pores) is not detrimental to the staining behaviour, probably because the large pores are easier to clean [5]. A prevalent influence of the surface morphology is confirmed by the relative weight of pore amount, size and shape, as measured by image analysis.

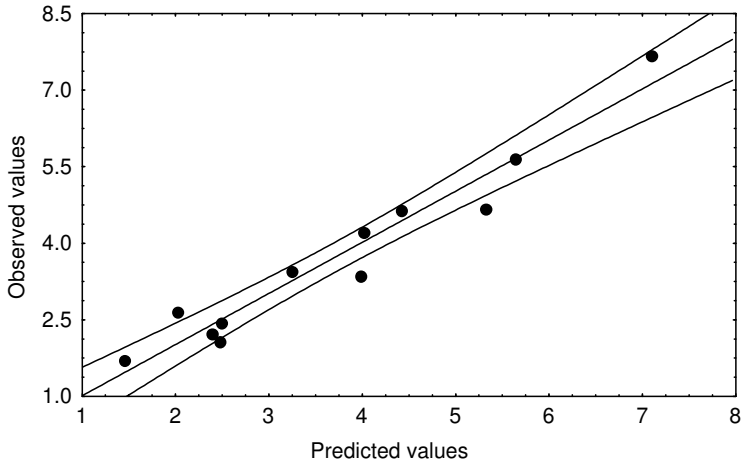


Figure 2 – Observed versus predicted values of resistance to stains from the predictional model achieved by multiple regression analysis.

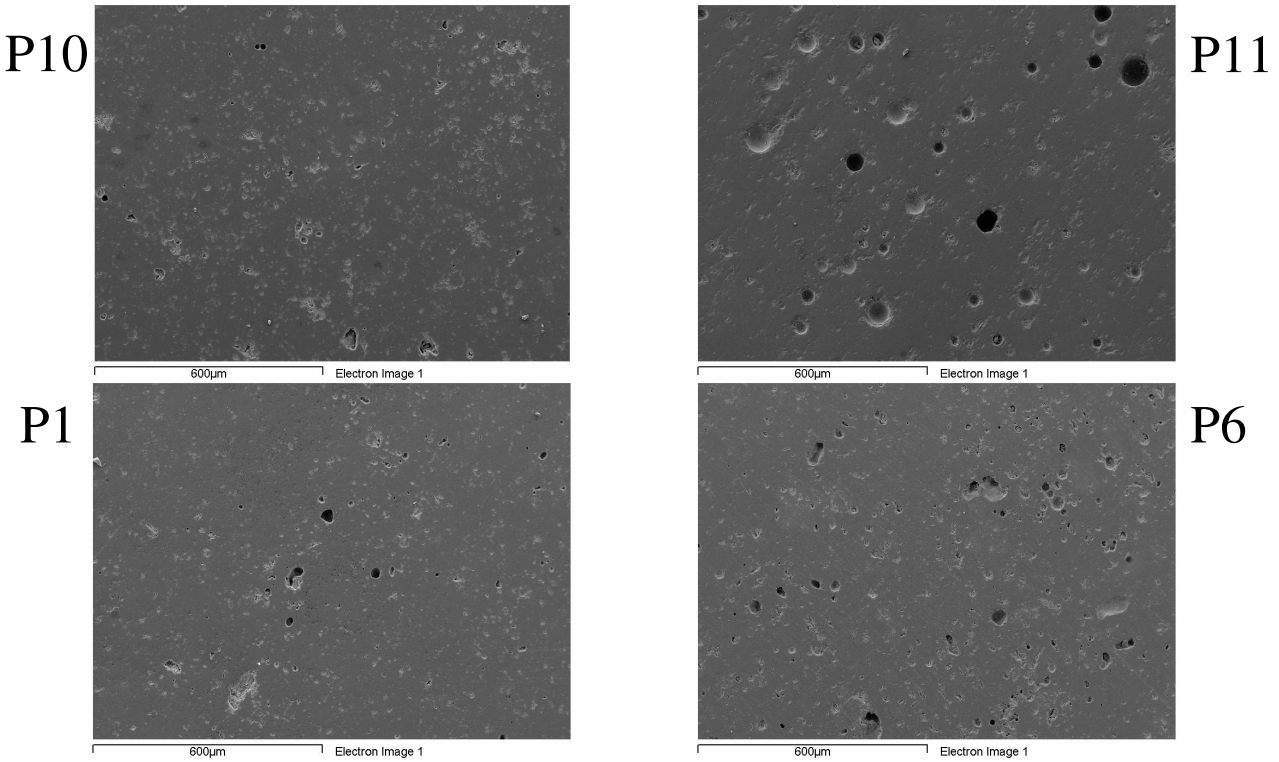


Figure 3.– Surface microstructure of different types of polished porcelain stoneware tiles.

The staining sensitivity of the tile surface depends on its microstructure (Fig. 3). Typical porcelain stoneware (P10, stain resistance ΔE=3.4) exhibits a wide spectrum of pore size and shape, with few spherical pores and several superficial flaws due to polishing. Products highly resistant to stains can be either compact, with few big pores and defects (P1, ΔE=1.7) or characterised by a smooth surface with big spherical pores (P11, ΔE=2.7). The worst performance is connected with pores presenting a rough internal surface (P6, ΔE=7.7).

Conclusions

The resistance to stains of polished porcelain stoneware tiles depends to a large extent on the surface microstructure. The statistical approach followed in this study has been able to highlight the primary role played by the surface roughness, as well as the important effect of the pore amount, size and morphology on the staining behaviour.

References

[1] T. Manfredini, G. C. Pellacani, M. Romagnoli: Am. Cer. Soc. Bull. Vol. 74 (1995), p. 77.

[2] L. Esposito and A. Tucci: Am. Cer. Soc. Bull. Vol.75 (2000), p. 59.

[3] V. Beltran, C. Ferrer, V. Bagan, E. Sanchez, J. Garcia, S. Mestre: Ceramica Acta Vol 4-5 (1996), p. 37.

[4] F. J. S. Arantes, D. F. Galesi, E. Quinteiro and A. O. Boschi: Ceramica Industrial Vol 6 (2001), p. 18.

[5] S. Di Primio, A. Argnani, R. Nofri, A. Gislimberti: Ceramica Informazione Vol 387 (1999), p. 264.