CLEANABILITY OF "LAPPATO" PORCELAIN STONEWARE

Maria Soranzo,[1] Elisa Rambaldi,[2]* Francesca Prete,[2] Giuliana Bonvicini,[2] Maria Chiara Bignozzi.[2,3]

[1] Fila Industria Chimica Spa, S. Martino di Lupari, Padova, Italy

[2] Centro Ceramico Bologna, via Martelli 26, Bologna, Italy

[3] Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, via Terracini 28, Bologna, Italy

1. ABSTRACT

With the arrival on the market of lapped porcelain stoneware tiles, several studies have focused on the improvement of the technical characteristics of these surfaces. In fact, surface lapping of porcelain stoneware tiles induces both aesthetical improvements and deteriorations of their performance. To overcome this problem, it is possible to protect the lapped surface with commercial waterproofing materials.

In this work, "Lappato" commercial porcelain stoneware tiles with a protective stain proofing agent, FILA PD15 and FILA 1239 Plus, were evaluated. The stain and chemical resistance results were correlated to the morphological surface characteristics of the products with and without protection. In particular, a systematic study of the surface porosity of the tiles was carried out. Results showed that a pore unprotected in time will tend to fill with dirt hardly removable with ordinary maintenance. If the pores are protected, however, the dirt from foot traffic over time will tend to be deposited, but only superficially.

2. INTRODUCTION

Porcelain stoneware is a product characterized by excellent technical performances: high density (water absorption <0.5%), abrasion and stain resistance, and surface hardness. When fired, stoneware tiles are exposed to very high temperatures, which allow an extremely durable and compact surface to be obtained. However, to attain aesthetic characteristics that are highly valued by the end user, porcelain stoneware tiles are often lapped to reduce the surface roughness and to increase their gloss.

Even if the lapping process improves the aesthetics of the product and increases its competitiveness with natural stones, it also induces several changes in the surface microstructure, as a result of the polishing procedure. A fine layer of the product is removed, causing the formation of cracks and flaws and revealing the closed porosity, initially located inside the material. This may compromise the technical and aesthetic performance of porcelain tiles, particularly in terms of cleanability and resistance to stains [1,2,3,4,5]: dirt can, in fact, penetrate into pores, grooves and scratches and its removal can turn out to be very difficult.

To achieve a high stain resistance and to preserve the aesthetic performance of porcelain stoneware, a protective stain proofing agent can be applied on the surface of the tiles. The role of the protective treatment is to fill up pores and holes, thus preventing the penetration of dirt and staining agents. The effect of some protective coatings [6,7,8] has been analysed in previous works and it has been demonstrated that the efficacy of the treatments depends on the characteristics of the treatment and on the characteristics of the surface on which it is applied. In this work the effect (stain resistance and chemical resistance) of two protective treatments on commercial lapped porcelain stoneware tiles has been studied: the first is a treatment directly applied on the industrial line (FILA FT1239 Plus) and the second one is applied after tiling (FILA PD 15).

3. MATERIALS AND METHODS

One type of commercial lapped porcelain stoneware tile (60x30 cm; white colour), referenced "A", was selected for this study. This type of lapped tiles was subjected to different treatment steps, referenced as follows:

- A1 – untreated tile;
- A2 – tile washed with a phosphoric based solution (to remove residuals of lapping process);
- A3 – tile washed with a phosphoric based solution and then treated with a protective agent (FT1239 Plus);
- A4 – tile washed with a phosphoric based solution and treated with two protective agents (FT1239 Plus and, subsequently, FILA PD 15).

The working surface of the tiles was subjected to a stain resistance test (according to ISO 10545-14), to the determination of the chemical resistance (according to ISO 10545-13 - glazed tile procedure) and to the analysis of the surface microstructure. For stain resistance, the staining agents were: green staining agent in light oil, iodine (13 g/l solution in alcohol) and olive oil. For the chemical resistance, the test solutions were: Ammonium chloride solution (100 g/l), Sodium hypochlorite solution (20 mg/l), Hydrochloric acid solution (3% V/V) and Potassium hydroxide solution (30 g/l). Both tests were performed on 3 different areas of each tile.

An optical microscope (Leica DMLM, D) was used to analyse the effect of the protective treatment on the working surface of the porcelain stoneware. The obtained digital images were analysed using the image software analysis Leica Application Suite (LAS) to calculate the percentage of the total porosity TP (mean of 5 images for each sample) and to evaluate their distribution, shape and size. Each tile was also examined by scanning electron microscope (SEM, Zeiss EVO 40, D) to investigate in-depth the effect of the protective treatment on the surface microstructure of porcelain stoneware. Further correlation between microstructure and cleanability was evaluated by spraying a solution of dirt (graphite based) and, after drying, by removing it with a wet cloth.

4. RESULTS AND DISCUSSION

The results of the resistance to staining (ISO 10545-14) are reported in table 1. All the samples belong to class 5 (the stain is removed with hot water) and no differences are observed among them, by using the selected staining agents.

Samples	A1	A2	A3	A4
Green staining agent in light oil	5	5	5	5
Iodine	5	5	5	5
Olive oil	5	5	5	5

Table 1. *Classes from 1 to 5 (ISO 105454-14). Class 1: stain not removed, Class 2: stain removed by dipping in a suitable solvent for 24 hours; Class 3 stain removed by mechanical cleaning and strong cleansing agent; Class 4: stain removed by manual cleaning with weak cleansing agent; Class 5: stain removed by means of hot streaming water for 5 minutes.*

The results of the determination of the chemical resistance (ISO 10545-13) are reported in table 2. A deterioration of the chemical resistance by using household chemicals (ammonium chloride and sodium hypochlorite solutions) was observed for sample A2.

By using hydrochloric acid (low concentration), a lower deterioration of chemical resistance was observed for samples having a protective treatment (A3 and A4) that belong to the class LB, while for tiles with no treatment (A1 and A2) the deterioration is more pronounced (class LC). By using Potassium hydroxide (low concentration) a marked deterioration of the chemical resistance was observed for all samples.

Samples	A1	A2	A3	A4
Ammonium chloride	A	B	A	A
Sodium hypochlorite	A	B	A	A
Hydrochloric acid	LC	LC	LB	LB
Potassium hydroxide	LC	LC	LC	LC
Pencil test	No	No	Yes	Yes
Reflection test	Yes	Yes	Yes	Yes

Table 2. *Classes from A to C (ISO 105454-14). For Ammonium Chloride and Sodium hypochlorite solutions (household chemicals): Class A: no visible effect; class B: discernible visible change in appearance; Class C: partial or complete loss of the original surface. For hydrochloric acid and Potassium hydroxide solutions (acid and alkalis in low concentration): Class LA: no visible effect; Class LB: discernible change in appearance; Class LC: partial or complete loss of the original surface.*

The results of the optical microscope analysis (bright field analysis) and of image analysis are reported in fig. 1. For sample A1 the value of the total porosity (TP) is quite high, 16.9%. The majority of the pores belong to the class 5-10 µm (fig. 1) and to the class 0-5 µm. Pores measuring>10 µm account for about 16% in all. In addition to the pores, grooves and scratches are also present, which contribute to the amount of total porosity.

For sample A2 (washed with a phosphoric based solution) the total porosity increases significantly, reaching a value of 30.9%, due to the effect of the acid that dissolves the glassy phase and creates, in addition to the intrinsic porosity, a large amount of small irregular cavities having a size <5 µm.

For sample A3 (treated with the proofing agent FT1239 Plus) the total porosity decreases to a value of 10.3% (fig. 1). A great part of the pores and cavities <5 µm, observed in sample A2, is filled and covered by the treatment. Pores measuring >10 and 20 µm are, instead, partially filled (this effect is more clearly visible in the SEM images, fig. 2).

For sample A4 the effect of the treatment is even more evident compared to sample A3. The total porosity decreases to a value of 6.3%. The most part of pores is filled and covered by treatments, only pores measuring >10 and 20 µm are not completely filled (as for sample A3, this effect can be more easily evaluated by SEM images).

The SEM analysis of the sample A1 (2a-2b) shows more clearly the shape of the pores: pores >10 µm mainly have a circular shape, while pores <10 µm are more irregular in shape and are often the result of the coalescence of small pores or of the coalescence of small irregular cavities formed as a result of the removal of material by lapping machines. Several marks and scratches made by the lapping process are evident on the surface of the sample.

The SEM analysis of sample A2 (fig. 2c-2d) shows the effect of the phosphoric solution on the working surface of the tile. The acid solution dissolves the glassy phase of porcelain stoneware creating a rough surface. Many irregular hollow spaces, together with the intrinsic porosity of the product, can be observed on the surface of this sample.

The SEM analysis of the sample A3 (fig. 2e-2f) shows how the proofing agent covers small pores, hollow spaces created by acid solution, and fills almost completely pores >10 µm. For sample A4 (fig. 2g-2h), the effect of the treatment is even more evident. Only pores >10 µm are clearly visible. These pores are almost totally filled by the proofing agent that appears cracked and, often, leaves a small circular hole inside the pore.

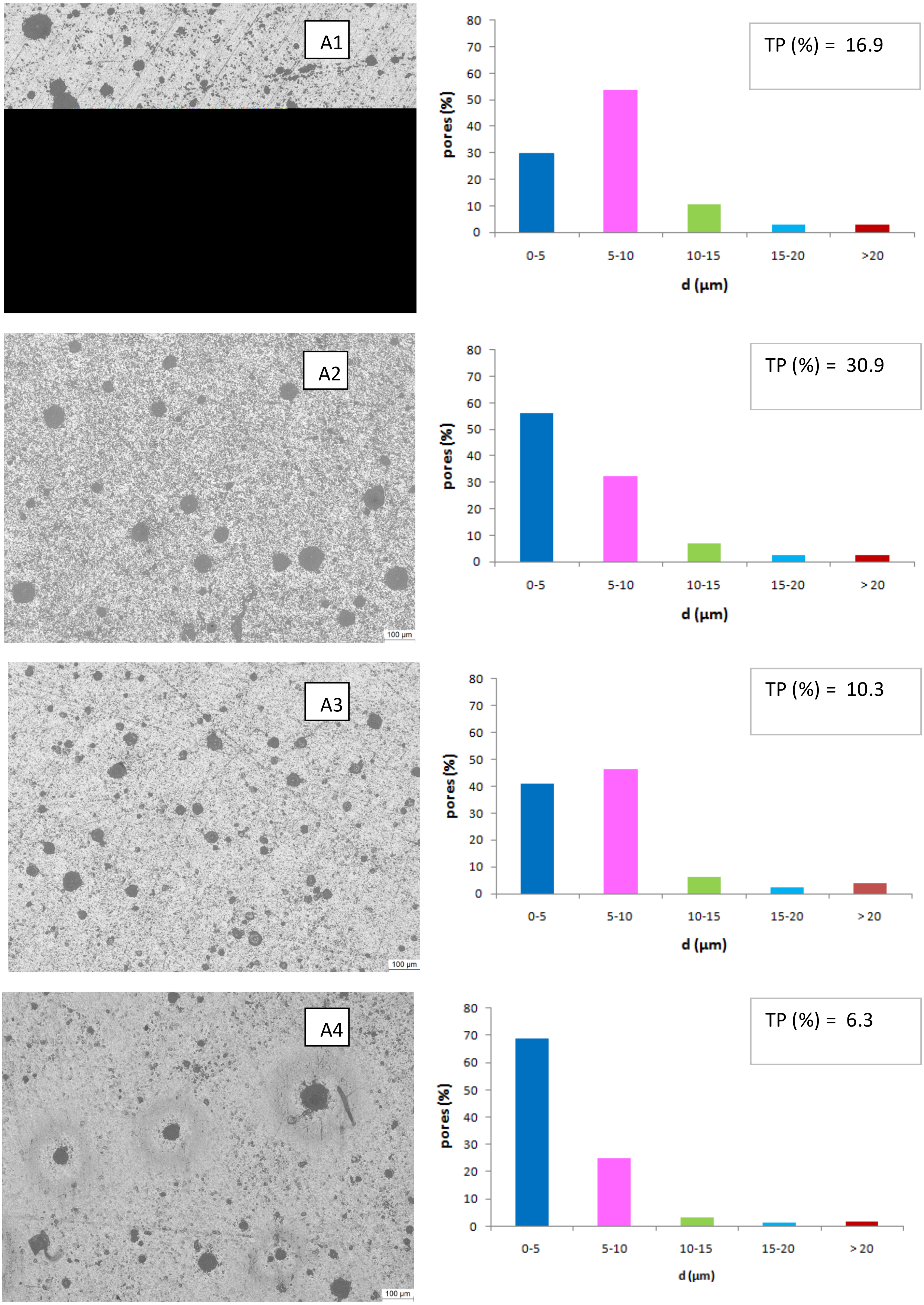

Fig. 1. *Optical microscope images (bright field) and pore size distribution for sample A1, A2, A3 and A4. TP = Total Porosity.*

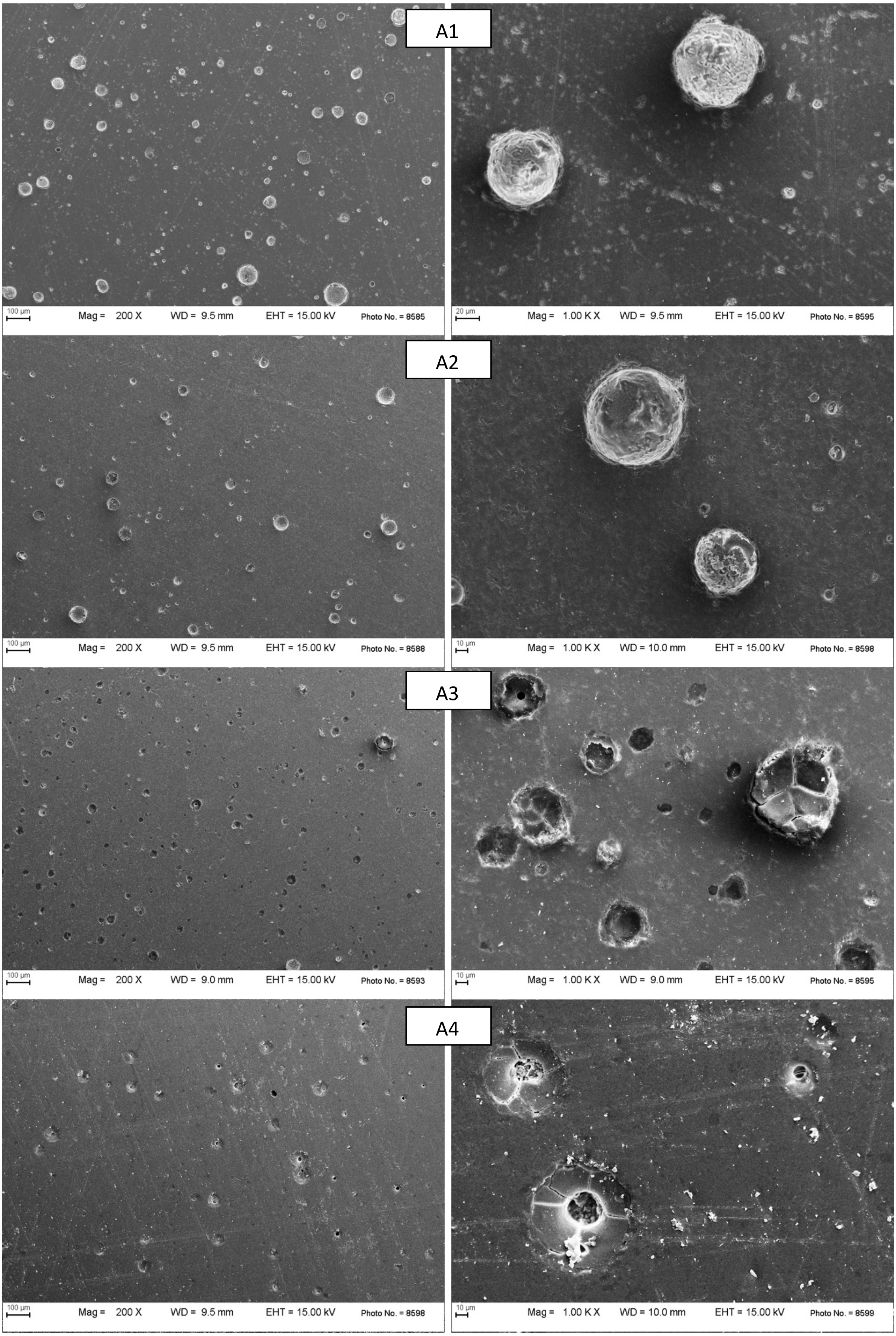

Fig. 2. *SEM images of sample A1, A2, A3 and A4.*

In Fig. 3, A1 and A3 photos are reported after the application of the dirt solution. The effect is clearly different. The unprotected and more porous A1 surface retains the dirt, while the protected surface A3 is clean.

Fig. 3. *Photos of a portion of the A1 and A3 tiles (15x5 cm) after the application of a solution of dirt and its removal with a wet cloth.*

5. CONCLUSIONS

Surface cleanability is an essential issue for porcelain stoneware tiles. The results of stain and chemical resistance - following the international standard tests - do not reveal any significant differences among the ceramic surfaces, protected or not. On the other hand, a simple laboratory test reveals substantial consequences in terms of dirtiness if the lappato tiles are not efficiently protected. This study clearly shows that the standard tests are not sufficient to highlight differences among commercial tiles, therefore more in-depth investigations (microstructural observation and pore-size distribution) should be considered in order to prevent cleanability issues after tiling.

With regard to the average life of a pavement, an alteration of lappato surfaces is rather predictable after long use. To avoid this, or at least to minimize this effect, the protection of the surface is fundamental to preserve the aesthetical appearance of the material.

REFERENCES

[1] Esposito L., Tucci A., Rastelli E., Palmonari C and Selli S., Stain resistance of porcelain stoneware tiles . Am. Ceram. Soc. Bull., 81(10), 38-42, 2002.

[2] Esposito L. and Tucci A., Porcelain stoneware tile surfaces. Am Ceram. Soc. Bull.,79(5), 59-63, 2000.

[3] Tucci A., Esposito L., Malmusi L. and Piccinini A., Wear resistance and stain resistance of porcelain stoneware tiles. Key Eng. Mater., 206-213, 1759-1762, 2002.

[4] Esposito L., Tucci A. and Naldi D., The reliability of polished porcelain stoneware tiles. Journal of the European Ceramic Society, 25, 1487-1498, 2005.

[5] Dondi M., Ercolani G., Guarini G., Melandri C., Raimondo M., Rocha e Almendra E, Tenorio Cavalcante P.M.., The role of surface microstructure on the resistance to stain of porcelain stoneware tiles. J. Europ. Ceram. Soc., 25(4), 357-365, 2005.

[6] Raimondo M., Zanelli C., Dondi M., Guarini G., Biasini V., Gardini D., Surface properties of porcelain stoneware tiles: the influence of different protective coatings, Proceedings of IX Qualicer, Castellon (Spain) February 12-15, P.BC 325-333,2006.

[7] Akarsu M., Burunkaya E., Tunalı A., Selli N. T., Arpaç E., Enhancement ofhybridsol–gel coating and industrial application on polished porcelain stoneware tiles and investigation of the performance. Ceramics International 40, 6533-6540, 2014.

[8] Miorin E., Pagura C., Battagliarin M., Fabrizio M., Guglielmi M., Miselli P., Stain-resistant sol–gel silica coatings on stoneware tile, Am. Ceram. Soc. Bull.82(3),52, 2003.