# SURFACE PROPERTIES OF PORCELAIN STONEWARE TILES: THE INFLUENCE OF DIFFERENT PROTECTIVE COATINGS

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## ABSTRACT

*In the last few years the demand of porcelain stoneware tiles, having even more improved aesthetic appearance, became very important, so that different product typologies, in terms of bulk and surface properties, came out. In particular, polishing process, which provides smooth and highly glossy surfaces compared to the as-fired ones, gives the product a very high aesthetic value. The industrial polishing process, however, causes the formation of superficial defects and inhomogeneities, leading to a worsening of product performances in working conditions. The aim of this work was to emphasize the role played by different chemical coatings on the surface microstructural features of different product typologies, through the investigation of their behaviour in terms of stain resistance and service life.*

## 1. INTRODUCTION

Among the available commercial products, porcelain stoneware stands out as a material in which the physico-mechanical properties determine excellent performances and service life[1]; in addition, the as-fired surface is characterized by excellent hardness, high fracture toughness and stain resistance[2]. In the last years, the great commercial success of porcelain stoneware tiles made it possible to concentrate considerable resources in developing different types of product, which can be classified on the basis of their different surface (rough, textured, polished, lapped, glazed, etc) or bulk properties (i.e. translucency, whiteness, etc.)[3, 4].

Among such different typologies, the last years recorded a significant advance in the production of polished tiles, having smooth and highly glossy surfaces compared to the as-fired ones[5]. However, the polishing process, which is industrially performed to improve the aesthetic appearance of the product, can promote irreversible damages, mainly due to the opening of the closed porosity and the formation of superficial flaws [5]. These drawbacks lead to a strength degradation of the processed surface with the consequent worsening of the functional properties in working conditions, especially in terms of stain resistance[6,7] and wear behaviour[8, 9]. In order to reduce these drawbacks, the possibility of surface coating with organic films was recently investigated as one of the most interesting solutions. Their role is to fill up the inhomogeneities and, in the same time, to waterproof the surface against the staining agents. Among the organic compounds, different kinds of resins are being utilized to improve the service performances of commercial products, even if a clear understanding of the interaction between the surface and the coating layer is missing. The comprehension of the interaction with the coating layer is fundamental in order to evaluate the behaviour of the material and to optimize the choice for suitable compounds and, hence, to design composite materials presenting innovative properties. The aim of this work is to assess the characteristics of two main porcelain stoneware typologies, glazed and unglazed, which have been industrially polished and subsequently coated with fluoro-carbon, silicon-based and UV thermo-hardened resins. The role played by each of them on the stain resistance and service life of tiles was thoroughly investigated.

## 2. MATERIALS AND METHODS

For this purpose, two different typologies of commercial porcelain stoneware tiles, glazed (G) and unglazed double-load (UG), were taken into account. Both typologies were industrially polished and subsequently coated with different kind of resins, in order to obtain the following different working surfaces:

- polished (GP and UGP);
- polished and treated with fluoro-carbon resin (GP1 and UGP1);
- polished and treated with silicon resins in non-aqueous medium (GP2 and UGP2);
- polished and treated with silicon resins in aqueous medium (GP3 and UGP3);
- polished and treated with UV thermo-hardened resin (GP4 and UGP4).

All products were extensively characterized by the determination of the main physical properties, obtaining data referring to both the bulk and the working surfaces. Open porosity and bulk density were quantified measuring the dry weight, the water-saturated weight and the weight suspended in water, according to ISO 10545-3. Total porosity was calculated by the ratio between bulk density and specific weight, this latter measured by He pycnometer (Micromeritics, Multivolume Pycnometer 1305); closed porosity was estimated by difference.

The wetting properties of the surfaces were furthermore investigated by measuring the surface energy and the contact angle with a polar ($H_2O$) and non-polar ($CH_2I_2$) liquids (DataPhysics Instrument OCA15).

The functional properties of all samples were evaluated in terms of stain resistance, according to ISO 10545-14, with 5 different staining agents: 1) green suspension of $Cr_2O_3$ and 2) red suspension of $Fe_2O_3$ in a low molecular weight oil; 3) iodine alcoholic solution; 4) methylene blue solution (0.01 N) and 5) water-resistant pen. The cleanability of the surface was investigated performing three different cleaning steps with warm water (WW), warm water coupled with a neutral pH detergent (ND), warm water coupled with an alkaline pH detergent plus vigorous brushing (AD), according to ISO 10545-14. The staining after each cleaning step was appraised through a colorimetric measurement (ISO 10545-16, Hunterlab Miniscan XE Plus): the difference between the surface colour before and after the staining and cleaning operations is expressed as: $\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$, where $\Delta L^*$, $\Delta a^*$ and $\Delta b^*$ are the differences of the CieLab parameters L*, a* and b*, considering the as-received polished surface as reference.

The working performance of the different surfaces was simulated by: a) chemical attack, utilizing dilute solutions of HCl, KOH and $NH_4Cl$ (ISO 10545-13); b) PEI abrasion after 50 and 150 steps (ISO 10545-7), c) the effect of temperature (60°C, 7 days) and d) brushing for 5 (B5) or 15 min (B15). The stain resistance and the cleanability of the surfaces after each of these treatments were appraised using only the red suspension of $Fe_2O_3$ as staining agent. The surface microstructure and the effectiveness of the different coating in reducing the superficial inhomogeneities were investigated through the SEM micrographs obtained with a Leica Cambridge Stereoscan 360 instrument.

## 3. RESULTS AND DISCUSSION

### 3.1. PHYSICAL CHARACTERISTICS OF AS-FIRED SURFACES

Water absorption, open, closed and total porosity, specific weight and bulk density of as-fired unglazed and glazed porcelain stoneware tiles are reported in Table 1. All data are referred to both the working surface and the bulk. Both product typologies exhibit very low values of water absorption (0.06%) of the bulk, this latter having a closed porosity in the 5-6% range. A higher degree of accessible pores (water absorption of about 0.3%) belongs to the working surface of both UG and G products, whose composition differs from the bulk one; their total porosity, indeed, is as high as 6% (G) and 7.5% (UG), respectively.

| PHYSICAL PROPERTY | UNIT | UNGLAZED PORCELAIN STONEWARE (UG) | | GLAZED PORCELAIN STONEWARE (G) | |
|---|---|---|---|---|---|
| | | Surface | Bulk | Surface | Bulk |
| Water absorption | % wt. | 0.28 | 0.06 | 0.32 | 0.06 |
| Open porosity | % vol. | 0.7 | 0.2 | 0.8 | 0.1 |
| Closed porosity | % vol. | 6.8 | 6.0 | 5.0 | 5.1 |
| Total porosity | %vol. | 7.5 | 6.2 | 5.8 | 5.2 |
| Specific weight | g $cm^{-3}$ | 2.467 | 2.414 | 2.463 | 2.451 |
| Bulk density | g $cm^{-3}$ | 2.450 | 2.410 | 2.443 | 2.448 |

*Table 1. Physical characteristics of the as-fired surfaces*

## 3.2. PHYSICAL CHARACTERISTICS OF PROCESSED SURFACES

In table 2 the values of the main variables influencing the surface wettability are shown; in particular, the contact angle with a polar (water) and a non-polar (diiodomethane, $CH_2I_2$) liquid, as well as the surface energy, in terms of both total value and disperse or polar component, are reported. These parameters are closely related to the affinity of the different surfaces towards the staining agents. The effect of the different treatments on the surface energy is also evident in figure 1. From the analysis of the data, the following conclusions stand out:

- the polishing process (UGP and GP samples) slightly lowers the surface energy, with the increasing of the polar component of unglazed surface with respect to the glazed one;
- the coating with all the different typologies of resins promotes a more or less pronounced reduction of the surface energy, with the silicon resin in non-aqueous media being the most effective; on the whole, all the other protective treatments promote an increasing of the polar/non-polar component ratio;
- as far as the surface wettability expressed by the contact angle values is concerned, the silicon in non-aqueous media treatment provides the less hydrophilic surfaces, while the UV thermo-hardened one increases the hydrophilicity especially in the case of the unglazed surface.

| SAMPLES | SURFACE ENERGY | | | CONTACT ANGLE (°) | |
|---|---|---|---|---|---|
| | Total (mJ $m^{-2}$) | Disperse component (%) | Polar component (%) | $H_2O$ | $CH_2I_2$ |
| UG | 55.8 | 52.6 | 47.4 | 45.3 | 58.6 |
| UGP | 52.0 | 34.1 | 65.9 | 46.3 | 57.4 |
| UGP1 | 31.4 | 20.1 | 79.9 | 73.0 | 89.2 |
| UGP2 | 19.9 | 71.9 | 28.1 | 91.4 | 78.7 |
| UGP3 | 30.4 | 38.6 | 61.4 | 73.4 | 92.3 |
| UGP4 | 54.3 | 38.6 | 61.4 | 43.4 | 50.8 |
| G | 58.0 | 29.9 | 70.1 | 38.5 | 56.0 |
| GP | 53.0 | 40.0 | 60.0 | 45.2 | 50.8 |
| GP1 | 24.0 | 14,3 | 85.7 | 83.5 | 101.4 |
| GP2 | 17.6 | 86.5 | 13.5 | 99.4 | 79.9 |
| GP3 | 24.6 | 29.5 | 70.5 | 80.8 | 89.4 |
| GP4 | 45.2 | 41.4 | 58.6 | 55.0 | 58.5 |

*Table 2. Chemical-physical characteristics of processed surfaces*

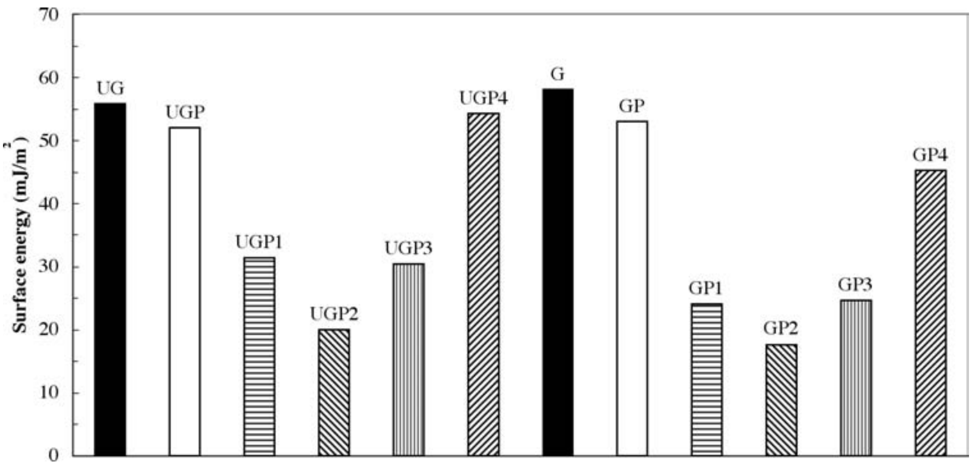


*Figure 1. Surface energy of as-fired (UG and G), polished (UGP and GP) tiles, polished and treated with con fluoro-carbon resin (UGP1 and GP1), silicon resin in non-aqueous medium (UGP2 and GP2), silicon resin in aqueous medium (UGP3 and GP3), UV thermo-hardened resin (UGP4 and GP4) tiles.*

## 3.3. MICROSTRUCTURE OF THE PROCESSED SURFACE

The SEM micrographs of the UG and G processed surfaces are reported in the Figures 2 and 3, respectively.

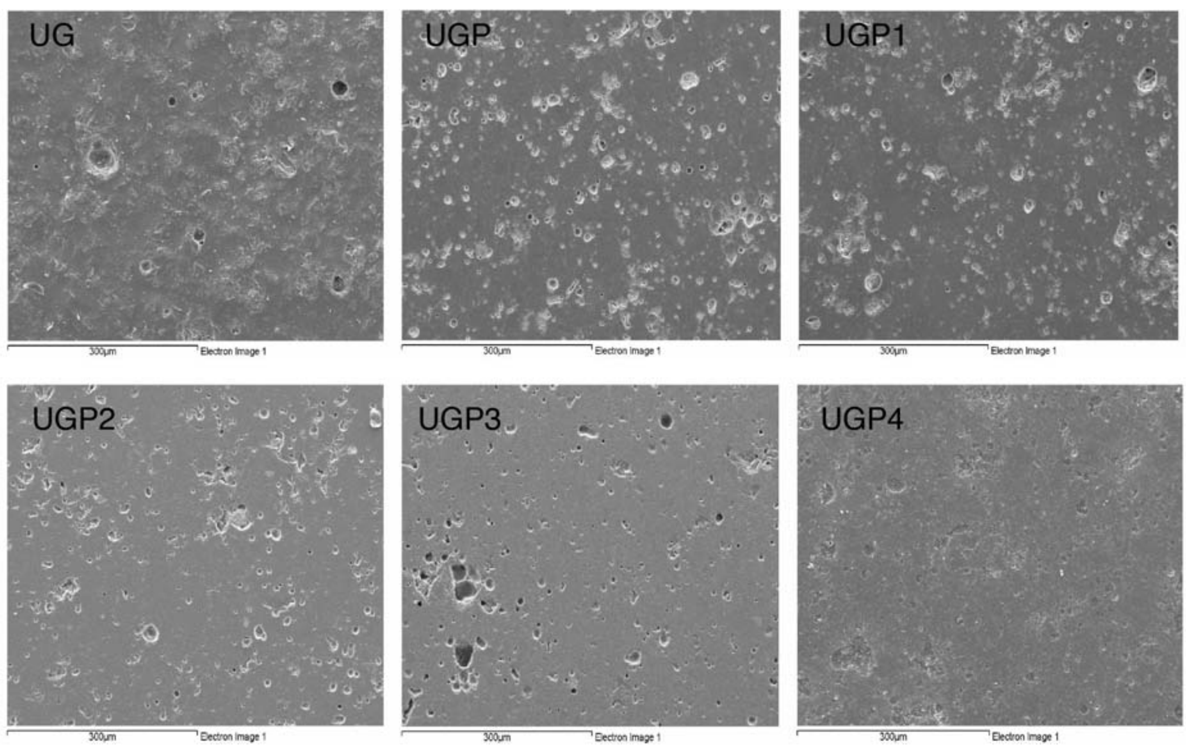


*Figure 2. SEM micrographs of as-fired UG, polished (UGP), polished and treated with fluoro-carbon resins (UGP1), silicon resin in non-aqueous medium (UGP2), silicon resin in aqueous medium (UGP3), UV thermo-hardened resins (UGP4) tiles.*

The as-fired surface of both product typologies is characterized by the typical roughness of the untreated surfaces, even if the unglazed one presents a porosity with a higher roundness degree. However, in both cases the polishing process seems not to promote significant damages on the surface, unless of areas having different density. The coating treatments #1 (UGP1 and GP1 samples) is just able to cover the small defects and it does not influence the size and shape of pores; the disappearance of smaller defects is more evident when the coating #2 is applied since it is able to smooth the greater pores and to partially fill them up. UGP3 and GP3 samples present a significant lowering of their roughness and a smoother surface, with the occlusion of the smaller defects. More pronounced effects are promoted by the coating with UV thermo-hardened resins in terms of both amount and size of filled pores; however, both surfaces show a low smoothness degree since the occurrence of many tiny humps with dimension under 1$\mu$m.

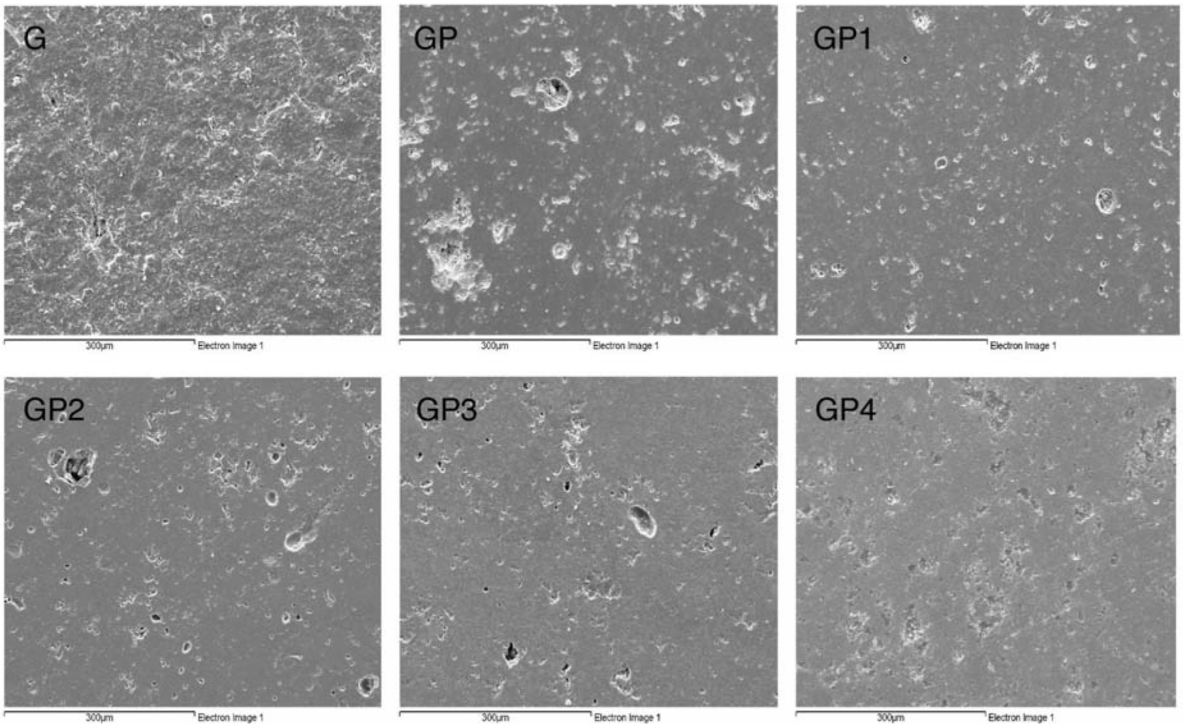


*Figure 3. SEM micrographs of as-fired G, polished (GP), polished and treated with con fluoro-carbon resins (GP1), silicon resin in non-aqueous medium (GP2), silicon resin in aqueous medium (GP3), UV thermo-hardened resin (GP4) tiles*

## 3.4. STAIN RESISTANCE OF THE NEW SURFACE

The staining after the three cleaning steps (WW, ND, AD) was appraised through colorimetric measurements; as an example, the colorimetric differences concerning the different staining agent, after the cleaning steps with warm water, are reported in table 3. The resistance to the red oily agent depends on both the surface typology (UG or G) and the different coatings; however, it results always higher when the UV thermo-hardened resins are applied. In this sense, note that this behaviour is consistent with the effectiveness of the treatment #4 in filling a significant amount of the greater porosity coupled with the more hydrophilic characteristics of the surface. In other words, the best performance of the surfaces when coated with UV thermo-hardened resins is the good agreement between the better stain resistance, due to the favourable surface microstructure, and the better cleanability, also without using any detergent, due to the increase surface affinity for water. As far as the other staining agents, the UG surfaces are generally more resistant than the G ones with respect to the alcoholic iodine solution; however, this solution show the drawback to chemically react with the UV thermo-hardened resin and, to a lesser extent, with the silicon resins in aqueous media leading to a worsening of the performances of the corresponding surfaces. On the other hand, the solution of methylene blue, with its high penetration capability, allows evaluating better the negative effect of the polishing process on the stain resistance; both G and UG surfaces practically behave in the same way, with the best cleanability provided by the coating with silicon resins in non-aqueous medium. Moreover, for both products typologies, the polished surfaces are more resistant towards the water-resistant pen than the as-fired ones. On the whole, looking at the results, the coating treatment #2 stands out as the only one able to provide an average protection against all the staining agents.

| SAMPLE | RED (Δa*) | GREEN (Δa*) | METHYLENE BLUE (Δb*) | IODINE (ΔE*) | WATER RESISTANT PEN (ΔL*) |
|---|---|---|---|---|---|
| UG | 0.19 | -0.23 | -2.35 | 0.53 | -37.68 |
| UGP | 2.36 | -0.59 | -8.08 | 0.21 | -12.36 |
| UGP1 | 3.45 | -1.12 | -8.62 | 0.87 | -9.88 |
| UGP2 | 1.87 | -0.46 | -2.56 | 1.38 | -33.09 |
| UGP3 | 1.53 | -0.72 | -4.66 | 4.38 | -12.19 |
| UGP4 | 0.07 | -0.10 | -6.00 | 11.62 | -18.84 |
| G | 0.80 | -0.18 | -3.09 | 0.56 | -40.26 |
| GP | 1.89 | 0.05 | -9.17 | 1.16 | -14.58 |
| GP1 | 1.99 | -0.52 | -9.06 | 1.31 | -3.72 |
| GP2 | 1.20 | -0.81 | -2.39 | 1.96 | -35.06 |
| GP3 | 2.67 | -0.04 | -5.96 | 6.60 | -8.93 |
| GP4 | -0.21 | -0.61 | -7.33 | 10.63 | -38.72 |

*Table 3. Stain resistance of as-fired UG and G tiles, polished (UGP and GP) and treated with the different resins (UGP1-4; GP1-4) after the cleaning step with warm water (WW).*

## 3.5. STAIN RESISTANCE AFTER AGEING TREATMENTS

The stain resistance to the red oily suspension (Δa* values) of the polished and coated surfaces is quite different after the simulation of the ageing treatments (i.e. chemical attacks, mechanical brushing, PEI abrasion and the effect of temperature) and the effectiveness of some of the chemical treatments, previously described, needs to be revised (table 4). At all events, the coating with UV thermo-hardened resins seems to provide again the best protection especially after the temperature aging and both the acid and alkaline attacks. Fluoro-carbon and silicon in aqueous medium resins are not able to protect the surface apart from the ageing treatment considered, resulting both not suitable to protect the ceramic surface in working conditions. As far as the effectiveness of treatment #2 is concerned, it provides still good performances after the ageing simulated with brushing and alkaline attacks, while it results not resistant to the action of acids and to the effect of the temperature.

Generally, however, performing the comparison of the action of the different chemical coatings, before and after the ageing treatment, it clearly stands out that, for both UG and G samples, coating does not provide in any case better performances than the untreated polished surfaces; data referring to UGP samples are represented in figure 4.

| SAMPLE | Δa* | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | B5 | B15 | P50 | P150 | HCl | KOH | $NH_4Cl$ | T (60°C) |
| UGP | 1.15 | 2.77 | 3.12 | 2.21 | 0.91 | 2.09 | 1.12 | 1.80 |
| UGP1 | 1.87 | 2.75 | 3.64 | 3.31 | 1.54 | 3.29 | 3.58 | 1.70 |
| UGP2 | 0.84 | 0.94 | 3.85 | 3.53 | 1.83 | 1.54 | 1.47 | 1.90 |
| UGP3 | 1.48 | 2.61 | 3.53 | 2.35 | 1.73 | 2.84 | 2.07 | 2.39 |
| UGP4 | 0.26 | 0.21 | 0.46 | 0.95 | 0.36 | 1.62 | 0.85 | 0.39 |
| GP | 2.57 | 2.22 | 2.15 | 2.18 | 0.98 | 1.48 | 1.94 | 2.05 |
| GP1 | 1.27 | 0.69 | 2.17 | 2.10 | 4.69 | 2.71 | 3.56 | 1.91 |
| GP2 | 1.36 | 0.83 | 2.56 | 2.81 | 1.19 | 1.33 | 1.43 | 1.87 |
| GP3 | 1.88 | 0.36 | 4.04 | 4.07 | 2.06 | 3.18 | 2.44 | 2.44 |
| GP4 | 0.29 | -0.17 | 0.58 | 0.55 | 0.58 | 0.56 | 0.16 | 1.74 |

*Table 4. Resistance to the red staining agent (Δa*) of UG and G processed tiles, after the ageing treatments (B5 = 5 min brushing; B15 = 15 min brushing; P50 and P150 = PEI resistance after, respectively, 50 and 150 steps)*

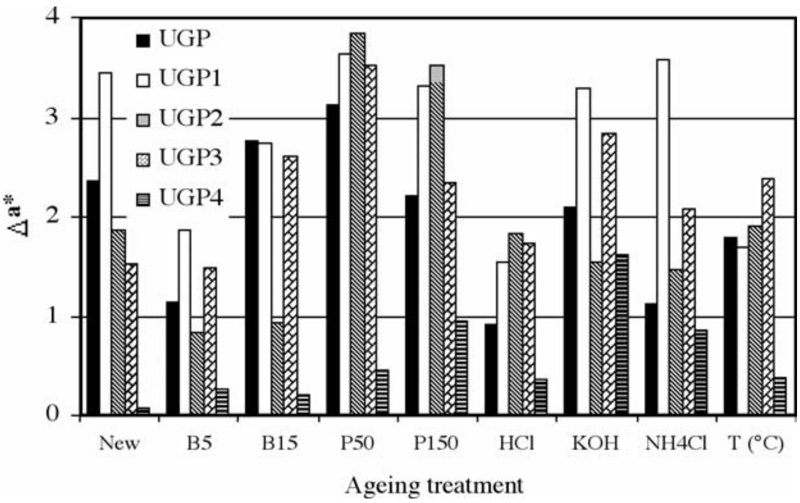


*Figure 4. Comparison of the stain resistance (Δa*) of the UGP processed surfaces before and after the ageing treatments.*

## 4. CONCLUSION

The characteristics of two typologies of porcelain stoneware tiles, glazed and unglazed, which have been industrially polished, and subsequently coated with fluorocarbon, silicon-based and UV thermo-hardened resins, were investigated in order to better understand the effect of each protective treatment on their performances and service life.

On the whole, the coating treatment generally promotes a lowering of both the surface energy and of the roughness, with a more or less significant removal of the defects occurring during the industrial polishing and the filling of the greater porosity; however, these effects are promoted in a different way by the chemical coatings taken into account and the effectiveness of each of them strictly depends on the amount of the physical and microstructural modification induced on the surface.

Stain resistance tests highlighted that all the surfaces give a quite complex picture of their behaviour as a function of the different chemical composition of the staining suspensions.

However, the UV thermo-hardened resin, which does not substantially change the total surface energy, improving its hydrophilicity and reducing the drawbacks introduced by the polishing process can be selected as the most suitable to protect the ceramic surface in working conditions. These positive effects are confirmed when the surface stain resistance is analysed, since the UV thermo-hardened resin provides good resistance against the red and green staining agents, which can be considered very representative in terms of the working conditions. However, while treatment #4 is not stable under the action of iodine solution and shows a negative performance when a methylene blue is utilized, the treatment #2, on the whole, seem to provide the best average protection.

Considering the stain resistance of the aged surfaces, it is important to note that all the surfaces, glazed and unglazed, coatings do not provide any improvement of their performances when compared to the untreated polishing ones. On this subject, the results provided by this work, which emphasize the role played by some chemical treatments on the surface microstructure, also suggest that the induced modifications should be planned in order to ensure durable performances in terms of service life of the product in the real working conditions. In other words, this means a need of a better understanding of the interaction mechanisms between the surface and the chemical nature of the coating, in order to design suitable ceramic composite materials having durable and innovative performances in working conditions.

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