# HIGH PERFORMANCE GLAZED PORCELAINIZED STONEWARE TILES

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## 1. INTRODUCTION

This article report results of a research work which the main goal is related to the development of a technical solution that considers the relationship between abrasion wear resistance and brightness and its understanding to obtaining glazed ceramic products with optimized properties and with high performance for a specific application considering the technical and aesthetical requirements attributed to a ceramic floor tile and also the market demanding. Thus, glazes formulated from a LZSA[1] glass-ceramic composition, which has coefficients of thermal expansions (CTE) between 46 e 75 x $10^{-7}$°$C^{-1}$, reinforced with crystalline alumina or quartz or zircon were prepared and characterized by scratching, abrasion wear and brightness measurements. Results show that is possible to obtain glazed ceramic tiles by combining good brightness (71BU) with high scratching (9 Mohs) and abrasion wear (PEI 5) resistances as well as with good staining resistance (Class 4).

## 2. EXPERIMENTAL PROCEDURES

For this work, glazes constituted (solid fraction) by a LZSA glass-ceramic frit ($19Li_2O.8ZrO_2.64SiO_2.9Al_2O_3$-molar basis) and by reinforcing crystalline particles (alumina or zircon or quartz) were formulated (Table I) and prepared. The LZSA frit, after sintering in the 700- 900°C temperature range, shows coefficients of thermal expansions between 52.8 and 51.4 x $10^{-7}$°$C^{-1}$ (25-325°C) according to Montedo.[1] The reinforcing industrial materials as received show main particle sizes, determined by laser diffraction, of 75.0 μm for alumina ($Al_2O_3$), 2.7 μm for quartz ($SiO_2$) and 6.6 μm for zircon ($ZrSiO_4$). Further details about processing and properties of the LZSA glass-ceramic frit can be found in Montedo's work.[1] In a successive step, the constituents of each formulated composition (Table I) were wet milled in a laboratory mill so that, after drying process, powders with particle sizes lower than 5 μm were obtained.

| CONSTITUENTS | COMPOSITIONS (wt-%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | P | P10A | P20A | P10B | P20B | P10C | P20C |
| LZSA Frit | 100.0 | 90.0 | 80.0 | 90.0 | 80.0 | 90.0 | 80.0 |
| $Al_2O_3$ | 0.0 | 10.0 | 20.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Quartz | 0.0 | 0.0 | 0.0 | 10.0 | 20.0 | 0.0 | 0.0 |
| $ZrSiO_4$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 10.0 | 20.0 |

*Table I. Investigated formulated and prepared glazes.*

The obtained powders were then mixed (55%) to an organic screen printing substance so that screen printing pastes (glazes) were obtained and applied on brilliant glazed porcelainized stone ware tile samples (scratch resistance 4 Mohs and CET = 64.0 x $10^{-7}$°$C^{-1}$) by using different screen printing screens (32 mesh) to reproduce the design as shown in Fig. 1 (a) which was obtained by scanning electron microscopy (SEM). The glaze screen printing applications were performed keeping the thickness layer (h) at about 75 μm. Subsequently; the glazed tiles were dried in a laboratory furnace at 110°C for 2 h and then heat-treated in a continuous roller furnace at 880°C for 41 minutes. After heat-treatments, the tiles, in appropriate formats, were subjected to scratching (NBR 13818/97 – Part V), surface abrasion wear (NBR 13818/97 – Part D), staining (NBR 13818/97 – Part G and ISO 10545-14/95) measurements. It was also determined the brightness of the ceramic tile surfaces (Tri-Gloss μ, angle = 60º). Finally, the ceramic tiles, after surface abrasion wear, were evaluated by comparing the area related to the removed material with the total area by using an image analyzer software (version 2.1.32) in an optical microscopy (OM).

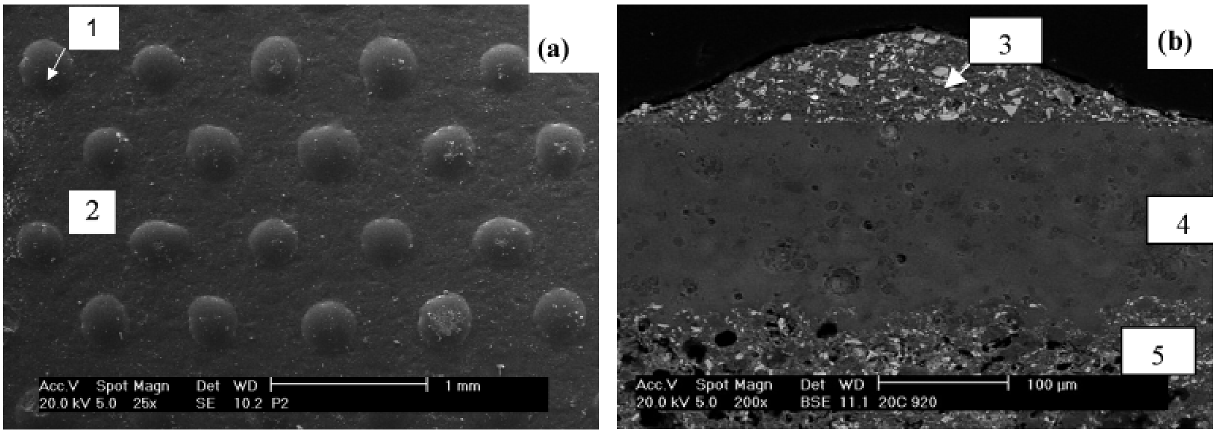


*Figure 1. SEM micrographs: (a) top view of a porcelainized stoneware tile coated with a LZSA glass-ceramic glaze (1) on a brilliant glazed surface (2); (b) cross section of a ceramic tile coated with the P20C glaze (100 X). (3) Glass-ceramic; (4) Glaze; (5) Ceramic body. Etching: HF 2%, 25s.*

## 3. RESULTS AND DISCUSSION

Looking to optimizes brightness, mechanical and chemical properties of the prepared mixtures, P10C and P20C compositions were fundamentally select for this study. Fig. 1 (b) shows a SEM micrograph of a sample, appropriated heat-treated, related to the P20C composition.

From the micrograph it can be observed that the vitreous glaze selected for the porcelainized stoneware tile shows low porosity, which is an important requirement to minimize the staining tendency. In the P20B composition, it was observed also that porosity and roughness are remarkable and for this reason it was not selected for this study since the intrusion of residues and consequently the staining are favoured in this case. Table II shows results related to the scratch resistance for P (LZSA glass-ceramic frit), P10C and P20C glaze compositions applied on the surface of glazed porcelainized stoneware tiles. From Table II it can be observed that the scratch resistance has a tendency to increases as the fraction of coated area by glaze ($f_{ac}$) was increased within the analyzed interval. On the other hand, as expected, the surface brightness decreases, as the $f_{ac}$ was increases since the composite glazes did not show appreciable brightness.

| COMPOSITIONS | $\lambda = 0$ $f_{ac} = 100$ | | $\lambda = 0.248$ $f_{ac} = 23.1$ | | $\lambda = 0.353$ $f_{ac} = 19.8$ | | $\lambda = 0.605$ $f_{ac} = 10.9$ | | $\lambda = 0.678$ $f_{ac} = 6.1$ | | $\lambda = \infty$ $f_{ac} = 0$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | B | M | B | M | B | M | B | M | B | M | B | M |
| P | 8.5 | 5 | 69.5 | 7 | 73.5 | 7 | 77.8 | < 7 | 84.8 | < 7 | | |
| P10C | 3.6 | 7 | 33.5 | 9 | 52.2 | 7 | 59.1 | < 7 | 64.3 | < 7 | 96.2 | 4 |
| P20C | 6.4 | 6 | 42.8 | 8 | 71.2 | 9 | 72.6 | < 7 | 75.8 | < 7 | | |

$\lambda$: Main free path (mm); $f_{ac}$: fraction of coated area (%); B: surface brightness (BU); M: scratch resistance (Mohs).

*Table II. Brightness and scratch resistance of tested samples.*

However, P composition for any of the mean free paths (λ) tested did not show the minimum necessary scratch resistance (>7 Mohs) according to the objectives of this work and so it was not used in the subsequent experiments even if it showed higher brightness. On the other hand, P10C and P20C compositions showed, under determined conditions, scratch resistance values equal to or higher than 8 Mohs. This means that the values, for the applied layer thickness (h) and the point diameters ($d_c$) used, the application of these compositions, with l values that allowed obtainment of such scratch resistance values, prevented the abrasive material contact with the original glazed surface producing in this way a self protection. This does not mean, however, that these materials did not have any wear as will be discussed later. For $f_{ac}$ = 23.1%, both considered sample compositions show scratch resistance at acceptable levels. However, the obtained brightness values were very low so that compositions, in these conditions, were approved by considering their scratch resistances but reproved respect to their brightness. Higher $f_{ac}$ were tested therefore, the applied points did not reach good resolution. Moreover, the scratch resistance values were very close to the respective monolith compositions and the brightness values were drastically reduced. Fig. 2 (a) shows scratches produced on the glazed surface without the protection layer after it was scratched by topaz (8 Mohs) while Fig. 2 (b) shows scratches produced on the glazed surfaces, with surface protections, after it was scratched with the same mineral.

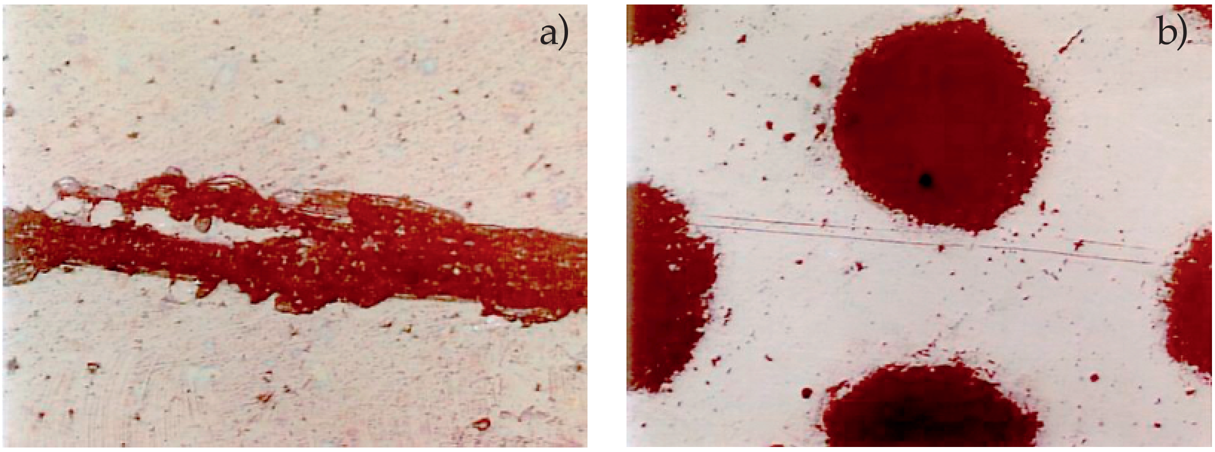


*Figure 2. Optical micrographs of samples scratched with topaz mineral:*
*(a) glazed surface without the protection layer;*
*(b) glazed surface coated with the P20C glaze (point application).*
*Magnification: 5 X.*

Fig. 2 (b) shows scratches crossing all the extension of the material surface, reaching the glazed surface and the applied composite glaze. It may be noted hat the intensity of the scratches produced on the glazed surface (protection layer) is much lower than that produced on the unprotected glazed surface by same abrasive material even when the scratches were produced on the composite glaze (protection layer) only. In fact, the protection layer created barriers against the action of the abrasive material becoming difficult the visualization of the generated scratches resulting in this way in high scratch resistance values. Thus, the P20C composition which $f_{ac}$ = 19.8% ($d_c$ = 0.316 mm and λ = 0.353 mm) was selected and subjected to surface abrasion wear. P20C composition, which was applied on the ceramic tile surface, was subjected to the PEI test at 2,000 revolutions. The evaluation was done taking in account the worn area fraction (fad) as shown in Table III.

| COMPOSITIONS | WORN AREA FRACTION (%) | | | | |
|---|---|---|---|---|---|
| | λ = 0.248<br>$f_{ac}$ = 23.1 | λ = 0.353<br>$f_{ac}$ = 19.8 | λ = 0.605<br>$f_{ac}$ = 10.9 | λ = 0.678<br>$f_{ac}$ = 6.1 | λ = ∞<br>$f_{ac}$ = 0 |
| P | - | 69 ± 4 | - | - | 77 ± 6 |
| P10C | - | 58 ± 1 | - | - | |
| P20C | 54 ± 1 | 44 ± 2 | 72 ± 5 | 74 ± 4 | |

*Table III. Worn area fraction (fad) of tested samples. λ: Main free path (mm); $f_{ac}$: Fraction of coated area (%).*

From the table it can be observed that there is a $f_{ad}$ reduction tendency as λ was decreased ($f_{ac}$ increases). P20C composition with λ = 0.353 mm ($f_{ac}$ =19.8%), shows the lower $f_{ad}$ among tested samples, probably due the reduction of the residual critical stresses which produce nucleation and propagation of lateral cracks.[2, 3] This means that the l value used is found in an optimal range respect to the applied glaze layer (h) and point diameter ($d_c$) selected, i.e., the $f_{ac}$ =19.8% value represents not only an optimal value respect to the relationship between scratch resistance and surface brightness but also a condition that makes it possible to provide a higher protection for the glazed surface among the tested values. On the other hand, the $f_{ad}$ increases for λ = 0.248 mm ($f_{ac}$ = 23.1%) can be explained by the remarkable increase of abrasive particles causing wear on the glazed surface generated by the wear on the glass-ceramic material. Moreover, Table III shows that for $f_{ac}$ =19.8% compositions P and P10C did not show the same performance as the P20C composition resulting in a higher wear on the glazed layer confirming in this way the low values of scratch resistance and brightness.

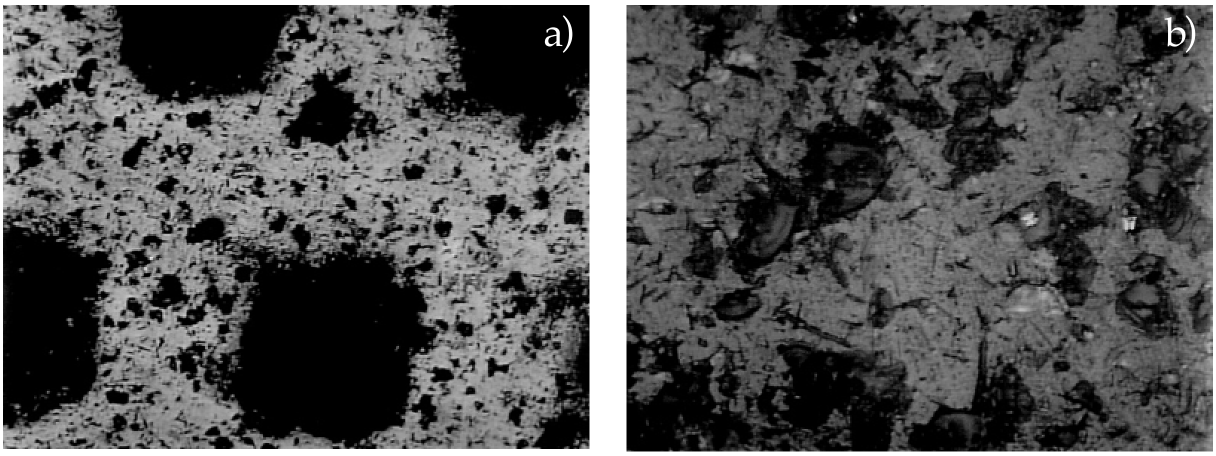


*Figure 3. Optical micrographs of glazed surfaces with application of protection glaze (points) after 2,000 revolutions in the abrasion equipment. (a) P20C (5 X); (b) P (20 X); (c) P10C (20 X); (d) P20C (20 X).*

In fact, Fig. 3 (a) shows a region between applied glaze points for a sample containing an application of P20C composition ($d_c$ = 0.316 mm and λ = 0.353 mm ($f_{ac}$ =19,8%)) after subjection to 2,000 revolutions in the abrasion equipment.

The considered glazed surface is amorphous and the fracture processes occurs in a fragile mode, i.e., showing few or not plastic deformation and in two steps: nucleation and crack propagation up to the final fracture.[4] In this case, the surface fracture aspect is denominated conchoidal type. Oliveira[3,4] studied the fragile fracture mechanism in ceramic glazes and he demonstrated that the fracture occurs with craters formation due the propagation of lateral cracks pointed out the similarity between the fracture model produced by a indenter and that produced on the glazed surface after an abrasion processes. The abrasion wear evolution on the glazed surface for a P20C composition point application (λ = 0.353 mm ($f_{ac}$ =19.8%) subjected to different abrasion cycles (N=number of revolutions) displayed cracks and removal caused by de abrasion wear. Subsequently, at 300 revolutions, the amount of removed material increases considerably. The processes evolve, until at 6,000 revolutions, the surface is completely worn and consequently brightness is almost null. Fig. 4 shows the abrasion wear evolution and the resulting brightness for samples with glaze points related to the P20C composition.

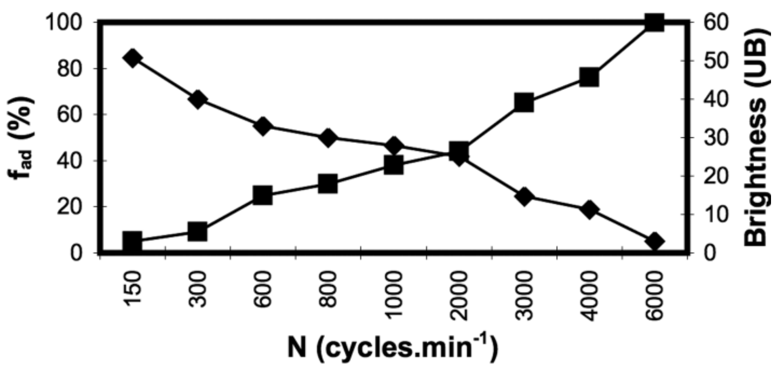


*Figure 4. Abrasion wear and brightness evolution of glazed samples coated with the P20C protection glaze composition. (♦: Brightness; ■: Worn area fraction).*

As expected by increasing N the amount of removed material also increased and the brightness decreases. However, from 2,000 revolutions the amount of removed material from the surface is very high compromising the surface brightness. This point (intersection in Fig. 4) could represent the material life. It is important to point out the effect caused by the protection glaze on the glazed surface, with respect to the glazed layer without protection. It can be further concluded that the area worn by abrasion ($f_{ad}$ = 44%) is significantly lower than that related to the protected surface ($f_{ad}$ = 77%). This means that the ceramic tile life can be duplicated using the protection layer application as shown in Fig. 4.

## 4. CONCLUSIONS

A glazed porcelainized stoneware tile coated with a layer glaze for the protection of the glazed surface, for which the scratch resistance is 4 Mohs and brightness is 96.2 BU, was obtained and characterized. Best results were obtained with P20C composition applied as a layer protection, circular points ($d_c$ = 0.316 mm and h = 0.075 mm uniformly distributed, λ = 0.353 mm; $f_{ac}$ = 19.8%). The finished product reached scratch resistance of about 9 Mohs and surface brightness of about 71 BU. It was evidenced that the scratch resistance increase occurred due the protection layer since it becomes difficult the abrasive particles contact with the glazed surface so that the generated scratches were not observed. After 2,000 revolutions in the PEI equipment the ceramic tile surface shows 44% of its glazed area removed and brightness of about 25 BU. This means that the ceramic tile life can be duplicated using the protection layer application. Finally, a brilliant (71 BU) porcelainized stoneware tile was obtained with high scratch resistance (9 Mohs), high abrasion wear resistance (PEI 5) and good stain resistance (Class 4).

## ACKNOWLEDGEMENTS

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