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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 (Li_2O-ZrO_2-SiO_2-Al_2O_3)[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).

Key words: Glazes, porcelainized stoneware tiles, abrasion wear, brightness.

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 (CILAS 1064L), 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 the 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.

Table I. Investigated formulated and prepared glazes.

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

The obtained powders were then mixed (55%) to an organic serigraphic substance supplied by ZSCHIMMER-SCHWARZ so that serigraph pastes (glazes) were obtained and applied on brilliant glazed porcelainized stone ware tile samples (scratching resistance 4 Mohs and CET = 64.0 x 10^{-7}°C^{-1}) by using different serigraph sieve screens (32 mesh) to reproduce the design as shown in Figure 1 which was obtained by scanning electron microscopy, SEM (Philips XL 30). The glaze serigraph 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 roll furnace at 880°C for 41 minutes. After heat-treatments, the tiles, in appropriate formats, were submitted 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 (BYK-GARDNER Instruments, Model Micro 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 microcopy, OM (Olympus model BX60M).

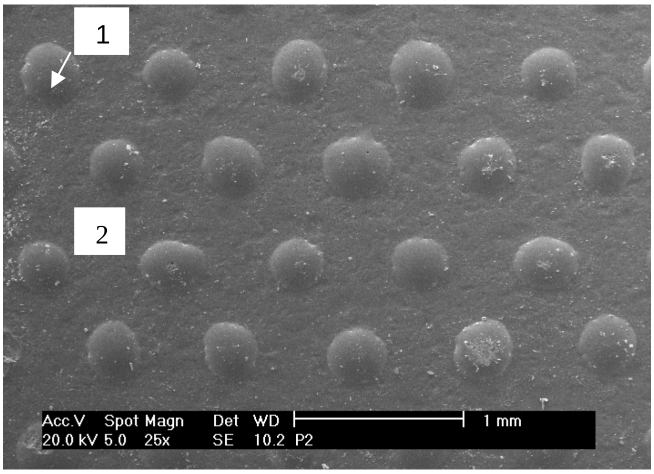

Figure 1. SEM micrograph related to the top view of a porcelainized stoneware tile coated with a LZSA glass-ceramic glaze (1) on a brilliant glazed surface (2).

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. Figure 2 shows SEM micrographs (cross sections) of samples, appropriated heat-treated, related to the P10C, P20C and P20B compositions.

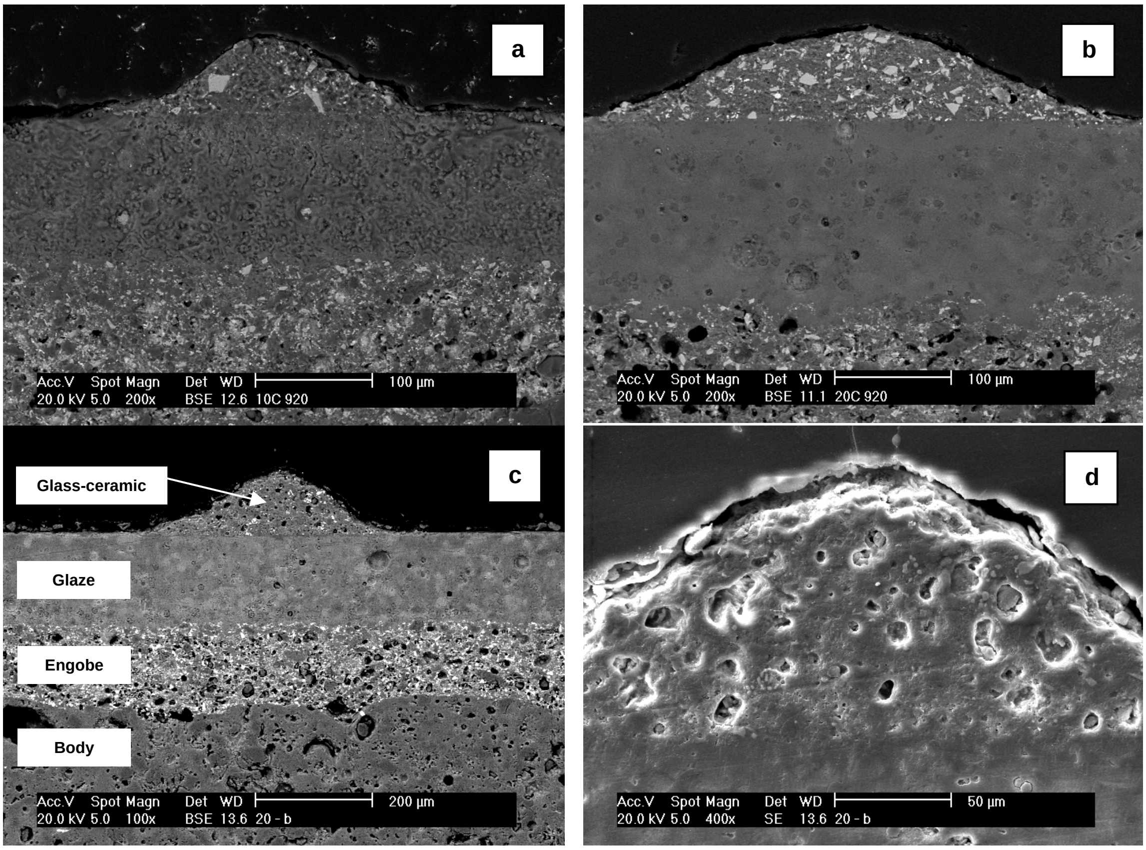

Figure 2. SEM micrographs of the cross sections of ceramic tiles coated with glaze compositions: (a) P10C (200 X); (b) P20C (200 X); (c) P20B (100 X); (d) P20B (400 X). Etching: HF 2%, 25s.

From the micrographs 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 micrographs of Figures 2 (c) and (d) which are related to the P20B composition, it can be 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 favored in this case. Table II shows results related to the scratching 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 scratching resistance has 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.

Table II. Brightness and scratching resistance of tested samples.

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	96.2	4
P10C	3.6	7	33.5	9	52.2	7	59.1	< 7	64.3	< 7		
P20C	6.4	6	42.8	8	71.2	9	72.6	< 7	75.8	< 7		

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

However, P composition for any of the mean free path (λ) tested did not shows the minimum necessary scratching resistance (>7 Mohs) according to the objectives of this work and so it was not used in the subsequent experiments even if it shows higher brightness. On the other hand, P10C and P20C compositions showed, under determined conditions, scratching resistance values equals or higher than 8 Mohs. This mains that the values, for the applied layer thickness (h) and the point diameters (d_c) used, the application of these compositions, with λ values that allowed to obtain such scratching resistance values, prevented the abrasive material contact with the original glazed surface producing in this way a self protection. This does not mains, however, that these materials did not have any wear as will be discussed latter. For f_{ac} = 23.1%, both considered sample compositions show scratching resistance at acceptable levels. However, the obtained brightness values were very low so that compositions, in these conditions, were approved by considering their scratching resistances but reproved respect to their brightness. Higher f_{ac} were tested therefore, the applied points did not reach good resolution. Moreover, the scratching resistance values were very closed to the respective monolith compositions and the brightness values were drastically reduced. Figure 3 (a) shows scratches produced on the glazed surface without the protection layer after it be scratched by topaz (8 Mohs) while Figures 3 (b), (c) and (d) show scratches produced on the glazed surfaces, with surface protections, after they be scratched with the same mineral.

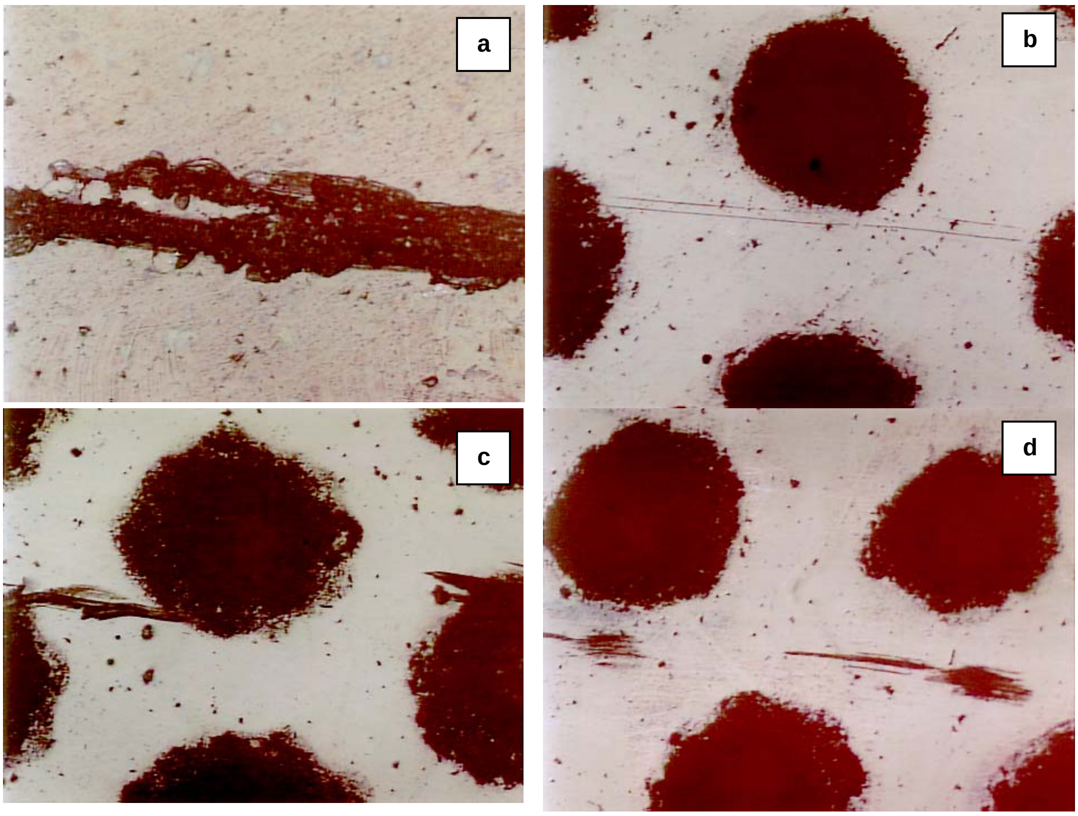

Figure 3. Optical micrographs of samples scratched with topaz mineral: (a) glazed surface without the protection layer; (b), (c) and (d) glazed surfaces coated with the P20C glaze (point application). Magnification: 5 X.

Figures 3 (b) and (c) show scratches crossing all the extension of the material surface, reaching the glazed surface and the applied composite glaze. It can realizes that 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 as shown in Figure 3 (d). 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 scratching 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 wearied area fraction (f_{ad}) as shown in Table III.

Table III. Wearied area fraction (f_{ad}) of tested samples.

Compositions	Wearied area fraction (%)				
	λ = 0.248 f_{ac} = 23.1	**λ = 0.353 f_{ac} = 19.8**	**λ = 0.605 f_{ac} = 10.9**	**λ = 0.678 f_{ac} = 6.1**	**$\lambda = \infty$ f_{ac} = 0**
P	-	69 ± 4	-	-	77 ± 6
P10C	-	58 ± 1	-	-	
P20C	54 ± 1	44 ± 2	72 ± 5	74 ± 4	

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 mains that the λ value used it 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 scratching resistance and surface brightness but also a condition that make 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 scratching resistance and brightness.

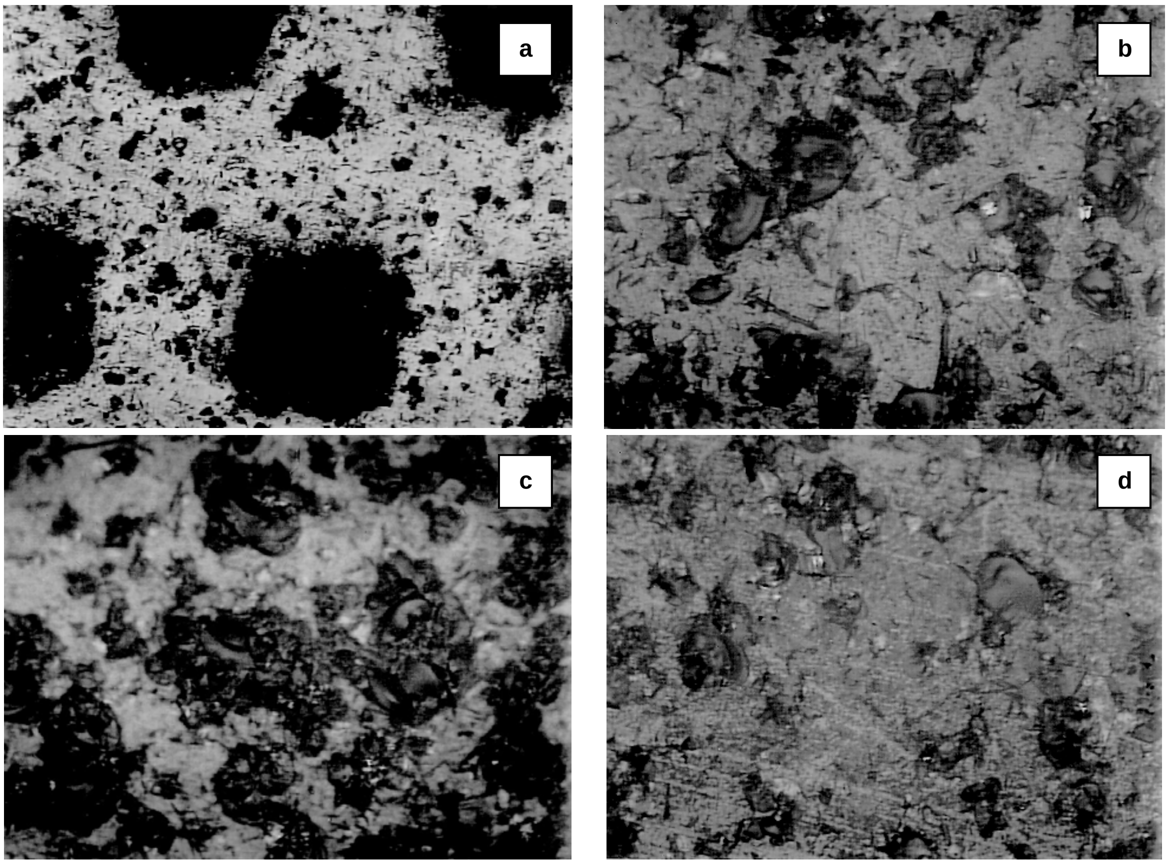

Figure 4. Optical micrographs of glazed surfaces with application of protection glaze (points) after 2,000 revolutions in the abrasion equipment. (a) P20C (5 X); (b) P (20 X); (c) P10C (20 X); (d) P20C (20 X).

In fact, Figure 4 (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.

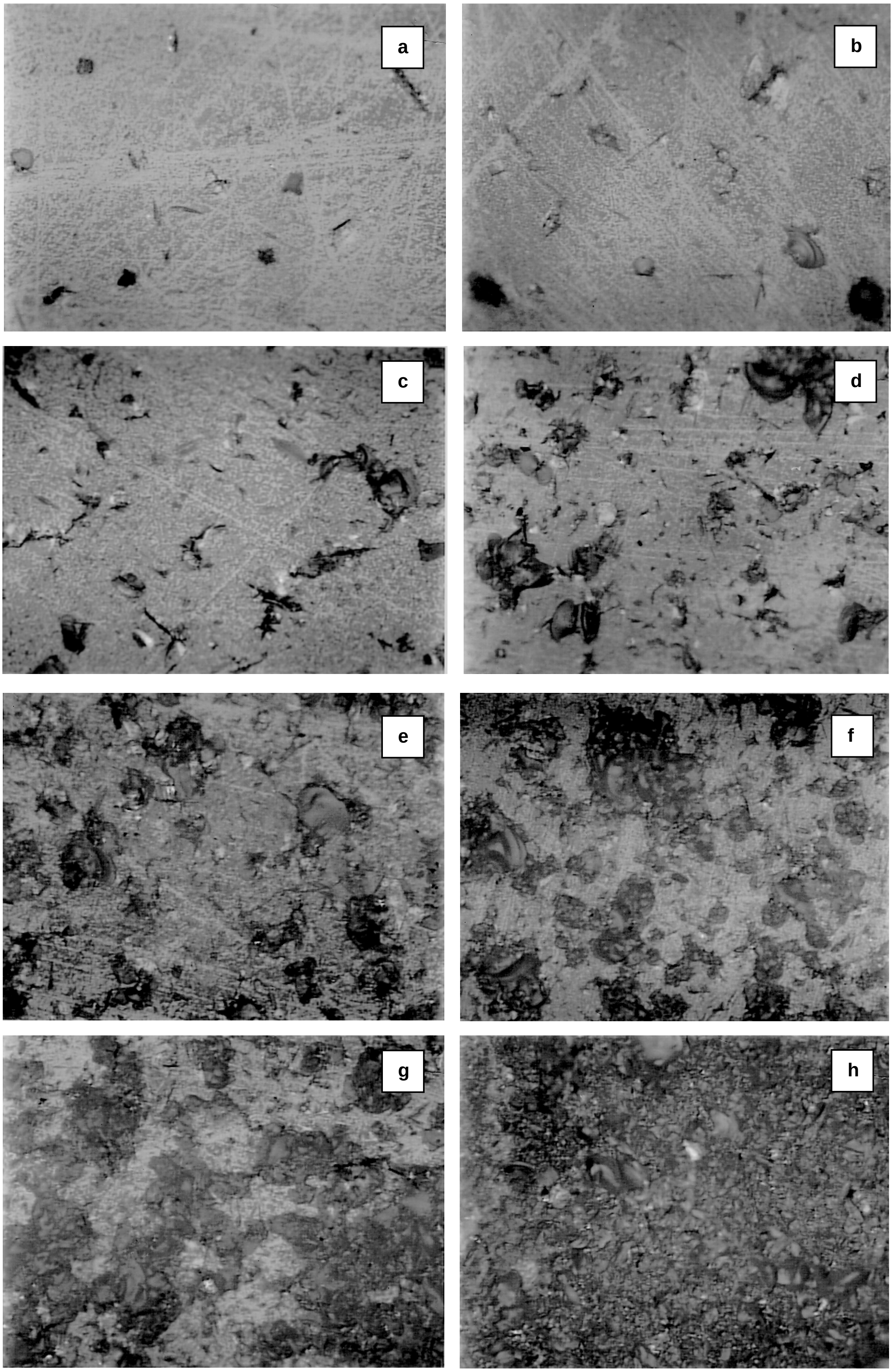

Figure 5. Optical micrographs of glazed surfaces with the application of protection glaze (P20C) points after N revolutions cycles in the abrasion equipment: (a) 150; (b) 300; (c) 800; (d) 1,000; (e) 2,000; (f) 3,000; (g) 4,000; (h) 6,000. Magnification: 20 X.

In this same figure can be observed yet the aspect and the predominant wear mechanism actuating on a glazed surface of a ceramic tile. 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.

Figure 5 shows 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). From Figure 5 (a) it can be observed a crack and shipping caused by de abrasion wear.

Subsequently, at 300 revolutions, the amount of removed material increases considerably. The processes evolutes until that at 6,000 revolutions the surface is completely wearied and consequently brightness is almost null. Figure 6 shows the abrasion wear evolution and the resulting brightness for samples with glaze points related to the P20C composition.

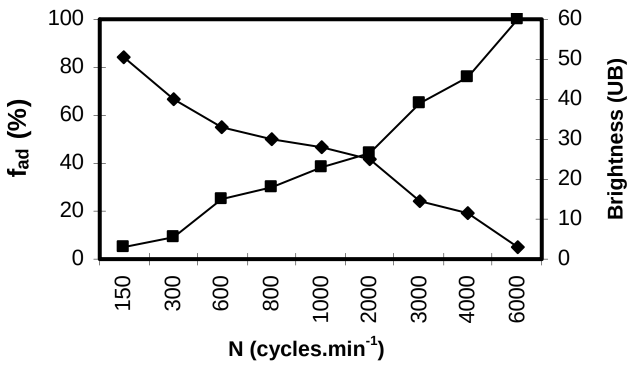

Figure 6. Abrasion wear and brightness evolution of glazed samples coated with the P20C protection glaze composition. (♦: Brightness; ■: Wearied area fraction).

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 Figure 6) could represent the material life.

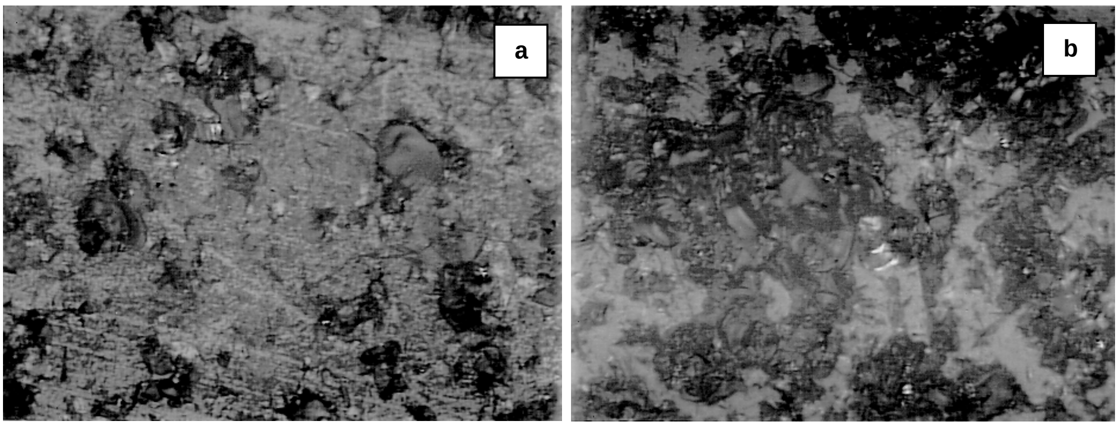

Figure 7. Optical micrographs of glazed surfaces with the application of protection glaze (P20C) points after 2,000 revolutions in the abrasion equipment. (a): With protection layer; (b): Without protection layer. Magnification: 20 X.

It is important to point out (Figure 7) the effect caused by the protection glaze on the glazed surface, Figure 7 (a) with respect to the glazed layer without protection, Figure 7 (b). It can realize yet from Figure 7 (a) that the wearied area by abrasion (f_{ad} = 44%) is significantly lower to that related to the protected surface (f_{ad} = 77%). This main that the ceramic tile life can be duplicated using the protection layer application as shown in Figure 6.

4. Conclusions

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A glazed porcelainized stoneware tile coated with a layer glaze for the protection of the glazed surface, which the scratching 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 scratching resistance of about 9 Mohs and surface brightness of about 71 BU. It was evidenced that the scratching resistance increasing 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 main 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 scratching resistance (9 Mohs), high abrasion wear resistance (PEI 5) and good staining resistance (Class 4).

Acknowledgements

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