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Research Article

Relationship between Surface Abrasion Wear and Brightness in Glazed Porcelainized Stoneware Tiles

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This paper reports the results of a research work whose main objective is related to the development of a technical solution that takes into account the relationship between the surface abrasion wear resistance and brightness of glazed ceramic tile products. Thus, glazes formulated from a glass-ceramic composition belonging to the LZSA system reinforced with crystalline particles of zircon were prepared and characterized with respect to their scratching and surface abrasion wear resistances and brightness. In this context, a bright (71.2 UB) porcelainized stoneware ceramic tile with high scratching resistance (9 Mohs), high surface abrasion wear resistance (PEI 5), and good staining resistance (Class 4) was obtained.

1. Introduction

In the last year it has been observed, taking into account the globalization, some changes in the world economic scenery which have impelled the companies, including also those of ceramic tiles, to look for the technological modernization and the competition as a manner to improve their positions as players. In fact, this world scenery has carried the brazilian manufacturers of ceramic tiles to the reducing of productive costs and even of the profits in toward to gain of scale.

Consequently, much has been invested during the last years with respect to automation technology and optimization of the productive processes as, for instance, wet milling, fast firing and drying in roller kilns and roller driers, respectively, automation and integration of the productive steps by means of control software, and so forth [1].

These changes are more and more available to all producers of ceramic tiles, which, having financial support, have had access to the most new world technologies that is, the difference between the bigger producers and the smaller ones, technologically, has been progressively decreasing. On the other hand, in Brazil the changes in the consumer's behavior such as their demand and the creation of the consumer's code have conducted the customer to demand technically differentiated products with esthetically and strong appeal to the quality. In this way, ceramic producers have been pressed to increase the value of their products in order to attract the customer's preference since more and more similar products in price and quality are available in the market. So the necessity of innovating has grown up by creating differentiated products, which are, safe and ecologically correct products, and showing technical solutions in response to the customer's appeals. Thus, the emerging technologies have allowed the development of new products such as those obtained by single fast firing, the "Trims," and the third firing products as well as, recently, the porcelainized stoneware tile (1984 in Italy and 1996 in Brazil). The porcelainized stoneware tile, even showing excellent properties as a material and as a ceramic tile, keeps its capacity of intrusion of the dirt after polishing since its closed porosity becomes open decreasing its staining resistance. So the product classification according to ISO 10545 is diminished. On the other hand, the overall market traditionally has demonstrated greater preference for products with high

Table 1: Compositions of the investigated glazes.

Constituents	Composition (wt.%)		
	P	P10C	P20C
Frit LZSA	100.0	90.0	80.0
Zircon	0.0	10.0	20.0

brightness indexes. To obtain porcelainized stoneware tiles with high brightness indexes and at the same time with high staining resistance, some producers have proposed an application of a vitreous coating on the surfaces of ceramic tiles to reduce the surface porosity. However, the applied vitreous coating (layer) shows low scratching resistance. Thus, came out an audacious challenge to be overcame that was imposed by the market to the producers of ceramic tiles, that is, to produce a technical product, with high brightness, high scratching, staining, and abrasion wear resistances, besides being esthetically pleasing and having a low price.

Taking into account this tendency of technological evolution, glass-ceramic materials could be an important alternative to obtaining technically differentiated glazed ceramic tiles. In fact, many research works about glass-ceramic materials were reported in the last years [2–10], including those ones related to ceramic tiles [1, 11, 12]. Some examples of successful application of glass-ceramic materials as ceramic tiles are the Italian product commercially named “Enduro” (ceramic tile coated with a glass-ceramic glaze), which is produced at more than 20 years by a process denominated “firestream” and the Japanese product named “Neoparies” (sintered glass-ceramic product). Both products, despite the success, are technologically difficult to produce today [13].

Among several investigated glass-ceramic systems came out LZS (Li_2O-ZrO_2-SiO_2) [14]. This glass-ceramic system showed some interesting properties, such as relatively high bending strength and high abrasion wear and chemical resistances. However, compositions belonging to LZS system have shown high linear coefficients of thermal expansion ($90–110 \times 10^{-7}{}^\circ C^{-1}$), making it difficult to use as a ceramic glaze. An alternative, on the other hand, can be the utilization of glass-ceramic compositions of LZSA (Li_2O-ZrO_2-SiO_2-Al_2O_3) system [15], since they have shown linear coefficients of thermal expansion (LCTE) between 46 and $75 \times 10^{-7}{}^\circ C^{-1}$. However, this new glass-ceramic system shows a relatively low scratching resistance (6 Mohs). Thus, the utilization of glass ceramics reinforced with high hard crystalline particles could be a solution. In fact, according to Montedo’s work [15], glass ceramics reinforced with zircon crystalline particles allowed to obtain materials with scratching resistance up to 9 Mohs.

In this context, this paper reports results regarding to the development of a technical solution that takes into account the relationship between the abrasion wear resistance and the brightness to obtain ceramic products with optimized properties and with high performance for application as floor tile.

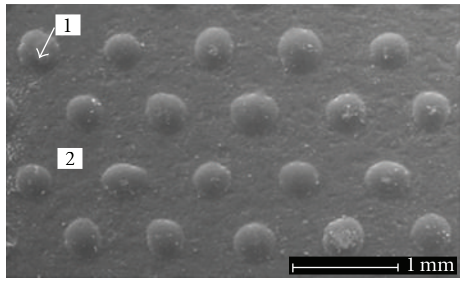


Figure 1: SEM micrograph (top view) of a ceramic tile sample coated with the LZSA glass-ceramic glaze (1) on the bright glazed surface (2).

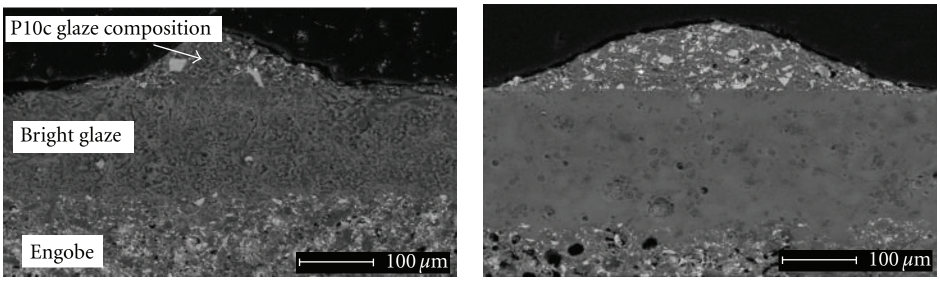
2. Materials and Methods

To perform this work, glazes constituted (solid fraction) by a LZSA glass-ceramic frit ($19Li_2O \cdot 8ZrO_2 \cdot 64SiO_2 \cdot 9Al_2O_3$) reinforced with hard crystalline particles of zircon were formulated and prepared as shown in Table 1. These compositions were chosen because of results presented in previous work [15].

The LZSA glass-ceramic frit, after sintering in the 700–900°C temperature range, showed a LCTE between 51.4 and $52.8 \times 10^{-7}{}^\circ C^{-1}$ (25–325°C), according to previous works [13, 15]. The reinforcing material as used in the industry showed mean particle size determined by laser scattering (CILAS 1064L) of 6.6 μm (zircon, $ZrSiO_4$). Additional details about the processing and the properties of the LZSA glass-ceramic frit can be obtained from Montedo’s work [15]. In a successive step, the constituents of each formulated composition (Table 1) were wet milled in water in a laboratory ball mill so that, after drying process, powders with particle sizes lower than 5 μm were obtained according to laser scattering measurements.

The obtained powders were then mixed with an organic vehicle (55 wt.%) supplied by ZSCHIMMER-SCHWARZ so that serigraphic pastes (glazes) were obtained and applied on the surfaces of glazed (bright) porcelainized stoneware tiles (scratching resistance of 4 Mohs and LCTE of $64.0 \times 10^{-7}{}^\circ C^{-1}$), using different serigraphic sieve screens (32 mesh) to reproduce the designed geometry as shown in the SEM (Philips XL 30) photograph of Figure 1.

The glaze serigraphic applications were performed in order to obtain a layer thickness (h) of approximately 75 μm. Subsequently, the glazed ceramic tiles were dried in laboratory furnace at 110°C for 2 h and then thermally treated in a continuous roller kiln so that a 41 min thermal cycle was performed at 880°C. Afterwards, all ceramic tiles, in appropriated formats, were characterized with respect to the scratching resistance (NBR 13818/97—Annex V), surface abrasion wear resistance (NBR 13818/97—Annex D), and staining resistance (NBR 13818/97—Annex G and ISO 10545-14/95). It was also investigated the brightness of the ceramic surfaces (BYK-GARDNER Instruments, model Micro Tri-Gloss μ, with a 60° angle). Finally, ceramic tile samples, after surface abrasion wear, were evaluated by comparing the worn area (area of removed material) with the



(a) (b)

Figure 2: SEM micrographs (cross sections) of glaze compositions: (a) P10C and (b) P20C. Etching: HF 2%/25 s.

Table 2: Brightness and scratching resistance of the tested samples.

Composition	$\lambda = 0$ mm $f_{ac} = 100\%$		$\lambda = 0.25$ mm $f_{ac} = 23.1\%$		$\lambda = 0.35$ mm $f_{ac} = 19.8\%$		$\lambda = 0.61$ mm $f_{ac} = 10.9\%$		$\lambda = 0.68$ mm $f_{ac} = 6.1\%$		$\lambda = \infty$ $f_{ac} = 0\%$	
	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		

λ: mean free path; f_{ac}: fraction area coated with glaze.

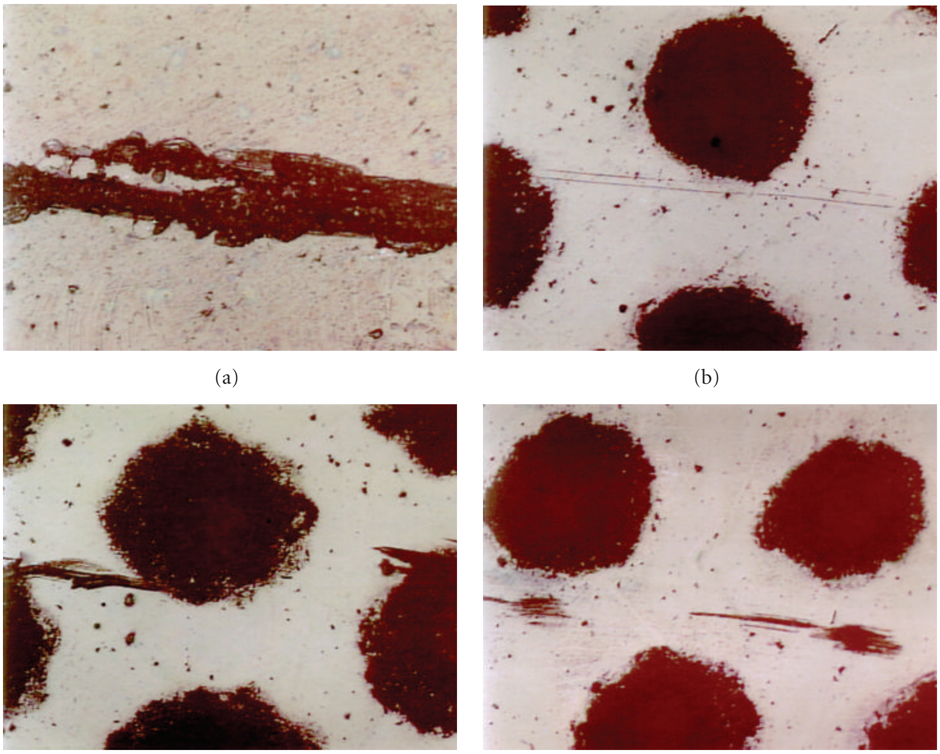
total area by means of a software (Imago 2.1.32) in an optical microscope (OM), Olympus model BX60M.

3. Results and Discussion

Montedo [15] studied LZSA system glass ceramics and found good and interesting results. However, the influence of reinforcing crystalline particles on the scratching and the surface abrasion wear resistances of the prepared glazes from the LZSA glass ceramic had not been evaluated yet. These compositions therefore constitute the main interesting focus of this work since the goal is to obtain glazed ceramic tiles matching the high brightness of the glazed layer on the porcelainized stoneware tile surface and the good abrasion wear, mechanical and chemical resistances of the prepared mixtures according to Montedo's previous work [15]. In this context and searching to optimize the brightness and the mechanical and chemical properties of the obtained mixtures, the P10C and P20C compositions for this study were selected, fundamentally. Figure 2 shows SEM micrographs of cross sections of samples, appropriated thermally treated, related to P10C and P20C compositions. From the micrograph analysis, it can be seen that the selected vitreous glaze used in the porcelainized stoneware tile showed low porosity which is an important requirement to minimize the staining tendency.

Table 2 shows results related to the scratching resistance of glaze compositions P (LZSA glass-ceramic frit), P10C and P20C, applied over the surfaces of the glazed porcelainized stoneware tiles.

Here, f_{ac} is the relation between coated area and total area of the surface ceramic plates, while λ is the average distance between the dots (glass-ceramic material applied over the ceramic plates). From Table 2, one can observe that there is a tendency to improve the scratching resistance as the fraction area coated with glaze (f_{ac}) increases, within the analyzed interval. On the other hand, as expected, the surface's brightness decreased as the f_{ac} was increased since the composite glazes do not show significant brightness. However, P composition, for any tested mean free path (λ) value, does not show the minimum necessary scratching resistance (>7 Mohs) according to the objectives of this work, not being therefore used in the subsequent experiments even showing higher brightness. Meanwhile, P10C and P20C compositions showed, under determined conditions, scratching resistance values equal to or higher than 8 Mohs. This means that for the used parameters (thickness of the applied layer glaze, h, and half-sphere dots diameter, d_c) the application (deposition) of these compositions, impeached the abrasive material contact with the glazed surface (unprotected glazed surface). In this way, some protection occurred. This does not mean, therefore, that these materials had not been worn as will be shown later. For f_{ac} equal to 23.1%, both considered sample compositions show scratching resistances at acceptable levels. However, obtained brightness value was very low so that in these conditions these compositions were approved in the scratching resistance criteria but reproved with respect to the brightness. Higher values of f_{ac} (over 23.1%) were tested, but enough definition was not achieved with respect to the applied half spheres (dots); that is, overlap of dots has occurred. Moreover, scratching resistances values are close to the respective monolithic compositions and brightness values were drastically reduced. As already signed, glazes from the prepared mixtures have not showed, after firing process, high scratching resistances. However, under determinate conditions, samples containing glaze coating



(a) (b) (c) (d)

Figure 3: OM micrographs (top views) of samples scratched by topaz: (a) bright glazed surface without the protective layer; (b), (c) and (d) bright glazed surfaces coated with the protective layer (half-spherical dots), P20C composition deposited in half-sphere geometry. Not etched. Magnification: 5x.

(dots) for the protection of the glaze on the ceramic tile surface show high scratching resistance, thus providing an effective protection or attenuation produced by the abrasion wear. Figure 3(a) shows scratches (groves) produced on the glazed surface without protective glaze dots after it has been scratched with topaz (8 Mohs). Figures 3(b), 3(c), and 3(d) show scratches produced on the glazed surface with surface protection after it has been scratched with topaz. Figures 3(b) and 3(c) show scratches that crossed all the material surface extension, so that they achieved the glazed surface and the protective composite glaze surface.

It can be realized that the dimensions of the groves produced over the protective glazed surface are much lower than that originated by the same abrasive material on the glaze surface without a protective layer even when they were produced in the protective glaze only, Figure 3(d). In fact, the protective layer (dots) created a barrier to the abrasive material action making the scratches difficult to be visualized. Consequently, high scratching resistance values were obtained. Thus, P20C composition with an f_{ac} corresponding to 19.8% ($d_c = 0.316$ mm and $\lambda = 0.35$ mm) was selected and submitted to the surface abrasion wear test for 2,000 cycles (revolutions or rotations). The evaluation of the tested samples was performed based on the fraction of the worn area (f_{ad}), and results are shown in Table 3.

From Table 3, one can observe that there is a tendency of f_{ad} reduction as λ decreased (f_{ac} increased). P20C composition with $\lambda = 0.35$ mm (f_{ac} =19.8%) shows a smaller f_{ad} among tested samples, probably by the reduction, in an optimized manner, of critical residual stresses which produce the nucleation and the propagation of lateral cracks [16, 17]. This means that the used λ value is appropriated since it allowed optimal correlation between the layer dots thickness (h) and dots (half-spheres) diameters (d_c) designed. So the f_{ac} value corresponding to 19.8% represents not only the optimized value with respect to the relationship between scratching resistance and surface brightness but also the condition that makes obtaining of a higher glaze surface protection among the tested values possible. On the other hand, the increasing of f_{ad} for a $\lambda = 0.25$ mm (f_{ac} = 23.1%) can be explained by the accentuated increases of abrasive material causing wear on the unprotected glazed surface occasioned by the wear generated in the own glass-ceramic material. Moreover, Table 3 shows that P and P10C compositions did not show the same performance for f_{ac} = 19.8% as for P20C composition resulting in a higher surface worn in the unprotected glazed surface, in agreement with the low scratching resistance and brightness values obtained. In fact, Figure 4(a) shows a region between dots in the unprotected glazed surface related to a sample whose P20C composition was deposited with dots diameter of 0.316 mm and $\lambda = 0.35$ mm (f_{ac} = 19.8%) after it has been submitted to 2,000 revolutions in the abrasion wear equipment. In that figure, it is possible to observe yet the aspect and the

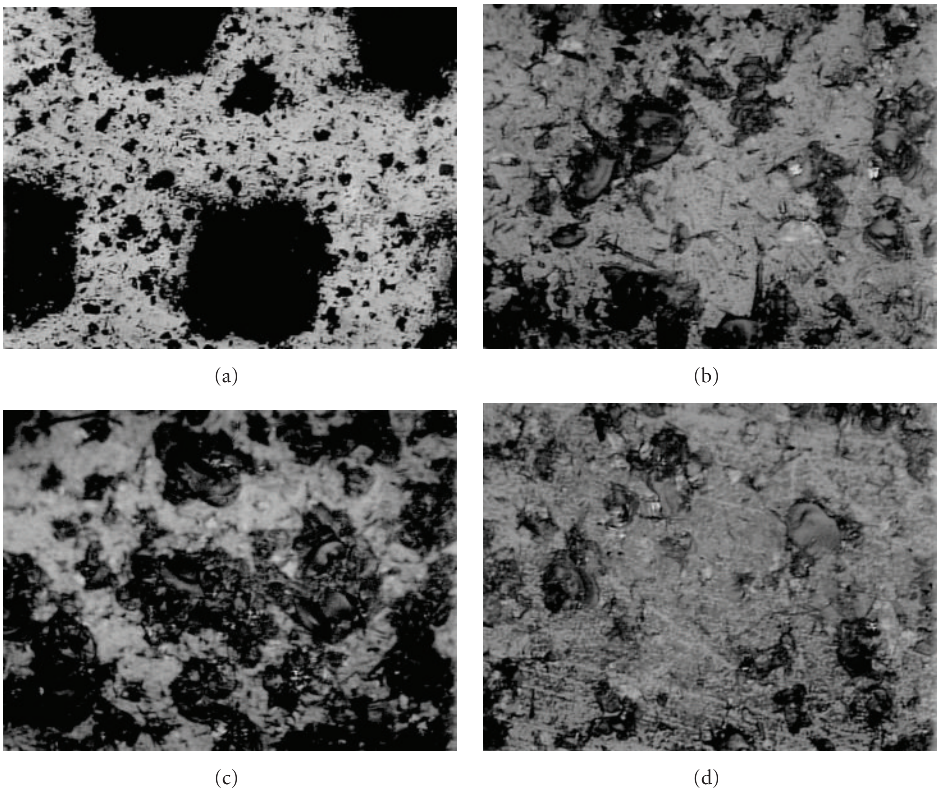


Figure 4: OM micrographs (top views) of bright glaze surfaces coated with the protective layer deposited in half-sphere geometry, after 2,000 cycles (revolutions): (a) P20C (5x), (b) P (20x), (c) P10C (20x), and (d) P20C (20x). Not etched.

Table 3: Fraction of the worn area (f_{ad}) of the tested samples.

Composition	Fraction of the worn area (%)				
	$\lambda = 0.25$ mm $f_{ac} = 23.1\%$	$\lambda = 0.35$ mm $f_{ac} = 19.8\%$	$\lambda = 0.61$ mm $f_{ac} = 10.9\%$	$\lambda = 0.68$ mm $f_{ac} = 6.1\%$	$\lambda = \infty$ $f_{ac} = 0\%$
P	—	69 ± 4	—	—	
P10C	—	58 ± 1	—	—	77 ± 6
P20C	54 ± 1	44 ± 2	72 ± 5	74 ± 4	

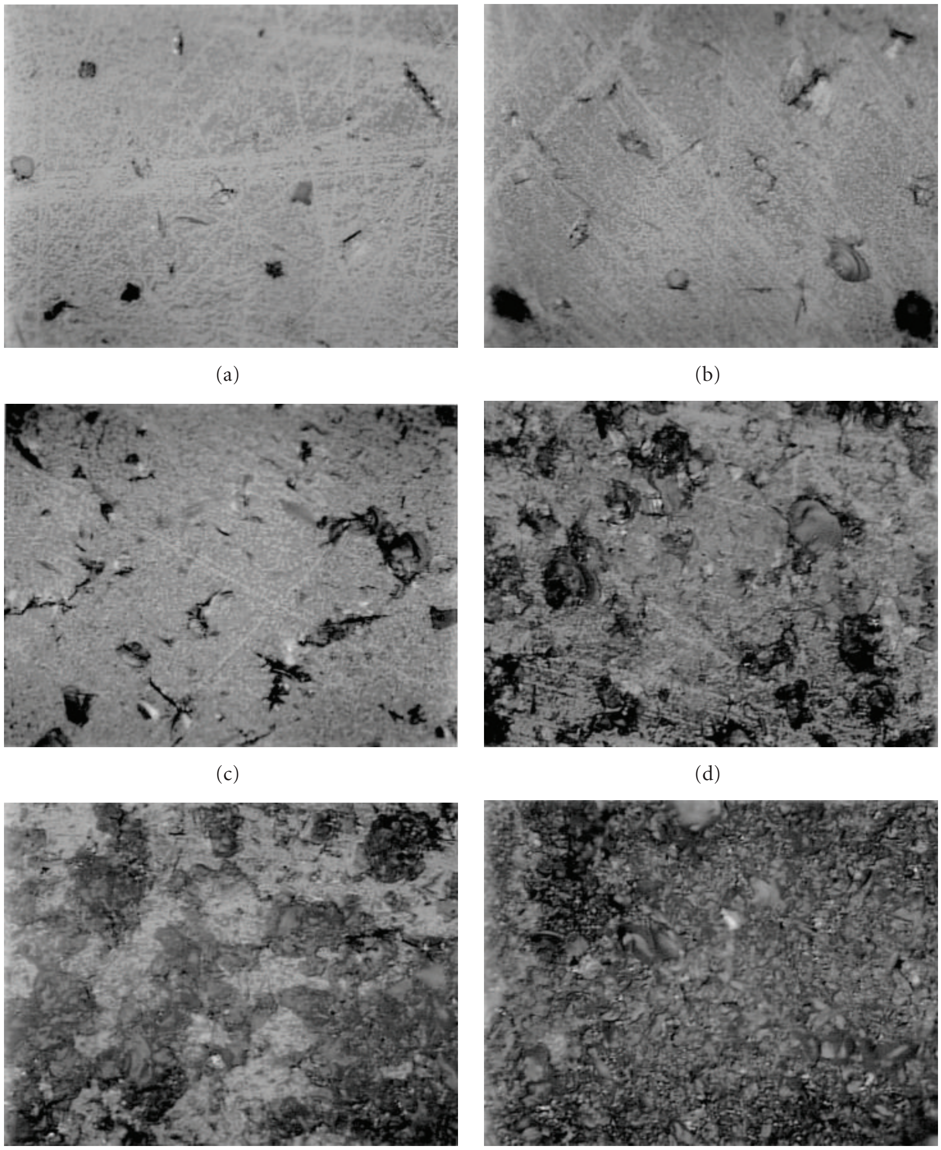
predominant wear mechanism operating on a glazed surface of a ceramic tile. Unprotected glazed surface analyzed is amorphous, and the fracture process occurs in a brittle way, that is, with small or any plastic deformation and in two steps: nucleation and crack propagation up to the final fracture [4]. In this case, the aspect of the fracture surface is denominated conchoidally.

Oliveira [16, 17] studied the mechanism of brittle fracture in ceramic glazes and demonstrated that it occurs with craters formation generated by the propagation of lateral cracks, evidencing the similarity between the fracture model produced by an indenter and that one produced on the glaze surface after an abrasion process. Figure 5 shows the wear behavior of a glazed surface with the deposition of the P20C composition (half-spherical dots) with $\lambda = 0.35$ mm ($f_{ac} = 19.8\%$) which was submitted to different abrasion levels, translated as number of rotations or revolutions (N) in the abrasion wear equipment.

In Figure 5(a) one can observe the existence of a crack and chippings generated by the abrasive wear. Subsequently, at 300 revolutions, the amount of removed material increased considerabely. The process developed, and at 6,000 revolutions the surface was completely worn and, consequently, the surface brightness was almost null.

Figure 6 shows the behavior of the occurring wear and the resulting brightness of samples with application of P20C glaze composition.

As expected, as N was increased, the amount of removed material also increased and the brightness decreased. However, from 2,000 revolutions the amount of removed material from the surface became excessively high committing the surface brightness. The interception point on Figure 6 could represent the useful material's life. It is important to underline (Figure 7) the effect generated by the protective glaze layer dots, Figure 7(a), related to the unprotected glazed surface, Figure 7(b). One can realize yet, from Figure 7(a),



(a) (b) (c) (d) (e) (f)

Figure 5: OM micrographs (top views) of bright glazed surfaces coated with the protective layer, P20C composition deposited in half-sphere geometry, after N cycles of abrasion: (a) 150 cycles, (b) 300 cycles, (c) 800 cycles, (d) 2,000 cycles, (e) 4,000 cycles, and (f) 6,000 cycles. Magnification: 20x. Not etched.

that the area worn by abrasion (f_{ad} = 44%) is significantly smaller than that related to the protected surface (f_{ad} = 77%). This means that the ceramic tile useful life with respect to the initial surface characteristics can be almost doubled by using the glaze protective layer as shown in Figure 6.

Considering the best results (optimized ones) with respect to the relationship between scratching resistance, surface brightness, and wear for P20C composition, λ = 0.35 mm (f_{ac} =19.8%), the abrasion wear resistance by the PEI test was evaluated. The porcelainized stoneware tiles glazed with a bright and white glaze and containing the P20C protective glaze (half-spherical dots) composition were characterized as PEI 5 according to NBR 13818/97—Annex D so that the wear was not visible after 24,000 revolutions in the abrasion wear equipment although it has been classified as Class 4 with respect to the staining resistance. Despite the staining resistance classification, the characteristics of the finished product are sufficient to evidence it commercially.

4. Conclusions

A glazed porcelainized stoneware tile coated with a composite glaze in a half-sphere geometry to protect the glazed ceramic surface, whose scratching resistance was 4 Mohs and brightness was 96.2 UB, was obtained and characterized. Best results were obtained with the P20C composition applied as a protective layer, half-spherical dots, with diameter (d_c)

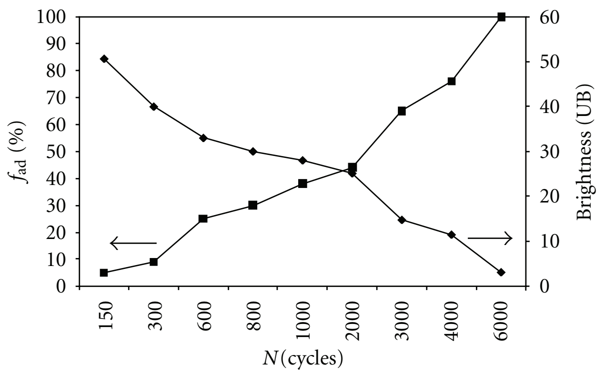
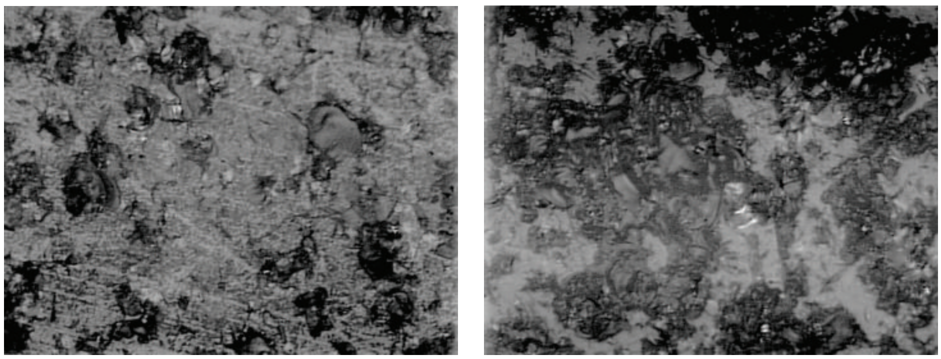


Figure 6: Evolution of the abrasion wear and brightness of glazed samples coated with the protective layer, P20C composition deposited in half-sphere geometry.



(a) (b)

Figure 7: OM micrographs (top views) of bright glazed surfaces after 2,000 cycles of abrasion: (a) coated with the protective layer, P20C composition deposited in half-sphere geometry; (b) unprotected glazed surface. Magnification: 20x. Not etched.

of 0.316 mm and thickness (h) of 0.075 mm distributed so that the mean free path (λ) was 0.35 mm and the fraction of coated area (f_{ac}) was 19.8%.

Thus, finished product achieved scratching resistance of 9 Mohs and surface brightness of 71.2 UB. It was verified that the scratching resistance increasing occurred due the fact that the protective layer, in the application conditions described before, created a barrier to the contact of the abrasive particles with the unprotected glazed surface in such way that the generated scratches could not be seen. After 2,000 cycles in the PEI abrasimeter, 44% of the glazed area was removed and brightness was 25 UB; having this value, its durability limit represents about 2 times the durability of the unprotected glazed layer.

In this way, a bright porcelainized stoneware tile (71.2 UB) was obtained with high scratching (9 Mohs) and surface abrasion wear (PEI 5) resistances and good staining resistance (Class 4).

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