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Low-gloss, silky matte glaze for porcelain tiles

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Abstract

Porcelain is a ceramic tile used worldwide, especially for its technical and aesthetic properties. In this increasingly competitive sector, innovative products are continually developed to meet the market's demands, such as glazed ceramic tiles with a matte surface, low surface gloss, and silky texture. In this research, a matte glaze for porcelain tiles with low surface brightness (9 to 14 UB) and silky texture was obtained. In particular, 16 formulations of ceramic glaze were studied, which were ground and applied to binil on a laboratory scale and then fired in an industrial kiln at 1192 °C for 45 min. The fired specimens were physically, chemically, thermally, and structurally characterized. The formulation that yielded the best results was tested on an industrial scale and technologically characterized. This formulation met the aesthetic (texture and gloss) and technological (resistance to staining, chemical attack, surface abrasion, and cracking) requirements of the Brazilian technical standard.
Keywords: matte glazing, silkiness, low gloss, porcelain tiles, ceramic coatings.

INTRODUCTION

Porcelain tiles have been gaining prominence in the international market owing to their glaze and low porosity. These characteristics provide the material with mechanical and chemical properties superior to those of other products in this category, i.e., high resistance to chemical attack, good cleanability of the coating, excellent abrasion resistance, high durability, and non-flammability [1]. In this context, the porcelain tile market has grown, especially that of glazed porcelain tiles with a low surface gloss and silky texture.

Ceramic glazes are formed from the combination of a dominant glass phase, closed porosity, and a small amount of crystalline phase. Sheikhattar et al. [2] quantified the maximum surface crystallinity of glazes as 25.4%. Parmelee and Harman [3] stated that controlling crystalline phase formation is critical to determining the amount of crystalline phase formed and thus the nature of the glazed surface (i.e., glossy, matte, or satin-finished). Amorós et al. [4] correlated the different typologies of unfired glazes during the sintering process. Low gloss glazes and satin glazes (silky texture) presented complex sintering processes in three parallel and overlapping steps that have been barely studied to date. Piccolo et al. [5] developed a translucent ceramic based on a porcelain stoneware paste modified by the addition of a frit to promote translucency. The reflectance spectrum of the better composition was, on average, 10% lower than that of the commercial sample used as a reference. The transmittance as a function of wavelength (400-700 nm) was 2% lower for the studied composition, reaching values of up to 12% for the reference sample. Moreover, the flexural strength was 50.12 MPa and the water absorption was 0.02%. Hupa et al. [6] stated that with increasing crystallinity of the glaze, the gloss values decrease and surface roughness increases. This microroughness or macroroughness is associated with the chemical composition of the crystalline phases on the surface, precisely the crystallinity of the glaze and the morphology of the crystals on its surface [2].

In this context, this work aimed to develop and characterize a matte glaze for porcelain tiles presenting a low-gloss surface (from 9 to 14 UB) and silky texture. There is a lack of knowledge about silkiness in ceramic tiles according to the existing literature. So, the novelty of this work is the development of a low-gloss, silky matte glaze for porcelain tiles from commercial raw materials, to understand the effect of composition on roughness and brightness. The presented paper makes a detailed analysis of 16 glaze formulations of commercial interest.

MATERIALS AND METHODS

The materials used and their corresponding results of X-ray fluorescence (XRF) spectroscopy (Epsilon 3XLE, Panalytical, Netherlands) are presented in Table I. Three matte frits available on the Brazilian market were selected, designated Frits 1 to 3, which featured high softening points for use in the manufacture of porcelain tiles. Sixteen glaze compositions were prepared using albite, kaolin, corundum, dolomite, nepheline, zinc oxide (ZnO), quartz, Frit 1, Frit 2, and Frit 3 (Table II), and their technical characteristics were evaluated at a firing temperature of 1192 °C.

Each composition was accurately weighed and wet-milled in a laboratory mill (CT 242, Servitech, Brazil) for 40

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Table I - Chemical composition (wt%) of the used raw materials.

Oxide	Albite	Kaolin	Corundum	Dolomite	Nepheline	ZnO	Quartz	Frit 1	Frit 2	Frit 3
Al_2O_3	17.27	37.27	98.26	-	17.40	0.12	1.11	19.58	19.63	18.79
CaO	0.49	-	0.08	28.10	0.59	-	0.05	23.76	12.56	21.12
Fe_2O_3	0.12	0.42	0.02	0.06	0.12	0.01	0.06	0.13	0.19	0.11
K_2O	1.57	0.03	-	-	2.01	-	0.05	0.22	1.67	1.50
MgO	0.19	0.28	0.22	24.68	0.21	-	0.08	7.58	0.56	8.29
Na_2O	8.37	-	0.41	-	8.32	-	0.11	0.20	4.81	0.36
P_2O_5	0.32	0.12	-	-	0.03	-	-	-	-	-
SiO_2	71.01	46.59	0.33	0.80	70.87	0.12	98.11	48.12	56.41	49.83
TiO_2	0.01	1.10	-	-	-	-	0.03	0.08	0.05	-
BaO	-	-	-	-	-	-	-	-	0.08	-
ZnO	-	-	-	-	-	99.30	-	0.11	4.04	-
ZrO_2+HfO_2	-	-	-	-	-	0.24	-	0.21	-	-
LOI	0.64	14.20	0.68	46.36	0.44	0.20	0.40	-	-	-

LOI: loss on ignition.

Table II - Studied glaze formulations (wt%).

Raw material	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16
ZnO	4.6	4.6	4.6	4.0	4.0	4.0	4.0	4.0	5.0	5.5	5.5	5.5	5.5	6.5	5.5	6.0
Corundum	3.3	3.3	3.3	4.5	4.5	4.5	4.5	4.5	3.5	3.0	2.0	3.0	4.5	4.5	3.0	4.5
Kaolin	9.2	9.2	9.2	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	13.0	13.0	12.0	11.0	12.5
Albite	35.5	35.5	35.5	34.6	34.6	34.6	-	-	-	-	-	-	-	-	-	-
Nepheline	-	-	-	-	-	-	34.6	34.6	34.6	34.6	34.6	32.6	31.1	31.1	32.6	31.1
Dolomite	13.8	13.8	13.8	13.8	13.8	13.8	13.8	13.8	13.8	13.8	11.8	11.8	11.8	11.8	11.8	11.8
Quartz	8.4	8.4	8.4	6.0	6.0	6.0	6.0	6.0	6.0	6.0	7.0	7.0	7.0	7.0	7.0	7.0
Frit 1	25.1	-	-	10.0	10.0	5.0	5.0	7.0	7.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Frit 2	-	25.1	-	-	15.1	15.1	15.1	10.1	10.1	11.1	13.1	13.1	13.1	13.1	15.1	13.1
Frit 3	-	-	25.1	15.1	-	5.0	5.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0

min. This procedure allowed the formation of a suspension (glaze) with a density of 1.83 to 1.85 g/cm^3 and flow time of 50 to 55 s in a Ford cup (4 mm opening); a residue of 0.30% to 0.50% was retained in the 325 mesh sieve. Subsequently, the obtained glazes were applied on porcelain tiles with the aid of a Binil with a 0.3 mm opening. The pieces (one of each formulation) were then fired in an industrial kiln (Icon, Brazil) at 1192 °C for a firing cycle of 45 min. These firing conditions are currently performed in the used industrial kiln, considering the working temperature (1192 °C) demanded by the ceramic support. After firing, the samples were subjected to visual analysis of the gloss (Glossmeter, KSJ, China) and roughness (Surftest SJ-301, Mitutoyo, Japan) using the methodology described in ISO 4288/1997 [7]. Four measurements of surface gloss were performed for each investigated formulation. The sixteen formulations were also analyzed using XRF spectroscopy (Epsilon 3XLE, Panalytical, Netherlands).

Based on the results of the physical and chemical analyses of the glazes, five formulations were selected for further analysis. Their linear thermal expansion coefficients (α), softening temperatures (T_s), and glass-transition temperatures (T_g) were determined using a contact dilatometer (DIL 402PC, Netzsch, Germany; heating rate of 7.5 °C/min, from 25 to 1200 °C). Heating microscopy (Misura HSM, Expert System Solutions, Italy; heating rate of 15 °C/min up to 1300 °C) was used to determine the sintering (T_{sint}), softening (T_s), and melting (T_m) temperatures of the selected formulations, and their viscosity curves were generated to elucidate their thermal properties. The crystalline phases present in the selected formulations were identified using powder X-ray diffraction (XRD, D8, Bruker, Germany; CuKα radiation, 1.5443 Å, 40 kV, 40 mA, 2θ from 5° to 75°, step size of 0.05°, time per step of 4 s, divergence and anti-scattering slits of 1/2°, and reception slit of 0.2 mm). These parameters were selected for phase quantification using the Rietveld method with the aid of software (X'Pert HighScore Plus, Philips, Netherlands). Microstructures of the studied glazes, in comparison to a commercial glaze (STD) with similar surface characteristics, were analyzed by scanning electron microscopy (SEM, JSM 6390, Jeol, Japan) with coupled energy-dispersive X-ray spectroscopy (EDS, Noran System Six X-ray Microanalysis System, Thermo Fischer Scientific, UK) to chemical microanalysis.

Next, the formulation that presented an adequate α value and the best gloss and texture for porcelain tile was selected for the industrial test. The sample was ground in a ball mill (Servitech, Brazil; 200 L, high alumina coating and balls). The produced glaze (100 L) had a density of 1.87 g/cm^3 and a flow time of 53 s; 0.28% residue was retained in the 325 mesh sieve. An industrial test was performed under production conditions, which involved the application of 132 g of this glaze on 60x60 cm tiles. The glazed tiles were fired in an industrial oven (Icon, Brazil; 45 min cycle at 1192 °C) and characterized according to the Brazilian technical standards [8, 9] in order to determine their resistance to staining, chemical attack, slipping, surface abrasion, cracking, and scratching according to the requirements of technical standard NBR 13.818/1997 - annex V [10]. The aesthetic characteristics of shine and texture were also assessed. Twenty-five specimens of Formulation 14 were used to perform the tests.

RESULTS AND DISCUSSION

Chemical characterization: Table III shows the XRF results of the studied formulations. Based on the data, the following conclusions can be drawn: i) the formulations with a non-compliant texture (05, 08, 12, 13, and 16; rough texture) contained the highest contents of alumina (Al_2O_3), ranging from 19.9 to 20.8 wt%. According to the literature, alumina is a highly refractory material and increases the viscosity of the melt. In addition, it is used to produce matte effects owing to its insolubility in the glass phase [11], which imparts a rough texture to the final product; and ii) the formulations with silky texture (01, 02, 03, 06, 09, 10, 11, 14, and 15) contained the lowest levels of alumina (Al_2O_3), ranging from 18.1 to 19.8 wt%, and high levels of zinc oxide (ZnO), which ranged from 4.5 to 6.6 wt%. Formulations 04 and 07 had a silky texture with high alumina (Al_2O_3) contents ranging from 20.2 to 20.7 wt% and low levels of zinc oxide (ZnO) ranging from 4.1 to 4.5 wt%; these formulations tended to adhere well to rough surfaces. As reported in the literature [11, 12], zinc oxide is an efficient melting agent at medium and high temperatures. At low contents, ZnO imparts a silky texture to the enameled surface.

Physical characterization: the physical characteristics of the tested formulations are presented in Table IV. The gloss measurements were taken using a surface glossmeter, the roughness was determined using a rugosimeter, and the texture of the material was classified based on the roughness data (Rz) of the surface. Considering the measured Rz and the corresponding tactile perception of the analyzed surfaces, the following working ranges were determined: a)

Table III - Chemical composition (wt%) of the studied formulations.

Formulation	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	P_2O_5	SiO_2	TiO_2	ZnO	LOI
01	18.3	10.1	0.1	0.7	3.8	3.0	0.3	50.5	0.1	4.5	8.6
02	18.3	7.6	0.1	1.0	2.6	3.8	0.2	52.3	0.1	5.3	8.7
03	18.1	9.5	0.1	1.0	4.0	3.0	0.2	50.8	0.1	4.5	8.7
04	20.2	9.8	0.2	0.8	4.0	2.9	0.3	49.3	0.1	4.1	8.5
05	20.3	9.8	0.2	0.8	4.0	2.9	0.3	49.5	0.1	3.8	8.5
06	18.6	9.1	0.1	1.0	3.4	3.8	0.3	50.7	0.1	4.6	8.4
07	20.7	9.0	0.2	1.0	3.5	3.0	0.1	49.8	0.1	4.5	8.3
08	20.5	9.0	0.2	1.0	3.4	3.2	0.2	50.3	0.1	3.9	8.2
09	19.8	9.1	0.2	1.0	3.5	3.0	0.2	49.2	0.1	5.3	8.7
10	19.4	9.0	0.2	1.0	3.5	3.0	0.1	49.4	0.1	5.7	8.6
11	19.2	8.5	0.2	1.0	3.2	3.0	0.2	51.0	0.1	5.9	7.8
12	19.9	7.0	0.2	1.0	2.3	2.8	0.1	55.0	0.1	5.8	5.9
13	20.8	7.0	0.2	1.0	2.2	2.8	0.1	54.0	0.1	5.8	6.1
14	19.7	9.7	0.2	0.9	3.7	2.5	0.2	49.0	0.1	6.6	7.6
15	19.4	8.8	0.2	1.0	3.3	3.1	0.1	50.7	0.1	5.8	7.6
16	20.6	8.6	0.2	1.0	3.2	2.7	0.1	49.5	0.1	6.4	7.6

LOI: loss on ignition.

Table IV - Physical characterization of the studied formulations.

Formulation	Brightness (UB)	Roughness, Rz (μm)	Texture
01	13±1	3.29	Silky
02	25±1	3.15	Silky
03	19±1	2.97	Silky
04	8±1	3.65	Silky*
05	8±1	3.80	Rough
06	23±1	3.66	Silky
07	12±1	3.54	Silky*
08	11±1	3.78	Rough
09	13±0	3.56	Silky
10	15±1	3.66	Silky
11	18±1	3.21	Silky
12	14±0	3.99	Rough
13	10±1	5.27	Rough
14	11±1	3.74	Silky
15	13±1	3.53	Silky
16	9±1	4.02	Rough

**: silky texture tending to be slightly rough.*

silky surface, Rz: 2.97-3.74 μm; and b) rough surface, Rz: 3.78-5.27 μm. Based on the analysis data, the formulations were classified as follows: i) formulations with non-compliant brightness (above the range specified for the work, from 9 to 14 UB): 02, 03, 06, 10, and 11 exhibited high brightness ranges, ranging from 15 to 25 UB; for this reason, these formulations were discarded; ii) formulations with nonconforming roughness and texture: 05, 08, 12, 13, and 16 exhibited rough textures, making them incompatible with the objective of the work, so they were rejected; and iii) formulations with texture and glosses consistent with the objective of the work: 01, 09, 14, and 15; formulations 04 and 07 showed silky textures tending to be slightly rough (to the touch); Formulation 04 was selected for study, as it had the lowest surface gloss (8 UB).

Based on the results of the physical and chemical analyses, it was evident that some of the studied formulations yielded textures and glosses compatible with the objective of this work. The five selected formulations (01, 04, 09, 14, and 15) were analyzed in depth. By specifically analyzing the texture of the selected formulations and correlating them with the respective chemical analysis results, zinc oxide was linked to a silky texture. As observed, Formulation 04 presented a slightly rough texture; the chemical analysis results listed in Table III showed that it comprised 4.1 wt% ZnO, which was a low ZnO content among the selected formulations. This content seemed to represent the boundary between a rough and silky texture for the range of studied compositions. The other formulations that presented silky textures showed ZnO contents ranging from 4.5 to 6.6 wt%. It is worth mentioning Formulation 14, which presented the highest ZnO content

Table V - Thermal characteristics of studied glazes.

Formulation	α (°C^{-1})	T_g (°C)	T_s (°C)	T_{sint} (°C)	T_m (°C)
01	6.6x10^{-6}	707	1101	1132	1218
04	6.3x10^{-6}	665	1106	1141	1220
09	6.1x10^{-6}	673	1082	1132	1244
14	6.0x10^{-6}	659	1064	1122	1212
15	6.0x10^{-6}	670	1072	1123	1238

α: thermal expansion coefficient (35-325 °C); T_g: glass-transition temperature; T_s: softening temperature; T_{sint}: sintering temperature; T_m: melting temperature.

and showed a very silky surface that was pleasant to the touch (Rz=3.74). A silky or satiny texture of opaque matte glazes is guaranteed by the presence of ZnO because this oxide increases the maturation interval of the glaze and promotes the stabilization of the acquired texture [13, 14]. Casasola et al. [12] stated that zinc oxide is widely used in glaze compositions with silky/soft textures. Zinc oxide is frequently employed in glazing compositions because it is an efficient fluxing agent, decreases viscosity, facilitates the spreading of the melt on the substrate, and facilitates the formation of a high-quality coating surface [12, 15].

Thermal characterization: the five selected formulations were subjected to thermal characterization by contact dilatometry. The results of α, T_g, and T_s are shown in Table V. The linear thermal expansion coefficient (α) of the studied glazes should lie between 6.0 and 6.5 x10^{-6} °C^{-1}. In this range, the glaze is expected to obtain adequate support/glaze coupling to avoid planarity defects after firing, since $\alpha_{support}$ ≅6.6x10^{-6} °C^{-1}, and the α value of the glaze must be slightly lower than that of the support in order to avoid cracking defects. A glassy layer under compression increases the resistance of the ceramic tile to mechanical stresses [12]. Considering the studied formulations, Formulation 01 exhibited an α value above that was considered appropriate for the production of glazed porcelain tiles and thus was not considered for the industrial application tests.

Based on the thermal characterization temperatures and on the viscosity (μ) values reported in the literature (theoretical values reported by Navarro [16] in the fixed points and viscosity ranges), the Vogel-Fulcher-Tammann (VFT) model [17, 18] was used to construct the viscosity curves as a function of temperature for the five studied formulations, as shown in Table VI and in Fig. 1. Based on these viscosity curves, the glazes' behavior at the firing temperature of the industrial kiln was evaluated. As described, the firing of the glazes in the industrial kiln took place at 1192 °C. This temperature was measured by the thermocouple fixed inside the kiln at a relative distance from the ceramic plate. Thus, it can be estimated that the temperature on the ceramic plate was ~50 °C lower than the temperature indicated by the thermocouple. As such, the firing temperature of the glazes was determined to be ~1142 °C for the used kiln.

In Fig. 1, it can be observed that Formulation 04 presented a higher viscosity at the firing temperature of the kiln (1192 °C, ~1142 °C on the ceramic plate), and this formulation also presented a higher softening temperature (T_s). Therefore, it can be concluded that this formulation, with its high viscosity and high T_s, yielded a higher content of suspended solids (i.e., insoluble), providing a more matte surface and thus a lower surface gloss, which was verified by the results of the surface gloss analysis (Table IV). Moreover, the formulations with the lowest viscosity values (i.e., 14 and 15) also had the lowest values of T_s. Thus, these formulations should present high liquid-phase contents and yield the glossiest surfaces. Glazes obtained at temperatures higher than their melt-phase composition and liquid temperature are more likely to be transparent and have brighter surfaces, whereas glazes obtained at firing temperatures lower than their melt-phase composition and liquid temperature are more likely to be matte or opaque [19]. In addition, formulations with lower viscosities enable better spreading of the glaze, improving the surface stretching and consequently the texture of the ceramic tile.

Table VI - Viscosity (μ) of the studied glazes.

T (°C)	Formulation 01	04	09	14	15	Log(μ) (Pa.s)
T_g	707	665	673	659	670	12
T_s	1101	1106	1082	1064	1072	9.25
T_m	1218	1220	1244	1212	1238	1

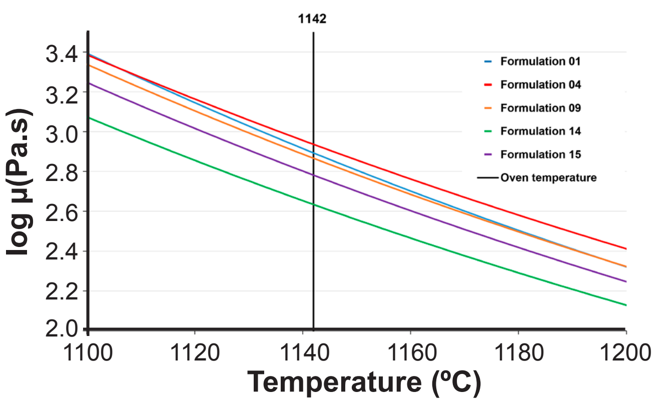

Figure 1: Viscosity curves of the studied formulations.

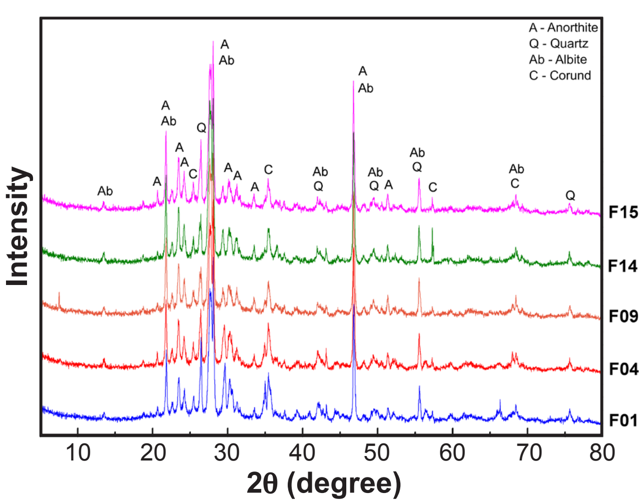

Figure 2: XRD patterns of the studied glazes.

Crystallographic characterization: the five studied formulations were also characterized using XRD (Fig. 2). Table VII provides the phase contents presented in these five formulations, as determined using the Rietveld method. The goodness-of-fit (GOF) is an index representing how well the calculated and experimentally obtained diffractograms correspond to each other. In practice, values below 5.0 represent a good refinement [20]. Based on the results of the quantification of the amorphous phase and quartz, which may be related to the surface gloss, the sum of these phases can be correlated with the results of the experimental analysis of the surface gloss, as shown in Table VIII.

Surface gloss depends on the surface properties, such as the roughness and present phases. It is expected that the lower the roughness Rz and the greater the sum of the amorphous and quartz phases, the greater the surface gloss of the obtained glazes. According to Table IV, Rz of the studied formulations showed the following behavior: 01<15<09<04<14. Table VIII shows a very close corresponding of surface gloss with Rz: 01=15=09>14>4. On the other hand, as can be seen in Table VIII, Formulations 09 and 15 had the largest sums of the amorphous and quartz phases (i.e., 35.6% and 34.9%, respectively), which gave rise to the highest surface gloss (13 UB). Formulations 04 and 14 presented intermediate sums; Formulation 14 was composed of 29.5% amorphous and quartz phases, consistent with intermediate surface gloss (11 UB). However, the formulation consisting of 30.8% amorphous and quartz phases (i.e., 04) exhibited

Table VII - Phase quantification (wt%) using the Rietveld method.

Formulation	Anorthite	Quartz	Albite	α-Al_2O_3	Amorphous	GOF
01	56.5	4.7	10.3	5.4	23.1	4.2
04	53.1	4.0	11.6	4.0	26.9	3.1
09	44.6	3.3	17.4	2.3	32.3	2.3
14	48.8	2.6	17.3	3.6	26.9	2.5
15	43.7	4.6	19.0	2.4	30.3	2.1

GOF: goodness-of-fit.

low surface gloss (8 UB), possibly owing to a low-gloss amorphous phase. In this formulation, two frits were employed (10.0% of Frit 1 and 15.1% of Frit 3), and the low surface gloss must be associated with Frit 3. However, considering the experimental data obtained in this work, Rz can explain the behavior of the surface gloss of the studied formulations better than the sum of the amorphous and quartz phases.

Table VIII - Results of surface gloss analysis of the studied formulations.

Formulation	Amorphous + quartz (wt%)	Brightness (UB)
01	27.8	13±1
04	30.8	8±1
09	35.6	13±0
14	29.5	11±1
15	34.9	13±1

Microstructural analysis: Fig. 3 shows the SEM micrographs of the studied glazes (non-chemically etched), in comparison to a commercial glaze (STD) with similar surface characteristics, which showed the vitreous (white arrows) and crystalline (black arrows) regions while Fig. 4 shows the SEM micrographs of the studied glazes (chemically etched, 2 vol% HF solution for 25 s). In Fig. 3, it can be seen the presence of crystalline, porous regions, which can decrease the surface gloss (Table VIII). On the other hand, although Formulation 04 presented an

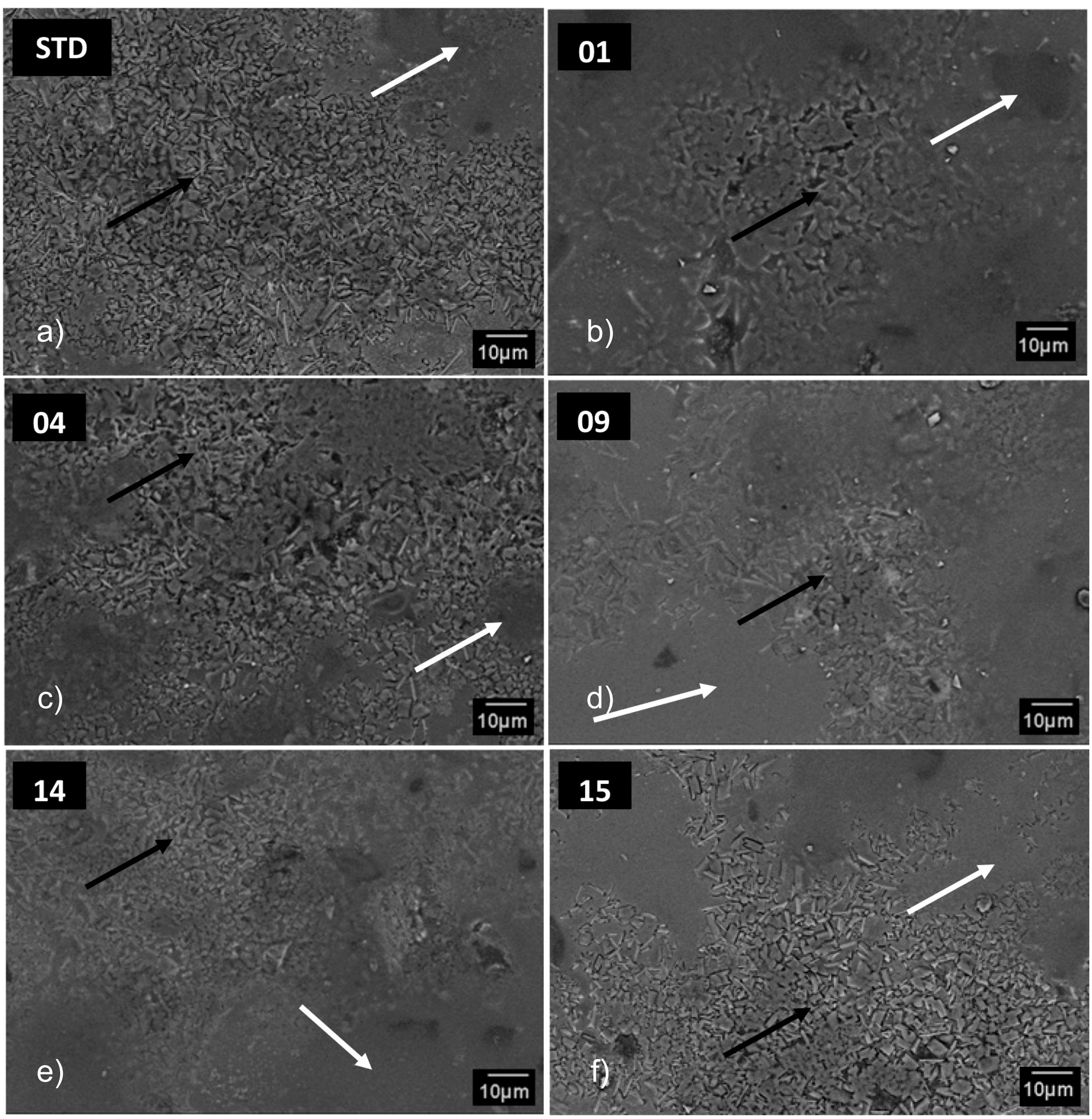

Figure 3: SEM micrographs of the studied glazes (non-chemically etched) showing the vitreous (white arrows) and crystalline (black arrows) regions.

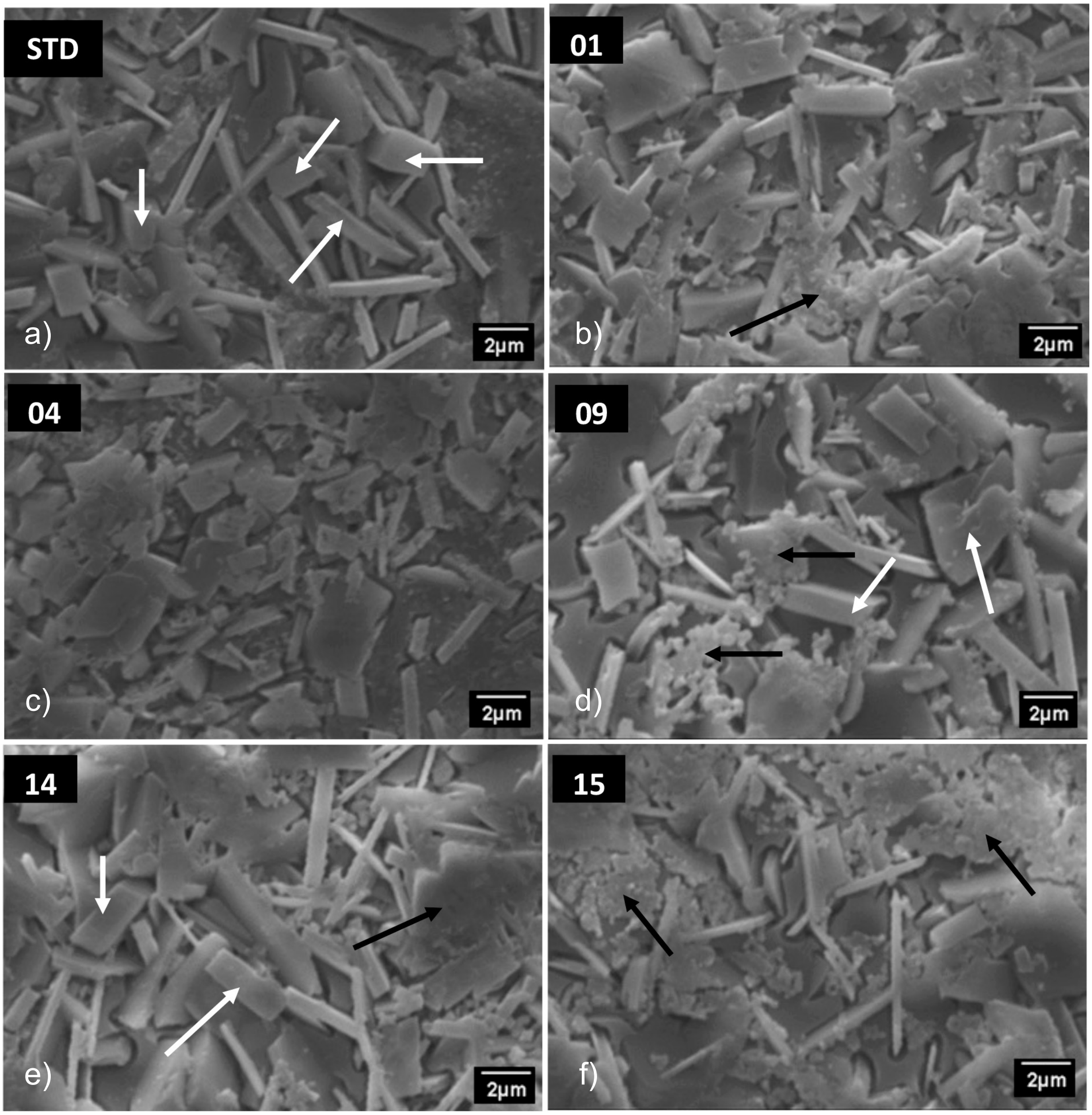

Figure 4: SEM micrographs of the studied glazes (chemically etched, 2 vol% HF solution for 25 s) showing the main identified crystalline phases: albite (black arrows) and anorthite (white arrows).

intermediate amount of amorphous phase (Table VII) in relation to the investigated formulations, it seemed that a smooth surface was shown. It is possible that the crystalline phases presented in Formulation 14 were immersed into the glassy matrix of the glaze, due to the low viscosity achieved by this formulation at the firing temperature (Fig. 1). Thus, the microstructure of Formulation 14 confirmed the results of adequate surface gloss and texture for using as low-gloss, silky matte glaze for porcelain tiles. In Fig. 4, the main crystalline phases were identified: albite (black arrows) and anorthite (white arrows), from the EDS analysis, in agreement with Table VII. It can be seen in Fig. 4 that the crystalline phases present in the investigated formulations (glazes) were the same as those found in the reference glaze (STD).

Industrial test: taking into account the aim of this work, to obtain a low-gloss, silky matte glaze for porcelain tiles, and based on the results of the laboratory experiments, Rz of 3.74 μm (silky surface) and brightness of 11 UB (low-gloss surface), Formulation 14 was best suited for application on an industrial scale. The glaze prepared for the industrial test was applied in industrial-production single-firing conditions using 60x60 cm tiles fired in an industrial kiln for 45 min at 1192 °C. A visual inspection of the surface finish of the glaze layer revealed no surface defects that could affect the quality of the product. The surface finish was similar to other comparable products on the market.

Finished product characterization tests: the most relevant technical characteristics of the glazing layer are surface texture, surface gloss, staining resistance, resistance

Table IX - Stain resistance results of Formulation 14.

Staining agent	Technical specification	Obtained value
Regulatory		
Chromium green oxide (penetrating action)	≥3	5
Iodine in alcoholic solution (oxidizing action)	≥3	5
Olive oil (film-forming agent)	≥3	5
Non-regulatory		
Red earth	≥3	5
Nugget shoe paste	≥3	5
Wine	≥3	5
Coke	≥3	5
Coffee	≥3	5

to chemical attack, and cracking resistance. In addition, scratch resistance (Mohs scale) and dynamic friction coefficient (wet) tests were also performed. The surface texture of the studied plates obtained from the industrial test was satiny with a silky touch, as desired. A surface gloss of 14 to 15 UB was obtained. The stain-resistance results are presented in Table IX. Besides the typical staining agents, some non-typical staining agents (i.e., red earth, Nugget shoe paste, wine, Coke, and coffee) found in daily life were also employed. For the three typical staining agents (green chrome oxide in light oil, iodine in alcoholic solution, and olive oil) and the non-typical staining agents, the samples were categorized into cleanability Class 5, which stains are easily removed by washing with warm water on the glazing surface.

The results of resistance to chemical attack are shown in Table X. Formulation 14 met the technical specifications, performing similarly to other comparable products on the market. No visible surface abrasion was observed for household or swimming pool chemicals (GA), that is, the glaze showed good resistance to these chemicals, as well as toward low-concentration acidic chemicals (GLA). However, changes in the surface (GLB) were observed when exposed to low-concentration alkali chemicals. In general, network-forming oxides-rich glasses (e.g., SiO_2) are more susceptible to alkaline attack [21]. These glasses are resistant to acid attack, but their resistance decreases upon incorporating network modifiers (alkali and alkaline-earth elements). Thus, the resistance to acid attack increases proportionally with the increase in silica content [22]. In the case of network-forming elements-poor glasses (SiO_2) and rich in network modifiers (alkali and alkaline earth metals), there is greater susceptibility to acid attack [21].

In the test of surface abrasion resistance, the tested slabs were grouped into PEI Class 4. This classification indicated high surface resistance, enabling the use of ceramic tile in high-traffic environments such as residences, garages, stores, bars, banks, restaurants, hospitals, hotels, and offices. In the literature, similar correlation values of gloss vs. surface-abrasion resistance (PEI) were reported for unfired glazes. Bright glazes show lower abrasion resistance (i.e., PEI classes 1 or 2), and low-gloss (frosted) glazes fall into PEI class 4 or 5. However, although these glazes, which contained quartz and corundum crystals, showed a higher classification (PEI 5), this type of unfired glaze does not meet the quality and aesthetic requirements for commercial glazes [23]. In the cracking resistance test, none of the specimens cracked before or after the test, demonstrating that the glaze did not undergo any kind of cracking, crazing, or chipping caused by a lack of coupling between the glaze and the ceramic support. In terms of scratch resistance, apatite had a hardness level of 5 on the Mohs scale, which begins to show a reduction of brightness and aesthetic change from orthoclase (hardness 6). The Mohs hardness of the glaze is influenced by the properties of the crystalline phase that devitrifies, depending on its nature and the distance between the crystals distributed in the glass phase. The closer the proximity of the crystals to each other, the greater the scratch resistance of the glaze [24].

The dynamic friction coefficient (wet) was determined to be 0.40, implying that the product is appropriate for normal installations. The surface roughness is strongly related to the crystallinity of the glaze and the morphology of the crystals precipitated on its surface [2]. Matte glazes exhibit high surface roughness, and their cleanability is influenced by the shape of the surface crystals, which can embed dirt on the rough surface. Shiny glazes naturally impart smoother surfaces than matte glazes owing to the lack of surface

Table X - Results of the chemical-attack resistance test of Formulation 14.

Chemical product	Solution	Technical specification	Obtained value
Household/swimming pool chemical	Ammonium chloride, 0.1 kg/L	GA	GA
	Sodium hypochlorite, 0.02 g/L	GA	GA
Low-concentration acid and alkali	Citric acid, 0.1 kg/L	GLB	GLA
	Hydrochloric acid, 3% (v/v)	GLB	GLA
	Potassium hydroxide, 0.03 kg/L	GLB	GLB

GA: effects of chemical attack not visible on the surface; GLA: effects of chemical attack not visible on the surface; GLB: chemical attack with discernible change in surface appearance.

crystallinity, which facilitates their cleanability [2, 25]. This correlation between the crystallinity of the glaze and its surface roughness (texture) was also observed in this work. Formulation 04 presented a matte surface with the lowest gloss (8 UB) and one of the highest contents of crystalline phases (72.7%) among the studied glazes; consequently, a silky surface tending toward rough was obtained. On the other hand, Formulation 09 exhibited the highest surface gloss (13 UB), low crystal content (67.6%), and high amorphous phase content (32.3%); as a result, the surface was very silky to the touch.

CONCLUSIONS

Experimental results of the development of a low-gloss, silky matte glaze for porcelain tiles from commercial raw materials (16 glaze formulations of commercial interest) to understand the effect of composition on roughness and brightness were presented. A silky matte glaze for porcelain tiles with a low surface gloss in the range of 9 to 14 UB was developed and studied. The chemical analysis results showed that the formulations with non-uniform textures (rough) contained the highest alumina contents (ranging from 19.9% to 20.8%), while the formulations with silky textures contained lower alumina contents (18.1% to 19.8%) and high ZnO contents (4.5% to 6.6%). Formulation 14 (6.5 wt% of ZnO, 4.5 wt% of corundum, 12.0 wt% of kaolin, 31.1 wt% of nepheline, 11.8 wt% of dolomite, 7.0 wt% of quartz, 6.0 wt% of frit 1, 15.1 wt% of frit 2, and 8.0 wt% of frit 3) displayed the lowest surface gloss and good glaze spreading, improving the surface stretching and consequently the texture. In the industrial test, the slabs glazed with Formulation 14 presented the same quality as those coated with the standard industrial glazes. The technological characterization results confirmed that the glaze met the standard technical requirements.

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