DEVELOPMENT OF PORCELAIN STONEWARE WITH HIGH SLIP RESISTANCE AND DURABILITY

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ABSTRACT

The surface characteristics of floor covering materials are one of the factors responsible for accidental slips and falls. To ensure safe use in areas with a high slip risk, such floor materials need to have specific surface profile characteristics, such as numerous high, sharp roughness peaks, to enhance the friction mechanisms at the interface with the shoes of the person walking on them. These rough textures, in the case of ceramic tiles, are usually achieved by applying grits to the surface of these products. However, high and sharp elements of surface roughness can easily wear away during the life of the tile, due to both pedestrian traffic and cleaning. Recent work showed that some ceramic tile surfaces that initially had satisfactory slip resistance for use in critical areas, no longer met the same safety requirement after being exposed to heavy pedestrian traffic. To avoid performance losses, the wear resistance of the granular materials applied to these surfaces needs to be improved in order to ensure that their non-slip properties perdure.

In this context, the aim of the present work was to develop porcelain stoneware tiles with high slip resistance by applying granular materials with high abrasion resistance to produce surface properties that would remain intact over the entire service life.

Granular materials with high modulus of elasticity and of varying compositions, particle sizes and shapes were applied to the surface of green industrial porcelain stoneware bodies. The samples were fired in a roller kiln up to 1190°C in 40-minute cycles. The different surface textures produced were then characterised. Slip resistance was measured using the British pendulum method. Stain resistance and chemical durability of the surfaces were assessed according to the tests described in international standard ISO 10.545. To simulate the wear that ceramic floors undergo during use, the surfaces were subjected to an accelerated ageing test using abrasion and mass loss was determined. The results showed that the surfaces produced with some of the granular materials in the study presented a high resistance to slipping and good ability to maintain their roughness and technical properties after accelerated wear.

1. INTRODUCTION

The surface characteristics of materials used as floor coverings are one of the factors possibly responsible for accidental slips and falls [1, 3]. For safe use in areas with high slip risk, floor materials need to have certain surface profile characteristics, such as numerous high and sharp roughness peaks to improve the friction mechanisms at the interface with pedestrians' shoes as they walk on the floor [4]. In the case of ceramic tiles, such rough textures are usually achieved by applying grits to the tile surface [5]. However, the elements of a surface with high sharp roughness can easily wear away during the service life of the floor due to pedestrian traffic [6], as well as from the great efforts applied to clean such surfaces.

Different research studies have been carried out in order to obtain glazes for ceramic tiles that meet the conditions of being both non-slip and easy to clean [7-10]. However, recent work showed that certain ceramic tile surfaces that initially had satisfactory slip resistance for application in critical areas according to standards, after being exposed for a time to high pedestrian traffic, no longer met that safety requirement [4].

To avoid a loss of non-slip performance, the wear resistance of granular materials that are applied to such surfaces needs to be improved in order to guarantee the durability of non-slip properties. In view of the above, by surface application of granular materials with high abrasion wear resistance, it was sought to develop porcelain stoneware ceramic tiles with high anti-slip resistance and the ability to maintain that characteristic throughout their service life.

2. MATERIALS AND METHODS

To undertake the work, granular materials with a high modulus of elasticity and of different compositions, particle sizes and shapes were used, which were applied to the surfaces of green porcelain stoneware tile bodies. The granular materials were proportioned in the amounts shown in Table I.

The seven compositions used are described below:

- STD: comprising a mixture of two commercial grits of different particle sizes commonly used in porcelain stoneware.
- SP50: comprising 50% commercial grits and 50% SP grains (spherical ceramic, aluminium oxide-based material with diameters classed between 105 and 200 µm).
- SP20: comprising 80% commercial grits and 20% SP grains (spherical ceramic, aluminium oxide-based material with diameters classed between 105 and 200 µm).
- BT50: comprising 50% commercial grits and 50% BT grains (brown fused aluminium oxide, with diameters classed between 63 and 105 µm).
- BT20: comprising 80% commercial grits and 20% BT grains (brown fused aluminium oxide, with diameters classed between 63 and 105 µm).
- AL50: comprising 50% commercial grits and 50% AL grains (white cast aluminium oxide, with diameters classed between 63 and 105 µm).
- AL20: comprising 80% commercial grits and 20% AL grains (white fused aluminium oxide, with diameters classed between 63 and 105 µm).

Samples	SP50	SP20	BT50	BT20	AL50	AL20	STD
Commercial grit C1 (75 – 150 µm)	25%	60%	25%	60%	25%	60%	50%
Commercial grit C2 (100 – 300 µm)	25%	20%	25%	20%	25%	20%	50%
SP Grains (100 – 200 µm)	50%	20%	-	-	-	-	-
BT grains (< 100 µm)	-	-	50%	20%	-	-	-
AL Grains (< 100 µm)	-	-	-	-	50%	20%	-

***Table I**. Compositions of anti-slip surface applications.*

The samples were proportioned, applied by vinyl on porcelain stoneware, and fired in a 40-minute cycle at a maximum temperature of 1190°C. Figure 1 shows the pieces obtained.

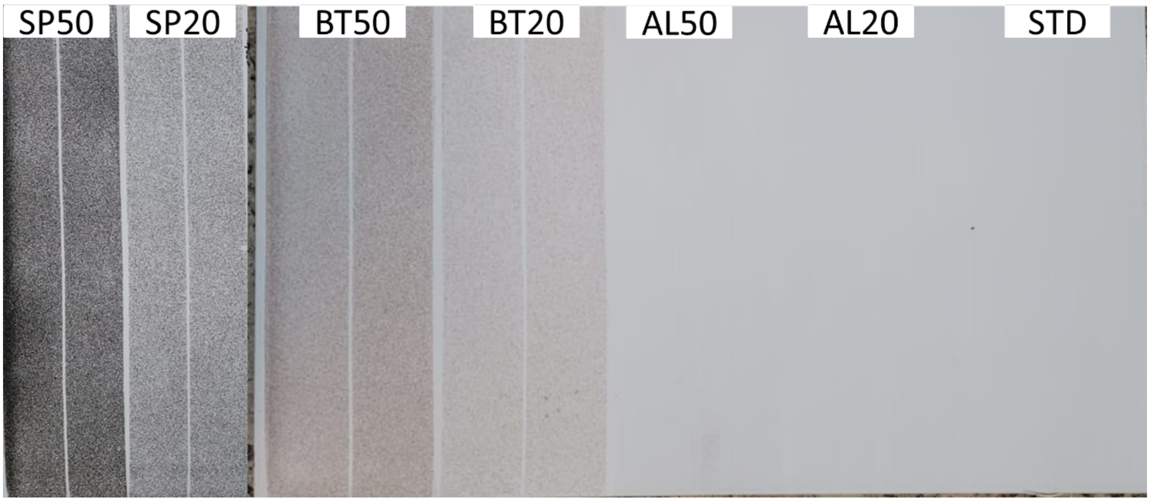

Figure 1. *Pieces of porcelain stoneware fired with the commercial grits and granular materials applied*

The surfaces of the pieces obtained were characterised as follows.

<u>Wear test as a function of time evaluated by mass loss:</u>

- Test specimens measuring approximately 5x5 cm were cut from the resulting pieces.
- The test specimens were fitted in the sample holder on the automatic polishing/abrasion device illustrated in Figure 2, with a standard load (300g) applied to the test specimens.
- They were then polished for 5, 15, 25 and 35 minutes and their mass was measured at the beginning and after each polishing cycle.

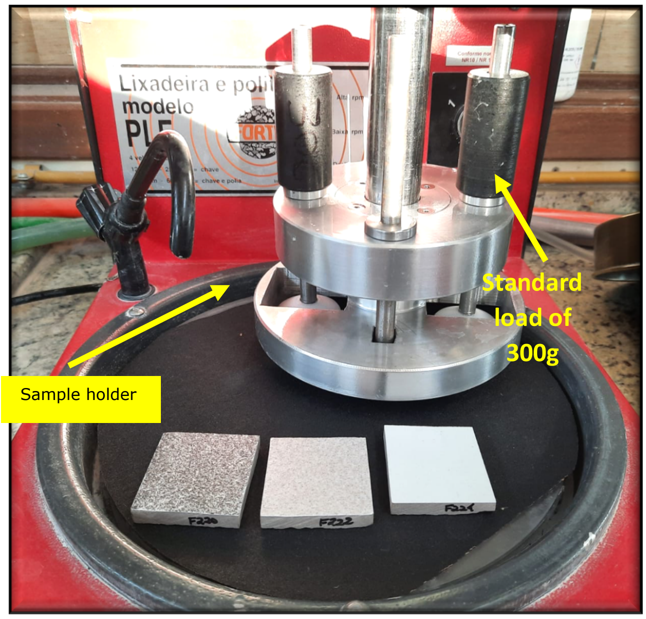

Figure 2. *Polishing/abrasion device with standard load fitted to a polisher.*

Chemical resistance test:

Test specimens measuring 5x5 cm were cut. Chemical attack was performed using the reagents detailed in ISO 10545, Part 13:

- Ammonium chloride (NH_4Cl) solution: 100 g/l for 24 hours
- Sodium hypochlorite (NaClO) solution: 20 mg/l for 24 hours
- Citric acid solution: 100 g/l for 24 hours
- Hydrochloric acid (HCl) solution: 3% for 96 hours
- Potassium hydroxide (KOH) solution: 30 g/l for 96 hours.

Resistance to stains test:

Test specimens measuring 5x5 cm were cut and stained with the agents detailed in ISO standard 10545, Part 14:

- Green penetrating staining agent in light oil (chromium oxide - Cr_2O_3)
- Chemical/oxidising staining agent: iodine/alcohol solution, 13 g/l
- Stains having filming action: olive oil.

Assessment of slip resistance by means of the British pendulum test:

Test specimens at least 20 cm long were removed along the vinyl application. The test equipment used is shown in Figure 3. The test was conducted in accordance with AS 4586/13 – Annex A. The result is obtained from the maximum angle that the arm on the equipment measures after contact with the surface. The scale varies from 0 to 100 PTV (pendulum test value), and its relation to slip potential is presented in Table II.

***Figure 3**. British pendulum.*

PTV	0-24	25-35	≥36
Slip potential	High	Moderate	Low

***Table II.** Safety limits for tiles according to the British pendulum.*

3. RESULTS AND DISCUSSION

Table III shows the chemical compositions and the main crystalline phases present in the abrasive grains that were mixed with commercial grits in the compositions and applied to the ceramic tile surfaces.

The three abrasives tested were prepared by electrofusion and have high concentrations of Al_2O_3. Corundum in the main crystalline phase. In the case of AL grains, the colouring is bright white, due to the high purity of the abrasive grains. BT grains, in turn, have a slightly lower concentration of Al_2O_3 and a higher proportion of silica and iron and titanium oxides, which gives them a brownish colour. Finally, SP grains have a significantly lower concentration of Al_2O_3 compared to the previous compositions, and a high proportion of silica, iron oxides and titanium. The presence of these elements in the SP grains leads to the formation of mullite and iron-rich crystalline phases together with corundum, which is the main crystalline phase. Depending on the chemical composition, SP grains are black in colour.

Oxides (%)	SP Grains	BT Grains	AL Grains
SiO_2	12.5	1.0	-
Al_2O_3	71.0	97.0	99.5
Fe_2O_3	13.0	0.9	< 0.1
TiO_2	1.8	1.6	-
Na_2O	-	-	0.4
MgO	-	0.2	-
Crystalline phases	**SP Grains**	**BT Grains**	**AL Grains**
Corundum	*	*	*
Mullite	*		
Iron oxides	*		

Table III. *Chemical compositions and crystalline phases present in abrasive grains.*

Images of the surfaces of the ceramic tiles obtained with compositions of grits and abrasive grains are shown in Figures 4 and 5.

Aesthetically, the presence of abrasive grains in the mixture with the grits alters the colour and texture of the resulting surfaces quite significantly. In general, abrasive grains help to increase surface roughness in the glazes by altering their tactile appearance, which creates more asperous surfaces.

From the visual point of view, the colour of the abrasive grains determines the overall colour of the surface, with the degree of whiteness being inversely proportional to the concentration of chromophore elements present in the chemical composition of the abrasive grains.

As far as morphology of the grains goes, the abrasives designated SP grains are seen to have greater sphericity, while the other two abrasives are formed by grains of an angular appearance. These differences are associated with the process used to make the SP abrasive grains, which is not used in the manufacturing process of the other two abrasives.

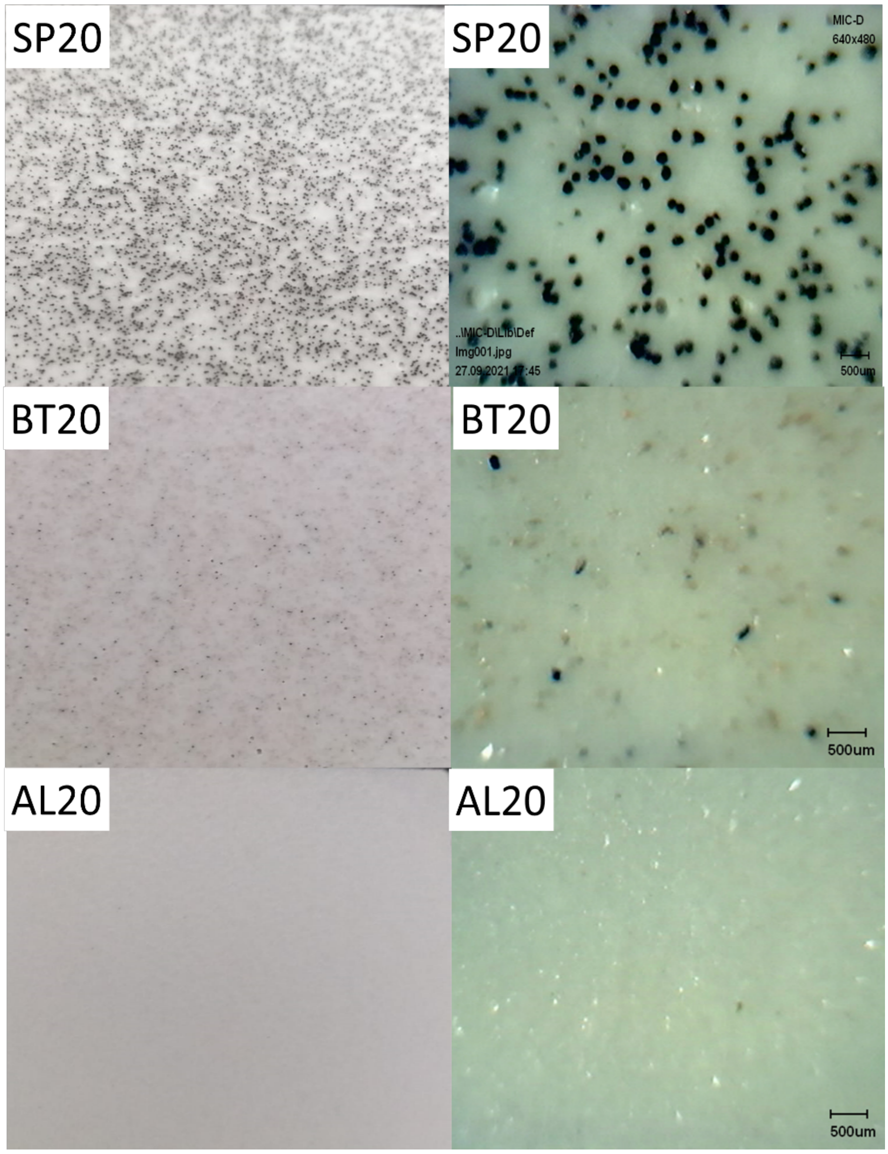

Figure 4. *Surfaces produced with 80% STD and 20% of the granular test materials. Top view of the covered area (left) and in detail (right).*

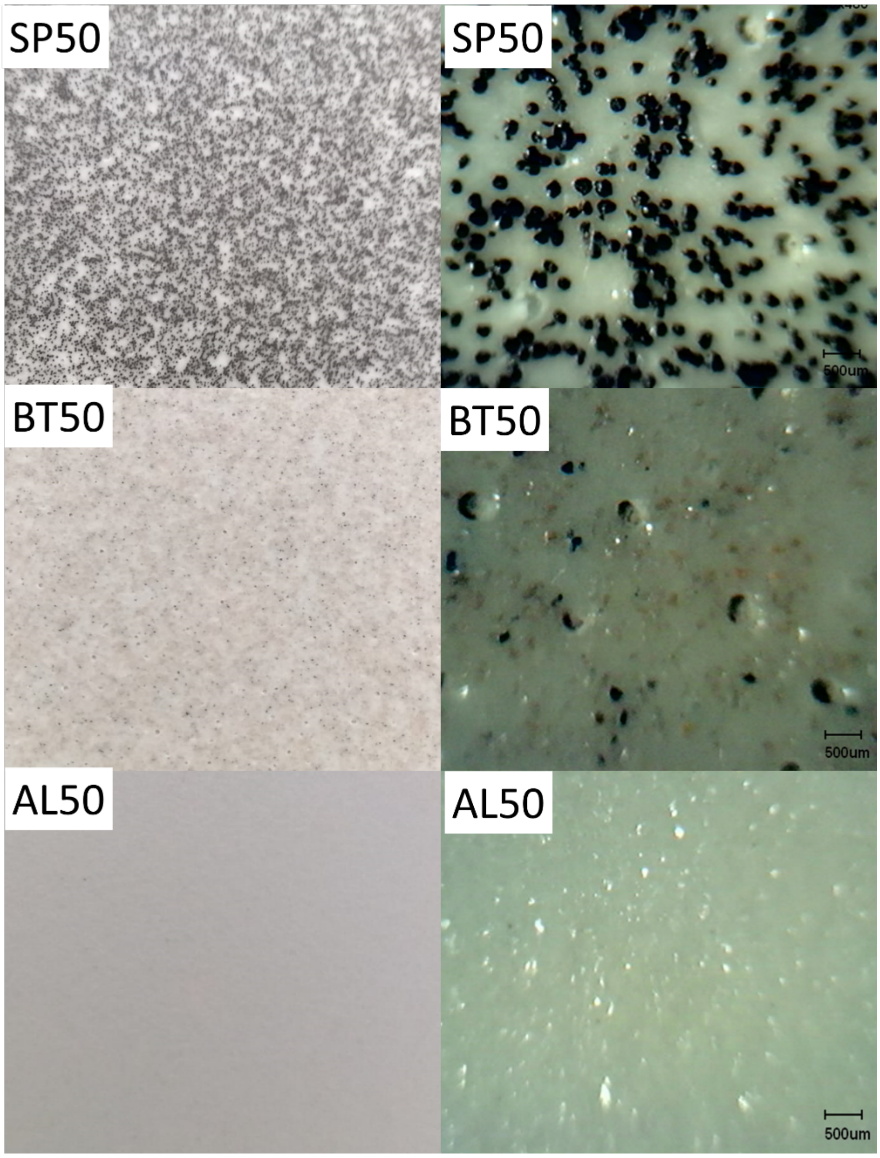

Figure 5. *Surfaces produced with 50% STD and 50% of the granular test materials. Top view of the covered area (left) and in detail (right).*

Figures 6 and 7 show the graphs of the mass loss tests as a function of abrasion time. All surfaces exhibit progressive mass losses as a function of the length of abrasive wear time in the apparatus used to carry out the mechanical degradation tests.

The pieces on which the STD grit formula was applied are seen to exhibit the most mass loss in relation to abrasion time, as verified by the angle coefficients of the resulting curves. The pieces with applications of the test formulations of granular materials were also seen to perform in a very similar manner, with mass loss after 35 minutes in the applications containing 50% test granular materials (Figure 7) being a little lower than the applications containing 20% (Figure 6).

The lower mass loss on surfaces containing abrasive particles relates directly to the higher modulus of elasticity of the grains included in the mixtures with the grits. Corundum has a modulus of elasticity of around 380 GPa, whereas glazes usually have a modulus of elasticity of between 50 and 90 GPa.

Although the modulus of elasticity of mullite (approximately 135 GPa) is closer to the modulus of elasticity of the glazes, and that phase is found in the composition with SP grains, the fact that corundum is the predominant crystalline phase in all the abrasives accounts for the much better mechanical performance of all test compositions compared to the STD composition. Naturally, the resulting mass loss from abrasive wear is less extensive in compositions that use high concentrations of abrasive grains mixed with milled frits (grits). However, these grains act as buffers that prevent the vitreous materials found in those buffers from wearing, so that even when they comprise a mere 20% of the applied compositions, these abrasive grains lead to significant increases in resistance to surface abrasion in the end products.

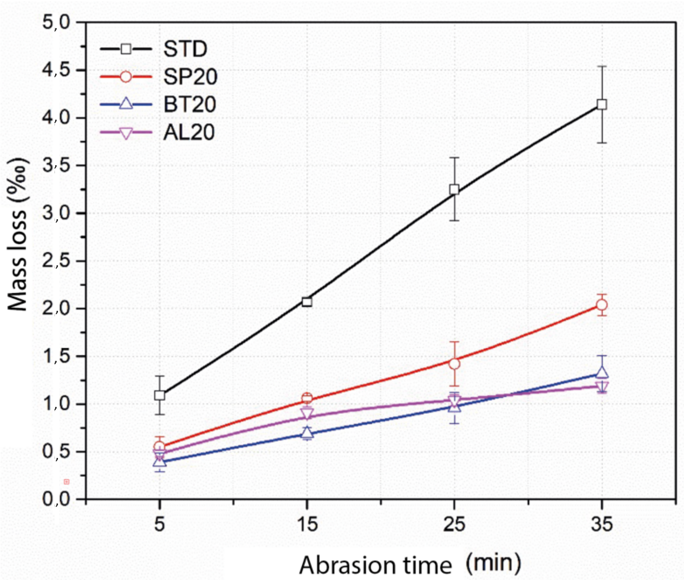

Figure 6. *Assessment of wear by mass loss of the product with STD grits and the tiles with 20% of test granular materials*

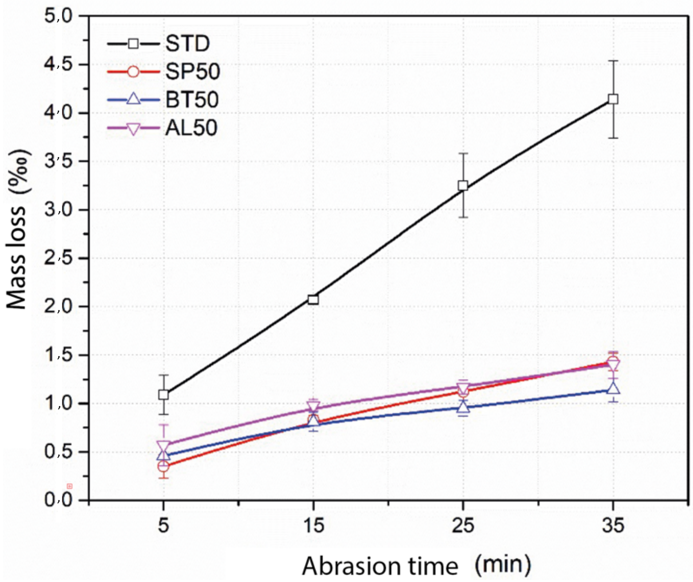

Figure 7. *Assessment of wear by mass loss of the product with STD grits and the tiles with 50% of test granular materials*

Tables IV and V show how pieces are classified in terms of chemical and stain resistance, respectively.

Reagents	SP50	SP20	BT50	BT20	AL50	AL20	STD
NH_4Cl	Class A	Class A	Class A	Class A	Class A	Class A	Class A
NaClO	Class A	Class A	Class A	Class A	Class A	Class A	Class A
Citric acid	Class A	Class A	Class A	Class A	Class A	Class A	Class A
KOH	Class A	Class A	Class A	Class A	Class A	Class A	Class A
HCl	Class A	Class A	Class A	Class A	Class A	Class A	Class A

Table IV: *Classification results of the products in regard to chemical resistance*

Reagents	SP50	SP20	BT50	BT20	AL50	AL20	STD
Oil	Class 5	Class 5	Class 5	Class 5	Class 5	Class 5	Class 5
Iodine	Class 5	Class 5	Class 5	Class 5	Class 5	Class 5	Class 5
Cr_2or_3	Class 5	Class 5	Class 5	Class 5	Class 5	Class 5	Class 5

Table V: *Classification results of the products in regard to stain resistance*

The results of the chemical attacks and staining show that the surfaces of the tiles with applications of grits and abrasive grains perform very satisfactorily, with maximum classification according to the dictates of ISO 10545, Parts 13 and 14. These results are thanks to the abrasive grains used having high chemical inertia and being well fixed to the surface of the glazes where they are applied. Therefore, surface porosity does not increase and the chemical resistance of the glaze and frit used as a grit is not altered by the presence of the abrasive grains.

Table VI shows the results of the pendulum test.

Parameter	SP50	SP20	BT50	BT20	AL50	AL20	STD
Result (PTV)	80	61	62	56	80	69	47
Class	Q5	Q5	Q5	Q5	Q5	Q5	Q4

Table VI: *Numerical results and classification from pendulum testing*

According to the results of this test, all the mixtures developed with abrasive grains may be deemed to display at least 19% higher slip resistance compared to the STD sample, as seen in the tile with the lowest friction index, while this may reach 70%.

The increase in anti-slip properties on surfaces with abrasive grains is thanks to higher surface roughness and, in particular, to the greater amplitude of peaks in the roughness profile. Abrasive grains, given their thermal inertia, do not exhibit softening and stretching phenomena at high temperatures, as is the case with frit particles. Therefore, the surfaces that contain the various abrasive grains tested are more slip resistant than the STD surface.

4. CONCLUSIONS

From the results obtained, the three abrasive grains (SP, BT and AL) incorporated in the commercial grits applied to the surfaces of the porcelain stoneware ceramic tiles have a better technical performance than the commercial grits used for the same purpose.

In regard to slip resistance, it was noted that the higher the proportion of abrasive grains, the greater the slip resistance, and regardless of that proportion, all PTV values were higher than in the reference (STD) sample. Within the abrasive grains, the SP and AL products produce the best results.

The newly developed mixes also performed better in the test to evaluate wear as a result of mass loss. The intention of this test was to simulate product durability: the greater the wear undergone due to pedestrian traffic, the greater the mass loss. In this regard, abrasive grains with a content rich in corundum lose much less mass compared to the reference product (STD) under the same mechanical degradation conditions. These results are thanks to the high elastic modulus of the abrasive grains used in this study.

Among the various abrasive grains tested, performance in terms of durability was very similar in all of them, even though grains with different morphologies and chemical compositions were tested. As the main crystalline phase in all grains is corundum, performances by mixtures containing those grains was always better than with the commercial grits.

In light of the results of the stain and chemical resistance tests, it may be said that the tested samples can potentially be applied in porcelain stoneware tiles to combine high slip resistance, cleanability, and greater durability.

Among the products tested, the AL product, being white in colour, should be more easily applicable for commercial uses as a function of colour, although the other test materials can also be used in product designs that seek darker colours.

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