ANTI-SLIP CERAMIC TILES OBTAINED BY INKJET PRINTING. THE PROBLEM OF CHEMICAL RESISTANCE

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RESUMEN

Non-rough anti-slip ceramic tiles were obtained by incorporating nanostructures and nano-materials on the tile surface, arrayed with a geometry resembling that observed on certain animal surfaces in nature, which exhibit hierarchised orderings. The nanostructures were incorporated in the pre-firing stage, using specially designed glazes that developed these structures during firing. The deposition methods used were rotogravure roller and inkjet application.

Ceramic suspensions were formulated with the characteristics required for application by the respective deposition method. These suspensions had a balanced chemical composition that provided the tiles on which they were applied with a non-slip capacity that had maximum chemical resistance.

The technical and aesthetic properties of the resulting ceramic tiles were appropriate for intended tile use. Slip resistance was evaluated by the pendulum test (UNE ENV 12633:2003) and the ramp test (DIN 51130), and chemical resistance was determined according to standard UNE EN ISO 10545-13, values being obtained of USRV>45 (Class 3) and GHA, respectively. The tiles obtained displayed no impairment of stain or wear resistance or of aesthetic characteristics, such as colour and gloss

1. INTRODUCTION

One of the technical characteristics that ceramic floor tiles must have is slip resistance, particularly in tiles intended for floors with heavy pedestrian traffic[1,2,3]. Conventional anti-slip treatments consist of increasing tile surface roughness by incorporating particles of components of high hardness, such as quartz or alumina, embedded in a bonding glassy matrix. Other treatments that also provide anti-slip characteristics chemically etch the surface or perform micro-perforations in the tile surface.

Figure 1 shows the appearance of conventional anti-slip ceramic tiles, in which slip resistance has been obtained by applying glazes containing hard components with a particular geometry.

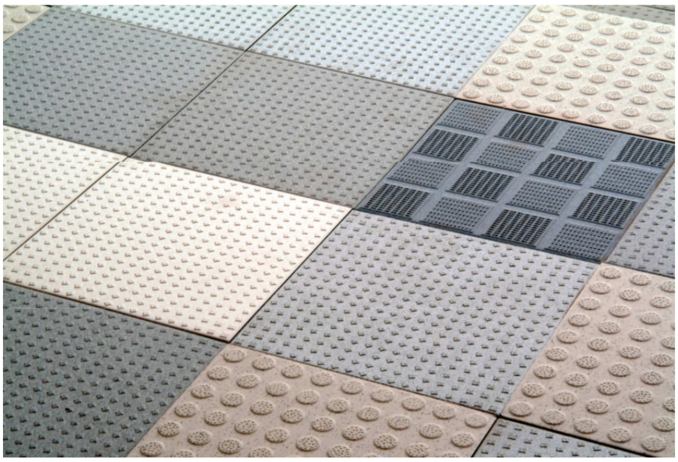

Figure 1. Industrially manufactured anti-slip tiles.

In general, the available methods for obtaining anti-slip ceramic tiles significantly alter tile surface appearance with regard both to aesthetic properties (change in texture, gloss loss, veiling of the decoration, etc.) and to technical properties (stainability, proneness of the treated surface to be attacked by chemical agents, etc.).

A great number of animals may be found in nature, such as certain insects, geckos[4] (popularly known in Spanish as salamanquesas) (Figure 2), and frogs[5] (Figure 3), which, in order to adhere to the surfaces on which they alight, have developed adhesive pads consisting of non-compact material in the form of foams or fibres that are spatially arrayed in a hierarchic ordering of thin walls or fibres whose dimensions decrease as they approach the outer surface.

This allows the animal to adhere to and detach itself from surfaces as it moves.

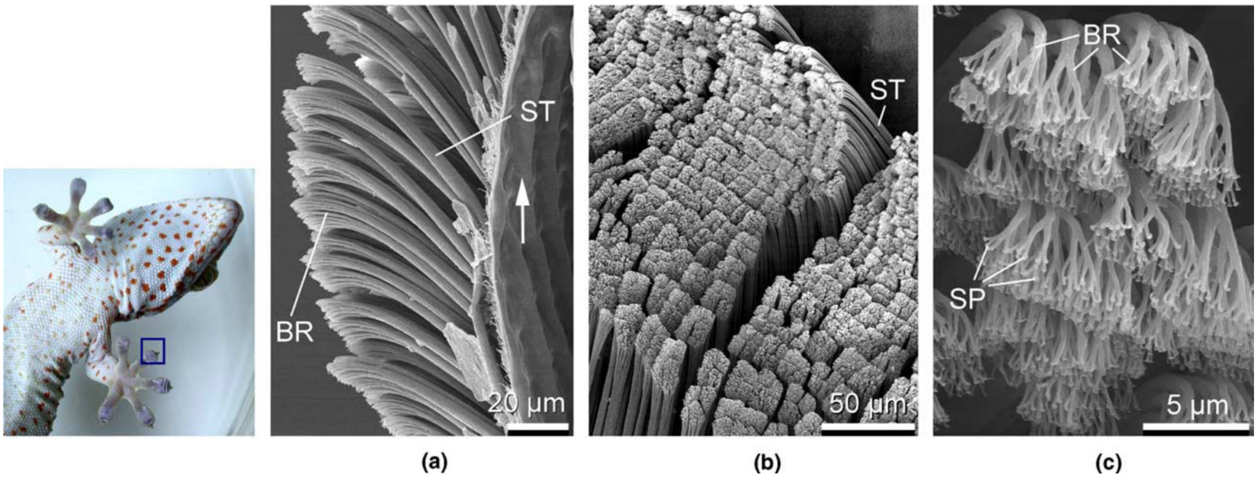

Figure 2. Views of the adhesive, hierarchised structures of gecko toe pads. a) and b) SEM of rows of the fibres at different magnifications. c) SEM of the smallest branches. A toe pad contains hundreds of thousands of "mushrooms" (ST), and one "mushroom" contains hundreds of "spatulas" (SP), which branch out very thinly at the end (BR).

The adhesive toe pads of a tree frog have a hexagonal design with 10 μm microstructures separated by 1 μm channels, subdivided into nanopillar orderings of 300–400 nm in diameter (see Figure 3). This structure allows the animal to drain away the fluids of the contact surface as it moves and to restore strong, dry contact on wet surfaces.

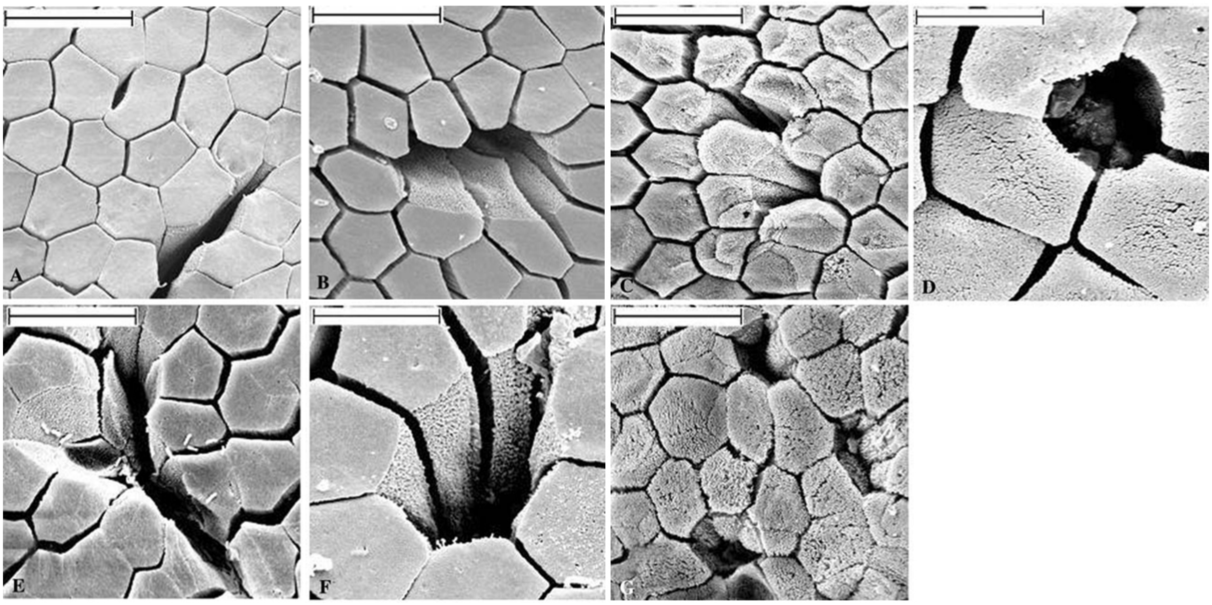

Figure 3. Typical structures of the adhesive pads of different types of frogs. A), B), C), and G), 25 μm rod. D) and F) 12,5 μm rod.

Studies of these adhesive mechanisms in nature[6] have enabled various research groups to develop artificial structures and small prototypes that imitate these structures [7],[8] (see Figure 4).

It is precisely these types of artificial structures that have been designed and applied on ceramic tiles to obtain anti-slip properties.

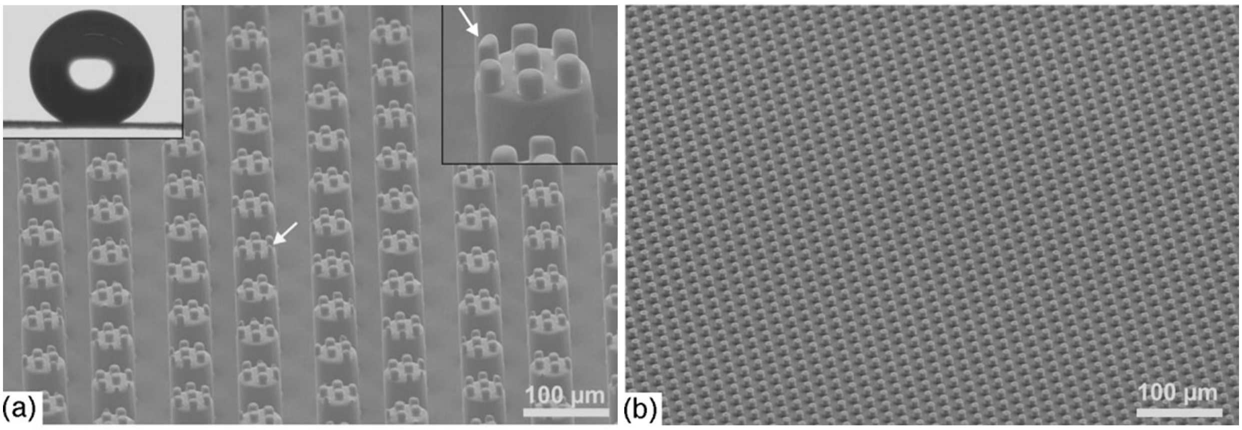

Figure 4. SEM images of PDMS pillars made according to different spatial geometries. a) Hierarchical array, b) Regular array of fine pillars.

A literature survey was performed in the present study on the preparation of anti-slip surfaces. The most common approach was found to involve a surface application, in the pre-firing stages, of inorganic materials that are widely used in the ceramic process[9],[10],[11] (aluminas, frits in the form of grits that devitrify components with high hardness, etc.), which generate a lumpy, slip-resistant surface with high hardness. Descriptions were also found of the creation of surface micro-relief by chemical etching, laser, or abrasive particles, as well as by the application of anti-slip particles in post-firing stages using a polymer binder. In these cases, the applied particle size was larger than 200 µm. In other works, patents were found that used different colloidal alumina and aluminium hydroxide suspensions[12].

In this study, various ceramic raw materials with very small particle sizes (between 15 and 0.5 µm) were used from which anti-slip inks with appropriate characteristics for use by rotogravure and inkjet printing were developed. The compatibility of the anti-slip inks with the different substrates on which they were applied, as well as the chemical resistance and anti-slip capacity of the resulting tiles, was studied.

2. EXPERIMENTAL

A series of ceramic raw materials were selected to prepare anti-slip inks for rotogravure and inkjet application (see Table 1).

The inks for rotogravure application were obtained from glaze compositions M-1 and M-2, which were wet milled and spray dried. The resulting powders were mixed with an appropriate screen printing vehicle to keep the suspensions stable and ensure that they had the required properties for the application technique.

Reference	Description	d90 (µm)	d50 (µm)	d10 (µm)
SL-1	Aluminosilicate type 1	43		
SL-2	Aluminosilicate type 2	14		
AL-1	Alumina type 1	2.2		
AL-2	Alumina type 2	0.59	0.23	0.09
Q-1	Quartz type 1	10	3	
M-1	Glaze with 40% SL-1 + 60% flux	22.3	8.1	2.2
M-2	Glaze with 60% SL-1 + 40% flux	21.6	7.9	2.2

Table 1. Materials selected for the preparation of the anti-slip inks.

The inks for inkjet application were prepared by dispersion of the solid materials in the selected organic medium that had been appropriately prepared with the necessary additives. A single-chamber bead mill with external recirculation was used. The mill consisted of a milling chamber into which the material to be ground (previously dispersed in the medium) and the milling balls (microbeads) were introduced, in addition to a rotor that provided the microbeads with a very high peripheral speed, producing progressive comminution by the effect of multiple impacts and shear actions on the material.

Two series of different anti-slip inks were prepared, which differed essentially in the nature of the inorganic components. In addition, different solids contents and different quantities of vehicles and additives were tested. The compositions of the inorganic part of the prepared inks are detailed in Tables 2 and 3. In the first series, the solids content of each ink is also indicated; in the second, this is not detailed because it remained constant at 40%.

Ink	Solids content (%)	Anti-slip material
TIAN-5	30	M-2
TIAN-6	30	SL-1
TIAN-7	30	AL-1
TIAN-8	30	AL-2
TIAN-17	40	85% SL-1; 15% Q-1
TIAN-20	40	SL-2
TIAN-22	40	75% SL-2; 20% Q-1
TIAN-24	40	75% AL-1; 20% Q-1

TTable 2. First series of anti-slip inks for inkjet application.

Anti-slip material	TIAN-40	TIAN-41	TIAN-42	TIAN-43	TIAN-44	TIAN-45	TIAN-46
AL-1	90	80	70	60	50	40	30
Q-1	10	20	30	40	50	60	70

Table 3. Second series of anti-slip inks for inkjet application.

The anti-slip inks obtained were characterised using the standard characterisation protocol established for each type of ink in which, for each ink, the following properties were determined: viscosity, surface tension, particle size, and stability with regard to sedimentation. When these properties were appropriate for the required deposition system, the inks were applied on porcelain tiles.

The tiles were prepared with ENDEKA base glazes (referenced B-1 and B-2), on which the anti-slip material was applied by the following techniques: rotogravure; spraying, simulating inkjet printing (spraying of the ink on the unfired glaze at a grammage of 14 g/m^2); and inkjet printing (directly via a laboratory printhead).

In the case of the tiles obtained by rotogravure application of the anti-slip material, a model with a geometric design was used that maintained certain proportions between the peaks and the valleys, as had been ascertained in the literature survey on the bio-inspired surfaces.

All the tiles obtained were fired at the KEROS facilities and subsequently characterised. The following tests were conducted: slip resistance by the pendulum method; slip resistance by the ramp method according to DIN 51130 (only in certain cases); chemical resistance according to the method described in clause 8 of standard UNE EN ISO 10545-13: 1998 "Ceramic tiles – Part 13: Determination of chemical resistance"; and stain retention and cleanability according to an own method that is more restrictive than the standard stain test.

A number of the tiles that exhibited chemical attack were studied from a microstructural viewpoint. This was done by cutting test pieces from tile areas that that had not been subjected to attack, as well as from tile areas that had been subjected to attack by 18% HCl (v/v). These test pieces were observed, photographed, and analysed with the backscattered electron signal of a scanning electron microscope, FEI Quanta 200 FEG-ESEM. The backscattered electron signal provides information on the topography and composition. The higher the average atomic number of the sample, the more intense is the signal, so that the lightest-coloured areas contain the heaviest elements (compositional contrast).

3. RESULTS OBTAINED

3.1. ROTOGRAVURE APPLICATION OF ANTI-SLIP MATERIAL

The tiles obtained with the glazes applied by rotogravure and fired according to the porcelain tile firing cycle, as well as the results of their characterisation, are detailed in Tables 4 and 5.

Tiles obtained			Slip resistance		Chemical resistance		
Reference	Base glaze	MP ink	USRV	Ramp	Reagent	Result	Classification
1P	B-1	M-1	65	R12	Hydrochloric acid 18% (v/v)	Definite change in appearance	GHB(V)
2P	B-1	M-2	71		Hydrochloric acid 18% (v/v)	Definite change in appearance	GHB(V)
3P	B-2	M-1	63		Hydrochloric acid 18% (v/v)	No visible effect	GLA*(V)
4P	B-2	M-2	70		Hydrochloric acid 18% (v/v)	No visible effect	GLA*(V)

Table 4. Porcelain tiles obtained and results of the slip resistance test according to the pendulum method (UNE-ENV 12633) and the ramp method (DIN 51130), and of the chemical resistance test according to standard UNE EN ISO 10545-13.

*Note: The test pieces displayed a slight change of colour. This is not deemed chemical attack according to standard UNE-EN ISO 10545-13

(V) Visual classification

Reference	ΔE			
	Retention	Cleaning 1	Cleaning 2	Cleaning 3
1P	3.8	0.9	0.8	0.7
2P	14.9	11.5	9.4	9.4
3P	9.6	6.6	5.4	5.3
4P	19.3	12.5	11.8	11.7

Table 5. Results of the stain retention and cleanability test of the tiles obtained.

Table 4 shows that using the same base glaze, with the ink prepared with raw material M-2 (which contained a greater quantity of anti-slip particles), a greater slip resistance was obtained by the pendulum method and a consequently greater anti-slip character.

The chemical resistance of the tiles obtained was better for the tiles with base glaze B-2, probably because of the nature of this type of glaze, which was formulated with a greater quantity of glassy materials and a smaller quantity of crystalline materials. No significant differences were observed with regard to the formulation of the anti-slip material.

However, it may be observed in Table 5 that tiles 2P and 4P, formulated with material M-2, exhibited greater stain retention and lower cleanability probably because this formulation contained a greater quantity of anti-slip particles.

3.2. TOPOGRAPHIC CHARACTERISATION DATA OF THE CHEMICALLY ATTACKED TILES

Micrographs of test pieces of the tiles prepared with the same base glazes (B-1 and B-2) and the same anti-slip material, from an original unattacked region as well as from an attacked region, are shown in Figure 5.

The glaze of the test piece prepared with base glaze B-2 was made up of abundant glassy phase that contained quartz, pigment, and zircon particles, in addition to some barium aluminosilicate crystals. Base glaze B-1 contained a very high quantity of devitrified barium aluminosilicate crystals and no quartz particles. In addition, in both test pieces there were particles of SL-1 from the anti-slip ink.

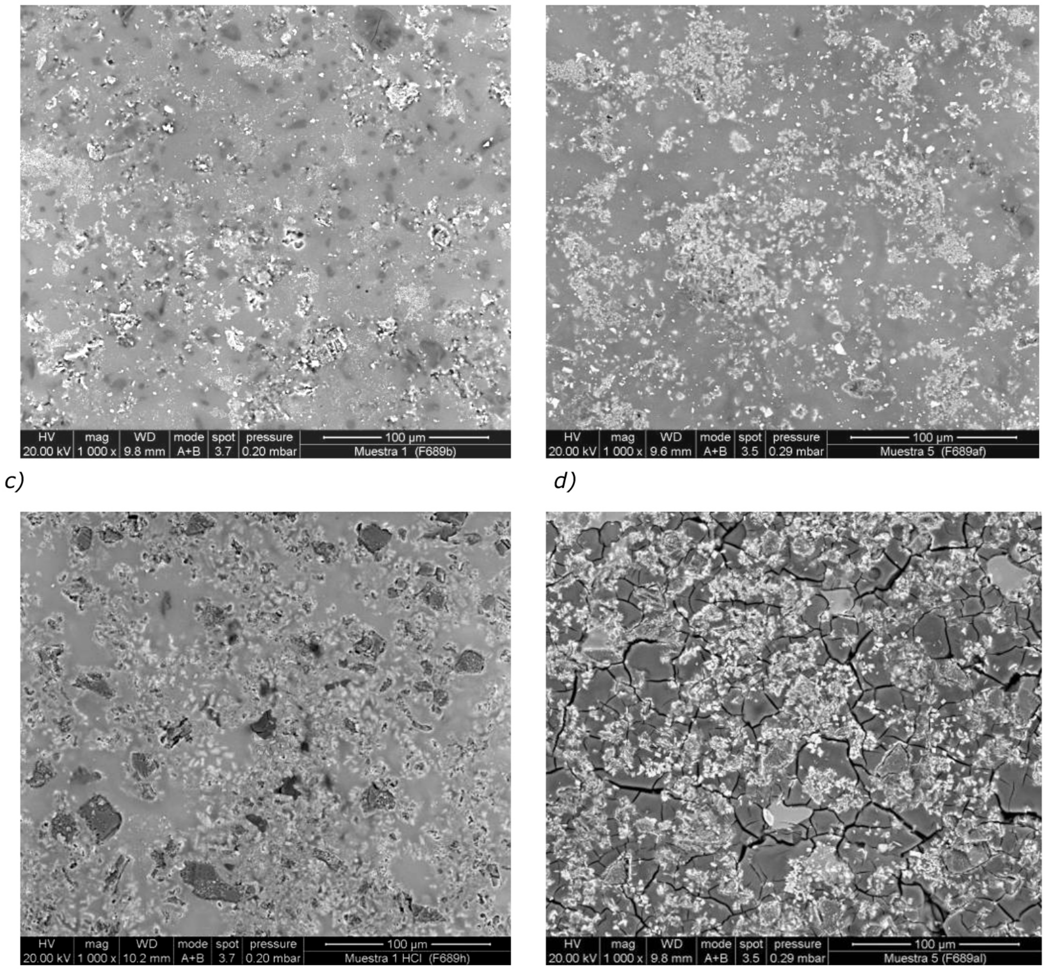

Figure 5. Micrographs of the test pieces prepared with different base glazes, same design and same anti-slip application content, in analogous regions. a) Original B-2 base; b) Original B-1 base; c) B-2 base attacked with HCl (18%); d) B-1 base attacked with HCl (18%).

The acid attack took place, in both cases, on the glassy matrix that surrounded crystals of the barium aluminosilicate type, the glassy matrix appearing darkened. When the attack was severe (as in the sample with base B-1), regions were observed in which the alkaline and alkaline-earth ions had been extracted, leaving a silica residue on which crystals were left that had initially been immersed in the glass. In areas with fewer devitrified crystals, the glassy phase did not appear to have suffered attack. However, the glass located next to these crystals had been attacked, probably because of the local enrichment in alkalis owing to Si-Al-Ba phase crystallisation.

In general, the attack on base glaze B-1 was much more severe than that on B-2, which contained quartz as raw material. The partial dissolution of quartz in firing probably generated a silica-rich melt that, after cooling, gave rise to a more siliceous glassy matrix, which was consequently less prone to attack by acids.

The interaction during firing between the different components that are applied to decorate ceramic tiles (base glaze, screen prints, etc.) gives rise to fired glaze coatings with a very heterogeneous microstructure. Consequently, the chemical attack that they undergo is not uniform either, which can lead to selective corrosion of the glazed surface[13]. However, knowing the attack mechanism could enable certain constituents to be introduced into the final applied composition (in this case, in the inks) to increase the chemical resistance of the surface, an approach carried out in phases that were conducted after the present work.

3.3. ANTI-SLIP MATERIALS DEVELOPED FOR INKJET APPLICATION

The characterisation data of the porcelain tiles obtained after the application of the first series of anti-slip inks prepared with different materials on base glaze B-1 are shown in Table 6.

Ink	Application	USRV	Chemical resistance (18% HCl (v/v))
TIAN-5	Spraying	63	GHB
TIAN-6	Spraying	65	GHB
TIAN-7	Spraying	69	GHB
TIAN-8	Spraying	74	GHB
TIAN-17	Inkjet printing	53	GHB
TIAN-20	Inkjet printing	50	GHB
TIAN-22	Inkjet printing	43	GHA
TIAN-24	Inkjet printing	63	GHB

Table 6. First series of tiles obtained with anti-slip materials for inkjet application, and tile slip resistance and chemical resistance data.

The table shows that all tiles obtained displayed very good slip resistance, though the tiles on which the anti-slip material had been sprayed exhibited higher slip resistance. However, in the case of chemical resistance, only ink TIAN-22 obtained the GHA rating.

Indeed, on closely studying ink TIAN-22 formulated with SL-2 and Q, it was concluded that the presence of quartz must be responsible for the significant improvement in chemical resistance, as had also been verified in section 3.2, though slip resistance worsened.

The chemical resistance and slip resistance data of the tiles prepared with the second series of anti-slip inks, applied on the same B-1 glaze base, are detailed in Table 7.

Property	TIAN-40	TIAN-41	TIAN-42	TIAN-43	TIAN-44	TIAN-45	TIAN-46
Chemical resistance (18% HCl (v/v))	GHB (V)	GHB (V)	GHB (V)	GHA* (V)	GHA* (V)	GHA	GHA
Slip resistance (USRV)	---	---	---	71	60	49	---

Table 7. Second series of anti-slip inks.

* Note: The test pieces displayed a slight change of colour. This is not deemed chemical attack according to standard UNE-EN ISO 10545-13

(V) Visual classification

It was verified that, as the ink quartz content increased, ceramic tile chemical resistance improved and slip resistance worsened.

A compositional equilibrium that provided good slip resistance and chemical resistance was obtained with composition TIAN-43, which appeared appropriate for this base and could be extendable to other bases of the same nature.

However, it was also verified that, with other types of bases with a greater glassy phase content, which were unaffected by the action of hydrochloric acid, inks could be used with 100% of the anti-slip components of the AL-1 or AL-2 type, without the presence of Q-1 in their composition.

4. CONCLUSIONS

The following conclusions were drawn from the project conducted:

- A new family of anti-slip products has been developed for use with rotogravure, which give rise to a pleasant texture and are applied on different bases, in addition to providing appropriate transparency and chemical resistance.

- A series of products for obtaining anti-slip tiles by inkjet printing have similarly been developed. These consist of a family of bases and two anti-slip inks. Depending on the degree of slip resistance and chemical resistance required, it is recommended that either one combination or other of the materials should be used.

- Anti-slip tiles can be obtained by applying the products that provide this property by a thin film application technology: rotogravure or inkjet printing. It is thus not necessary for the anti-slip product to cover the entire tile. The appropriate use of design helps obtain anti-slip tiles.

- New anti-slip materials are already available for thin film application on ceramic tiles by rotogravure and inkjet techniques, which exhibit enhanced aesthetic properties compared with those obtained with traditional approaches (in regard to transparency, smoothness to the touch, roughness, etc.), without impairing the required technical properties, and which are appropriate for intended tile use:

    - Slip resistance, evaluated by means of the pendulum test (UNE ENV 12633:2003).

    - Stain resistance, evaluated according to UNE-EN ISO 10545-14, and chemical resistance, according to UNE-EN ISO 10545-13.

- New graphic designs have been developed, applying geometric concepts from the literature on natural elements that exhibit high dry and wet adhesive strength (bio-inspired).

7. ACKNOWLEDGEMENTS

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