A NOVEL SUSTAINABLE MATERIAL FOR DECORATIVE AND TECHNICAL SURFACE EFFECTS FOR TILES

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1. ABSTRACT

This paper reports synthesis and application of silicate-based high surface area amorphous material on wall and floor tile surfaces. The material is very effective for obtaining various novel surface effects which include a smooth super matt effect, granilla-like effect, anti-slip effect etc. by simple airless spraying of its aqueous suspensions. Similar effects can also be obtained by digital application of its inks and the obtainment of these effects by digital application is also a novelty. The material is synthesised at very low temperatures compared to frits that are used to get the granilla effect and no organic medium is needed during its application unlike frit suspensions. With these features, the synthesised material presents energy and environmentally efficient solutions for various surface decorative and technical effects in ceramic tile production.

2. INTRODUCTION

Materials that give decorative effects and technical characteristics to tile surfaces are continuously being investigated [1]. A wide variety of materials for the decorative and technical effects are present in the tile industry, including crushed and sized frits (granillas) as well as anti-slip materials. For a granilla effect, generally specific frit compositions have to be produced for different surface appearances such as matt, satin, glossy or the so-called sugar effect on wall and floor tiles. Production of the crushed frits involves melting of a particular composition at high temperatures (usually >1500 °C), solidification, crushing and sizing. All these steps are rather energy intensive processes causing substantial CO_2 emissions [2], which presents challenges for the European Green Deal Act [3]. Furthermore, wet application of the crushed frits usually necessitates the use of high-viscosity organic mediums in order to reduce settling in a suspension and these organic mediums are released into the environment from the furnaces during firing, which places an additional burden on the environment.

One of the technical characteristics of tile surfaces is their anti-slip property. Accidents due to slipping in residential and commercial buildings are placing a major burden on economies due to loss of labour and health cost [4]. Therefore, there is an increasing awareness regarding surfaces with non-slip properties in the construction industry. Ceramic tile companies produce anti-slip tiles by making surfaces rough to reduce possible slipping. This is achieved by adding either hard particles, such as corundum, or crushed frit particles to glazes or applying them directly over the glaze surface to provide required roughness. However, the main problem with these methods is that the induced surface roughness makes the tile unpleasant to look and touch as well as being unpreferable design-wise. In addition, there is a health hazard due to rough surfaces causing knee, elbow injuries etc. when there are slip-falls. Another approach is to chemically treat the surfaces by hydrofluoric acid to dissolve the amorphous phase and create a topography [5]. This method is quite successful but the use of hydrofluoric acid makes the process rather dangerous. Therefore, developing materials that could provide smooth anti-slip surfaces without impairing a tile's aesthetic appearance is of interest [6].

In this study, application possibilities of a synthesized novel effect material based on silicates to achieve various decorative and technical effects on tile surfaces will be addressed. The decorative effects include an effect similar to the crushed frit effect (so-called granilla effect) and extremely smooth, non-reflective super matt effect, while the technical effect includes a very smooth anti-slip surface effect. While the granilla-like effect could be a sustainable alternative to crushed frits, the smooth anti-slip and/or non-reflective surface effects may provide further design possibilities, as well as widespread use of anti-slip surfaces in both indoor and outdoor applications without impairing the aesthetic value of ceramic tiles.

3. EXPERIMENTAL

The experimental flow chart of the synthesis of the material for the different effects is shown in Figure 1. For proprietary and commercial reasons, detailed information about the processing conditions is not given. Nevertheless, the required reactants with their desired compositions are mixed in water and reacted in a sealed container at temperatures up to 150 °C. Compositions could easily be modified as required depending on softness/refractoriness of the final material and lie between 55-65% SiO_2, 17-35% Al_2O_3, 5-20% alkali/alkaline/zinc oxides and 1-5% B_2O_3. Mainly amorphous silicate-type reaction products were then dried and milled, either in water for airless spraying applications down to an average particle (agglomerate) size of 5 micron or in organic media for digital applications down to an average particle size of 0.3 micron at a concentration of 40 wt%. The aqueous suspensions were applied by airless spraying in an amount between 5-70 g solid/m^2 by diluting the aqueous suspension down to 5-30 wt% solid loading, depending on the desired surface effect. The aqueous suspension is also mixed with top glazes in order to see its effect on surface texture development. In this case, the solids concentration of the mixed glaze suspension was kept the same as the top glaze in application. For digital applications, two types of inks were prepared, namely anti-slip ink and effect ink. The anti-slip ink was applied up to 16 g ink/m^2 while the effect ink was applied between 15-60 g ink /m^2. Surface features after application of the synthesized material were examined by a stereo microscope or a scanning electron microscope.

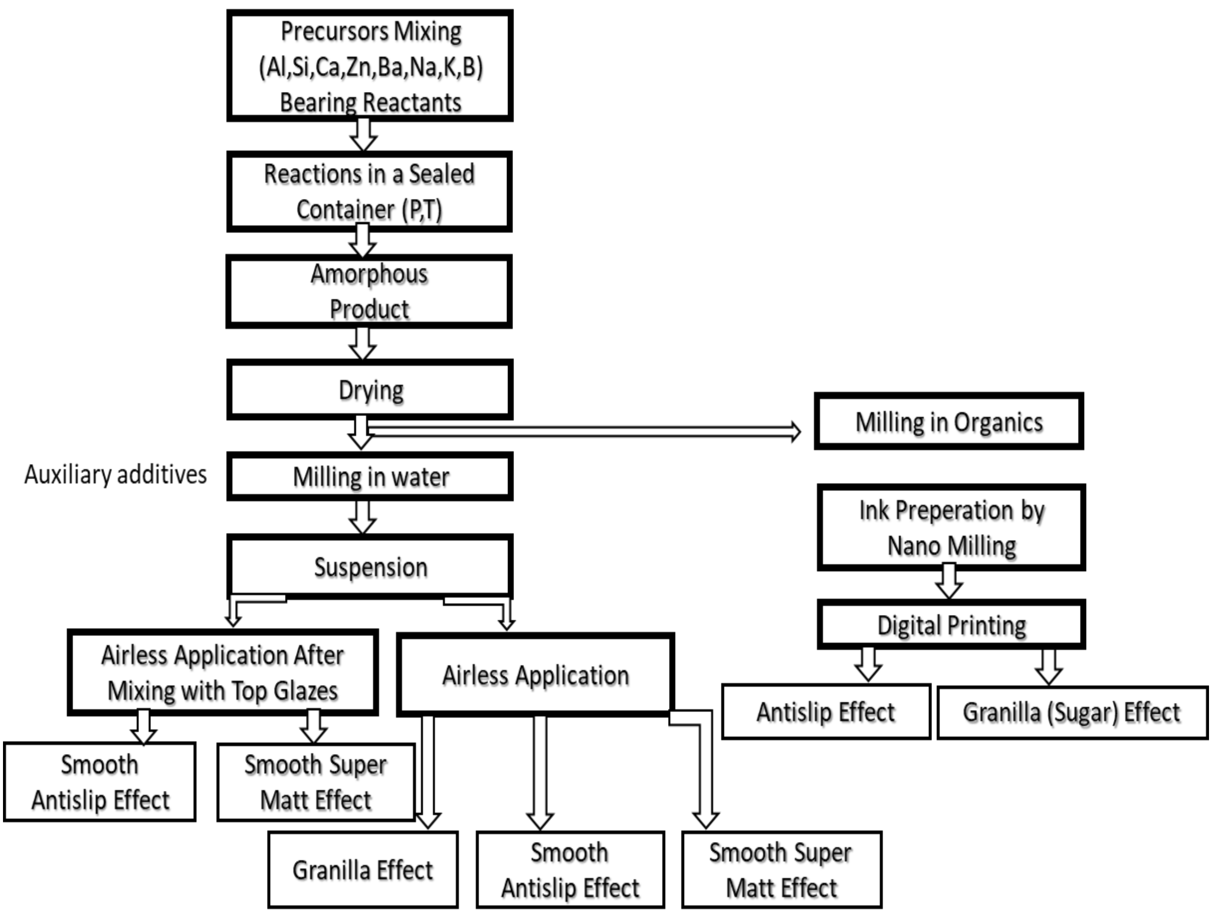

Figure 1. *Experimental flow chart*

4. RESULTS AND DISCUSSION

4.1 THE SYNTHESISED MATERIAL

Closed container synthesis of the material develops vapour pressure inside the container due to water evaporation which may help the dissolution and precipitation process. After synthesis, the material has an amorphous structure with rather fine precipitates having a specific surface area ranging from 15-30 m^2/g and shows a good densification behaviour after firing under industrial fast-firing conditions. The fired product can remain amorphous or be made crystalline as desired, depending on the composition.

4.2 GRANILLA-LIKE EFFECT

When the aqueous suspension with 5-micron-sized particles was applied as a top glaze in an amount between 40-70 g solid/m^2 solid by using 20-30 wt% solid loading by airless spraying, a very homogeneously distributed granilla-like effect is obtained as seen in a stereo microscope image in Fig. 2. The appearance of the granilla-like surface could be modified from very matt to shinier-looking by controlling the morphology of the grits simply by adding fluxing agents such as zinc oxide, boric acid etc. to the base composition. Fluxing agents cause spreading of the grits with flatter top, while more refractory compositions cause rounder grits which reduce the shininess by causing multiple reflections. The grits could also be colour-shaded by adding pigment particles to the suspension to enhance its decorative property. The size of these regions usually varies between 150-250 micron depending on the amount of material applied. The reason for the development of the granilla effect is the drying cracks that form as a result of excessive shrinkage due to the high surface area of the synthesized material.

Figure 2. *Stereo microscope image of granilla-like effect. The amount of applied material is 60 g solid/m^2.*

4.3 SMOOTH MATT EFFECT

If the amount of the aqueous suspension application as a top glaze is 10-20 g solid/m^2, rather fine and homogeneous grits with sizes of about 80-100 micron form over the glaze surface (Fig. 3). In this case, the suspension's solid content should be between 5-15% in order to be able deposit a large enough amount of solid material with good coverage by airless spraying. Comparison of Fig. 2 and 3 clearly shows that lowering the amount of the applied solid results in a much finer grit size without any visible granilla-like effect. Since these grits are difficult to feel physically by touching, particularly due to their amorphous nature, and reflect the light in all directions, they make the surface extremely matt with a very smooth touch. In fact, gloss values of 2.2 and 1.9 at 60° and 85° are achieved, respectively. In particular, a very low gloss value of 1.9 at 85°at high smoothness is interesting because such low gloss values are not easy to produce by current matt glazes without compromising smoothness and cleanability. This is because, mattness in current matt glazes is usually increased by adding corundum to crystalline glazes at the expense of losing smoothness.

Figure 3. *Stereo microscope image of a smooth matt surface showing very fine granular structure. Application amount is 15 g/m^2.*

The behaviour of the material is also interesting when mixed with common top glazes that are used to cover and protect the digital decoration. The top glazes are mostly matt glazes but they have the problem of undesirable glossy appearance at higher angles of incidence of light, which degrades the design quality and surface attractiveness of the tiles. Increase glossy appearance at high angles of incidence of light is probably due to the morphology of the surface crystals being parallel to the surface. In this case, they are less able to reflect the light to different directions. When the synthesized material is added to the top glaze, it does not tend to react with the glaze and forms a semi-circular topography at the tile surface. Fig. 4 shows stereo microscope pictures of a matt glaze surface and of a surface with the same glaze containing a 15% addition of the synthesized material.

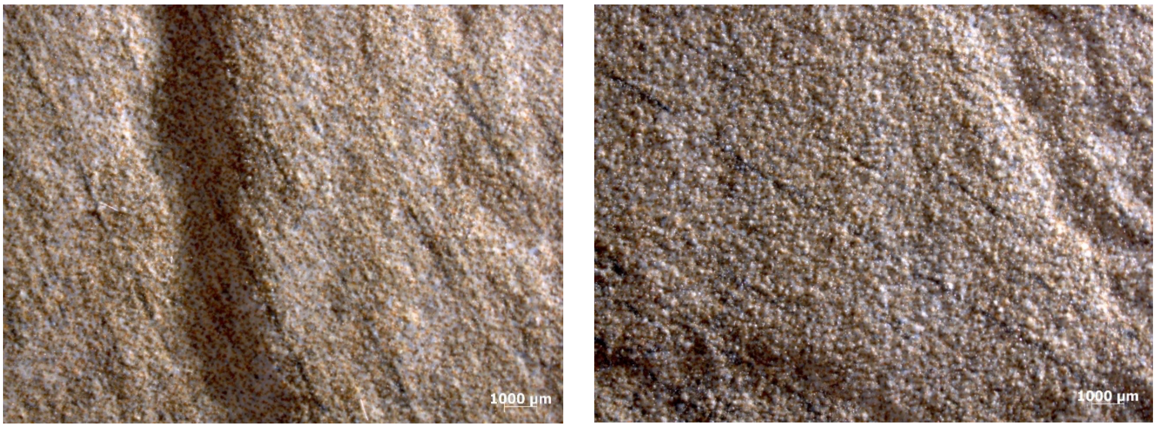

Figure 4. *Stereo microscope image of surfaces of (a) matt top glaze and (b) matt top glaze containing 15% of the synthesized material.*

The development of a fine topography is clearly visible when these two pictures are compared. It is the development of this topography that make the surface matter without inducing undesirable roughness, which is confirmed by measuring 85° gloss values, these being 8.5 for the matt glaze surface and 2.5 for the same glaze containing 15% of the synthesized material. The addition of the synthesized material not only reduces the gloss values of the surface but may also improve its anti-slip property depending on the amount of addition. In this particular example in Fig. 4, the slipping angle according to DIN 51130 was determined to increase from 10° to 19°with 15 wt.% addition of the synthesized material. These observations clearly show that the synthesized material could be used as a simple additive to improve the mattness, as well as the anti-slip behaviour of top glazes, depending on the amount added, without inducing roughness and losing their existing texture.

4.4 DIGITAL ANTI-SLIP/ANTI-GLOSS INKS

The firing behaviour of the synthesized material, forming a topographical surface as explained above, was also exploited to produce anti-slip ink for digital applications. In order to make the amorphous topographic regions with smooth surface seen in Fig. 2 resistant to slipping, some unreactive hard particles such as nano-size alumina or mullite were mixed with the synthesized material. The nanoparticles create fine-scale perturbations on the surfaces of the topographic regions making them non-slippery. It should be stressed that nano-size hard particles should not disturb the sinterability of the synthesized powder. Fig. 5a shows a scanning electron microscopy image of the fired tile surface containing digitally applied anti-slip ink. The nano-size hard particles creating the anti-slip effect can be seen embedded in the synthesized material. The effect of different amounts of anti-slip ink application on colour performance is compared in Fig 5b. It shows that the colour interactions, although they depend on underlaying glaze hardness and composition, are not significant. The anti-slip values of the tile surface containing 16 g/m^2 digital ink, seen in Fig. 5b, according to DIN 51097, DIN 51130 and BS7976, are given in Table 1 together with the R_a surface roughness value.

As seen in Table 1, excellent anti-slip values with very low surface roughness are achieved by the digital ink.

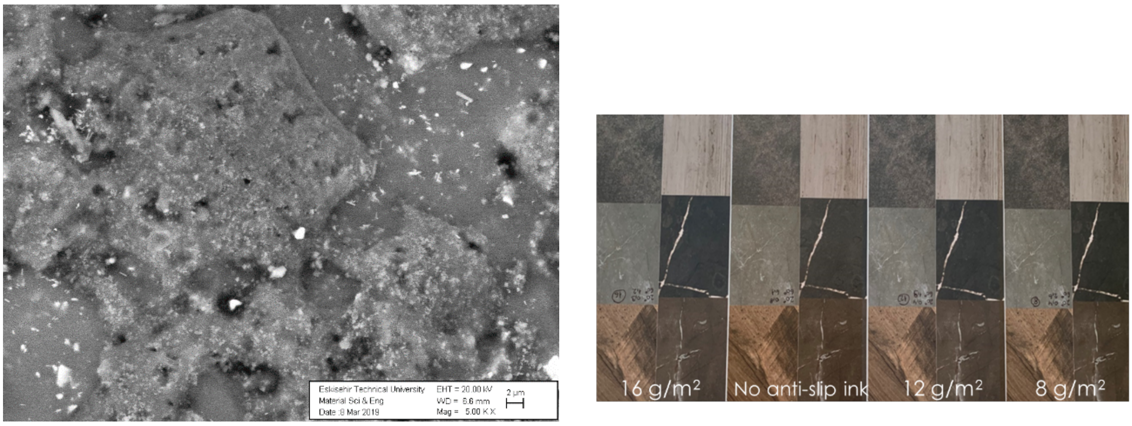

Figure 5. *(a) Scanning electron microscopy image of digital ink applied surface and (b) visual picture of surface of tiles with different amount of ink application together with the pristine surface.*

Application amount (g/m^2 ink)	DIN 51130 Ramp value	DIN 51097 Ramp value	Pendulum BS 7976-2:2002 (wet)	Surface roughness (Ra, micron)
16	R11 (22˚)	Class B (21˚)	55	4,3

Table 1. *Anti-slip values of a tile surface with 16 g/m^2 ink applied by different standards*

If the ink does not contain any hard particles and is deposited between 30-60 g/m^2, particularly on satin and matt surfaces, it also develops a topography during firing. Scanning electron microscopy image of such a topography is given in Fig. 6a together with visual photographs of the surfaces with an ink application (Fig. 6b&c). As seen in Fig. 6b&c, this type of topography provides the so-called sugar effect on tile surfaces. The sugar effect is normally achieved by crushed frit application using conventional techniques. Therefore, achievement of the sugar effect with some relief by digital application of an ink appears to facilitate processing as well providing new design possibilities.

Figure 6. *(a) Scanning electron microscopy, (b) and (c) visual photographs of wall tile surfaces with 60 g/m^2 digital ink application.*

5. CONCLUSIONS

A silicate-type amorphous material has been synthesised. When this material is applied over a glaze on wall and floor tile surfaces by airless spraying of its aqueous suspension, it creates semi-spherical topographic features. The size of the features range from about 80 micron to 250 micron, increasing with the applied amount of synthesised material. While the small-size features give very smooth and extremely matt surfaces, the larger sizes create a granular effect that resembles the application of crushed frits (granilla effect). Depending on the composition of the synthesized material, these surfaces could be made anti-slip. When the features contain added hard particles and/or are made more refractory by compositional adjustment during synthesis, they become resistant to slipping and provide an anti-slip surface effect. Similar surface features can also be obtained by applying the synthesized material in the form of digital inks.

6. REFERENCES

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