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

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1. ABSTRACT

This paper reports syhthesis and application of silicate based high surface area amorphous material on wall and floor tile surfaces. The material is very effective to get various novel surface effects which include smooth super matt effect, granilla-like effect, antislip 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 novelity. 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 respects, 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. 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 granilla effect, generally specific frit compositions have to be produced for different surface appearances such as matt, satin, glossy or so called sugar effect in 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, which presents challenges for European Green Deal Act. 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 to the environment from the furnaces during firing which gives additional burden to the environment.

One of the technical characteristics of tile surfaces is their antislip property. Accidents due to slipping in residential and commercial buildings are causing major burden to economies due to loss of labour and healt cost. Therefore, there is an increasing awareness about surfaces with non-slipping property in construction industry. Ceramic tile companies produce anti-slip tiles by making surfaces rough to reduce slipping tendency. This is achieved by adding either hard particles, such as corundum, or crushed frit particles into 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 designwise unpreferable. In addition, there is a health hazard due to rough surfaces causing knee, elbow injuries etc. when fallen. Therefore, developing materials that could provide smooth anti-slip surfaces without loosing tile's aestatic appearance is of interest.

In this study, application possibilities of a synthesized novel effect material based on silicates to get 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 the crushed frits, the smooth anti-slip and/or non-reflective surface effects may provide further design possibilities as well as a wide spread use of anti-slip surfaces both indoor and outdoor applications without comprimising from the aestatic value of ceramic tiles.

3. EXPERIMENTAL

Experimental flow chart of the synthesis of the effect material is shown in Figure 1. Required reactants with desired compositions are mixed 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 lies 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 solid 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 solid 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.

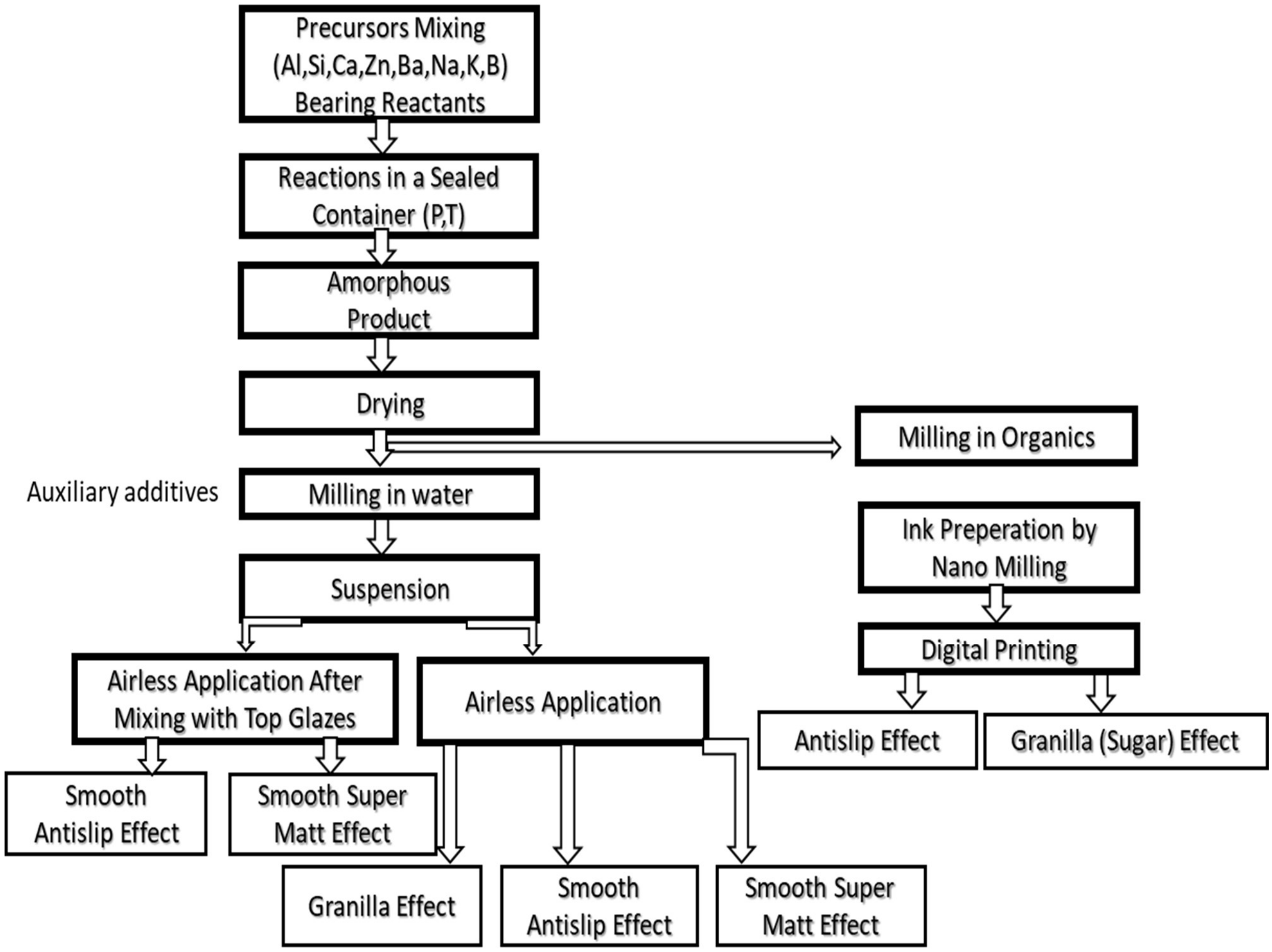

Figure 1 *Experimental flow chart*

4. RESULTS AND DISCUSSION

4.1 THE SYNTHESISED MATERIAL

The material after synthesis has amorphous structure 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 a 5 micron particles size 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 are obtained as seen in a stereo microscope image in Fig. 2, respectively. 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 into the suspension to enhance its decorative property. The size of these regions vary usually between 150-250 micron depending on the amount of material applied.

Figure 2 *Stereo microscope image of granilla-like effect. The amount of applied material is 60 g solid/m2.*

4.3 SMOOTH MATT EFFECT

If the amount of the application of the aqueous suspension as a top glaze is 10-20 g solid/m^2, a rather fine and homogeneous grits with sizes of about 80-100 micron are formed 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 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 solid applied results in 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. Particularly, 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.

Figure 3 *Stereo microscope image of a smooth matt surface showing very fine granular structure. Application amount is 15 g/m2.*

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. When the synthesized material is added into the top glaze, it does not tend to react with the glaze and form a 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 15% addition of the synthesized material.

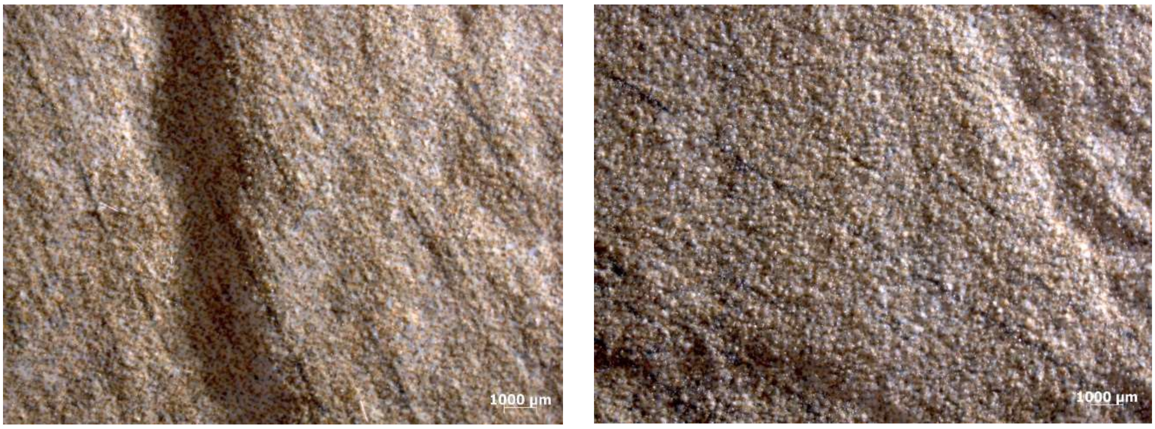

Figure 4 *Stereo microscope image of surfaces of (a) matt top glaze and (b) matt top glaze containing 15 % of the synthesized material.*

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, 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 also may improve its antislip property depending on the amount of addition. In this particular example in Fig. 4, 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 antislip behaviour of top glazes, depending on the amount of addition, without inducing roughness and loosing their existing texture.

4.4 DIGITAL ANTISLIP/ANTIGLOSS INKS

The firing behaviour of the synthesized material, forming a topographical surface as explained above, was also exploited to produce antislip 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 nano particles creates 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 sythesised powder. Fig. 5a shows a scanning electron microscopy image of the fired tile surface containing digitally applied antislip ink. The nano size hard particles that are creating antislip effect can be seen as embedded in the synthesized material. The effect of different amounts of antislip ink application on colour performance is compared in Fig 5b. It is seen that the colour interactions, although depends on underlaying glaze hardness, are not significant. The antislip 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 R_a surface roughness value. As seen in Table 1, excellent antislip values with very low surface roughness are achieved by the digital ink.

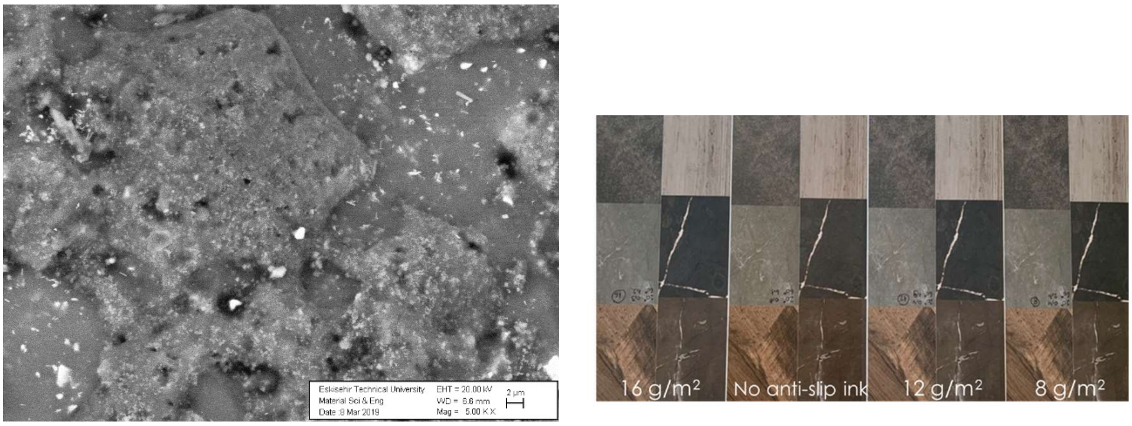

Figure 5 (a) *Scanning electron microscopy image of digital ink applied surface and (b) visual picture of surface of tiles with different amount of ink application together with pristine surface.*

Table 1. *Antislip values of a tile surface with 16 g/m² ink applied by different standards*

Application amount (g/m² 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

If the ink does not contain any hard particles and is deposited between 30-60 g/m², 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 ink applied surfaces (Fig. 6 b&c). As seen in Fig. 6 b&c, this type of topography gives so called sugar effect on tile surfaces. The sugar effect is normally achieved by crushed frit application. Therefore, achievement of the sugar effect with some relief by digital application of an ink appears to present process ease as well new design possibilities.

Figure 6 *(a) Scanning electron microscopy, (b) and (c) visual photographs of wall tile surfaces with 60 g/m2 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 amount of application of the 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). When the features contain added hard particles, they become resistant to slipping and give antis-slip surface effect. Similar surface features can also be obtained by applying the synthesised material in the form of digital inks.