GLOSSY COATINGS OBTAINED BY INKJET. INFLUENCE OF THE NATURE OF THE BASE GLAZE

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1. SUMMARY

In recent years, inkjet inks used in the ceramics industry have evolved considerably and have gone from being pigment inks, necessary for chromatic decoration of ceramic tiles, to effect inks used to modify mechanical, chemical or aesthetic surface properties. In these cases, the inks do not contain ceramic pigments, but are suspensions of other inorganic materials which, after firing, generate different effects: gloss, matte, reactive (chameleon), lustre, etc. Therefore, inkjet technology is used only as a means of deposition, and the greatest difficulty lies in selecting and optimising the composition and thickness of the different layers applied.

This paper examines the variation of gloss in the glossy coatings obtained after application of inkjet effect inks on unfired ceramic tiles glazed with different types of base glazes, followed by subsequent ceramic firing. On correlating this property with the microstructure of the resulting coatings, it was verified that this depended on the *effective thickness* of the coating. The resulting thickness was determined, in addition to the grammage applied, by the nature of the interface produced by the interaction between the deposited material and the base glaze components.

2. INTRODUCTION

Ceramic tile decoration by (inkjet) digital printing has considerably increased decoration possibilities since the so-called "effect inks" were developed, which include "gloss inks" that define glossy areas of the piece when applied on matte glazes¹.

Gloss inks need to be able to generate smooth glazes, in which incident light reflection is mostly specular, minimising diffuse reflection as much as possible. The most important factor affecting surface gloss is roughness, there being a direct relationship between gloss and surface roughness. In paints, inorganic fillers are used to modify surface roughness and to control gloss. These fillers lead to surface lumps that increase diffuse reflection and decrease gloss, which depends on the size, shape and concentration of the particles at the surface of the coating^{2,3}.

Other factors also influence the perception of gloss⁴: thus, when observing two objects with identical surface characteristics (the same amount of specular and diffuse reflection), the darker surface appears glossier. The contrast between specular and diffuse reflections of the surroundings of the surface under study also affects the perception of gloss. Hunter⁵ identified six types of gloss perception. These include what he called contrast gloss, which is due to the contrast between the specularly and diffusely reflected radiation fraction from the surface at issue and its surroundings.

This perception of gloss by the observer is what has been targeted in this study, using inkjet technology to apply ink that will provide a glossy finish, on surroundings with a significant percentage of diffuse reflection (matte glaze).

3. EXPERIMENTAL

The gloss of glazes resulting from inkjet application of different thicknesses of a gloss effect ink on five matte glazes of different compositions was studied: three for porcelain stoneware tiles (M1 to M3) and two for red-body tiles (M4 and M5).

In both cases the references assigned to the glazes were the matte base glaze followed by a dash and a sequentially higher number coinciding with the increased amount of applied ink. The correspondence between the references and the g/m^2 applied ink is detailed in Table 1 for base glaze M1. For the other base glazes, the correspondence is identical.

Table 1. Designation of the glazes obtained using M1 as a function of the base glaze and amount of applied ink.

reference	M1-0	M1-1	M1-2	M1-3	M1-4	M1-5	M1-6
Applied ink (g/m²)	0	13.3	26.6	39.9	53.2	66.5	79.8

Table 1. Designation of the glazes obtained using M1 as a function of the base glaze and amount of
applied ink.

These amounts of applied ink, taking into account a 50% solids content and a molten glass density of about 2.6 g/cm³, would correspond to a layer thickness of about 2.6 μ m per 13.3 g/m², so that when 79.8 g/m² ink was applied, a resulting layer about 16 μ m thick would be expected after firing.

The red-body and porcelain stoneware tiles were fired in industrial furnaces with the corresponding thermal cycle. Glaze gloss was measured with a Rhopoint NOVO-GLOSS glossmeter at an angle of 60°. Polished cross sections of the glazes were prepared, observed, photographed and analysed using the backscattered electron signal of a scanning electron microscope (SEM). The photographs were treated using MicroImage 4.0 image analysis software to determine the thickness of the interaction layer between the ink and the base glaze, which was calculated as an average of 10 measurements. An average value was determined from the cross-sectional area without crystalline phases in the vicinity of the glazed surface.

4. **RESULTS**

4.1. EVOLUTION OF GLAZE GLOSS WITH THE AMOUNT OF APPLIED INK

Figure 1 shows the evolution of the gloss of the pieces glazed with the porcelain tile base glazes (M1 to M3) and the red-body tile base glazes (M4 and M5) on varying the applied amount of inkjet ink. It may be observed that, although the gloss values of the base glazes without ink application were very similar (between 12 and 17), each piece exhibited a different trend; lines have been drawn to join the points of the series to facilitate observation of the data.



Figure 1. Evolution of gloss of the pieces glazed with porcelain tile base glazes (M1 to M3) and red tile base glazes (M4 and M5) on varying the applied amount of inkjet ink. The points have been joined by lines to facilitate observation.

The gloss of pieces M1 to M3 approaches a limit value as the amount of ink increases, a maximum gloss that seems to be very similar for the three pieces. M4 and M5 also reached an identical gloss value after application of 66.5 g/m² ink, though this was considerably lower than in the case of the three previous base glazes.

4.2. PORCELAIN STONEWARE TILE: GLAZES OBTAINED WITH BASES M1 TO M3

4.2.1. MICROSTRUCTURE OF THE ORIGINAL FIRED GLAZES

The original microstructure of the fired glazes is shown in cross section in Figure 2. M1 was a barium matte glaze in which most of the crystals, which provided the matte finish, were barium silicoaluminates, indicated in the figure as SiAlBa. The glaze also contained zirconium silicate (ZS) and alumina (A) additions and some zirconium oxide (ZO) devitrified by partial dissolution of the ZS in a melt relatively poor in silica.

Glaze M2 was a calcium matte containing devitrified anorthite and zirconium silicate additions, which have been labelled in the figure as An and ZS, respectively.

Glaze M3 was a zinc/barium matte and the identified crystalline phases were barium silicoaluminates (SiAlBa), in a smaller amount than in M1, and zirconium silicate (ZS) and alumina (A) additions.





Figure 2. Cross section of bases M1 to M3 without application of ink. SiAlBa: barium silicoaluminates, ZS: zirconium silicate, A: alumina, ZO: zirconium oxide, An: anorthite.

4.2.2. MICROSTRUCTURE OF PIECES WITH INK APPLICATION ON

THE BASE GLAZES

Figures 3 to 5 show how the microstructure of the glazed porcelain stoneware tiles varied with increasing amounts of ink applied on the three test base glazes.

In the case of M1, it is observed that, as the quantity of applied ink increased, the upper part of the piece became a homogeneous glass. The interaction between the ink and the base glaze was already very significant in M1-2, where alumina and zirconium silicate particles from base glaze M1 were observed at the surface of the piece, indicating that the ink had penetrated the base glaze and had been integrated into it.

In the right part of the micrograph, the presence of the ink is more evident, as the amount of glass had increased and many of the barium silicoaluminates from base glaze M1 had disappeared.

In any event, M1-2 ink thickness was very thin, much thinner than that of M1-4 and M1-6, which would explain the comparatively small increase in gloss on applying 26.6 g/m^2 ink to base glaze M1. (see Figure 1).

The appearance of the intermediate pieces of series M1 (M1-3 and M1-5), which have not been included in the figure, was also very similar. The interaction zone could be defined as one in which the barium silicoaluminates from base glaze M1 disappeared. To facilitate identification of the interaction zone, in Figure 6 the zone outline has been marked on glaze M1-5, manually drawn to determine its thickness by image analysis. It may be noted that, in every case, interaction zone thickness varied significantly within the same micrograph.

The M2 series exhibited a similar behaviour. In this case, interaction between the ink and the base glaze resulted in the disappearance of the anorthite crystals from the M2 base glaze. The zirconium silicate particles from base glaze M2 (lightest grey areas) could be used as markers to indicate where the ink application had ended and base glaze M2 had started. However, it may be seen that, in every case, the interaction zone lay below the zirconium silicate particles (area without anorthite), indicating that the ink had diffused to a greater depth.

According to these criteria, the M2-2 and M2-4 interaction zones were larger than those of M1-2 and M1-4, respectively, while the interaction zone of the pieces with the largest ink application (M1-6 and M2-6) would be similar. Figure 6 includes the outline of the M2-5 interaction zone by way of example.

The pieces obtained with M3 are shown in Figure 5. As the curve of M3 gloss development was peculiar, micrographs of all applications have been included here. In every case it may be seen that the zirconium silicate, from base glaze M3, lay well above what would have been the interaction zone between the ink and the base glaze, which could be defined as that where the Ba/Zn silicoaluminate crystals, responsible for the matte texture of M3, had disappeared. On thus defining the interaction zone, it may be observed that M3-1 and M3-2 had practically the same interaction thickness and, therefore, very similar glosses (see Figure 1). This interaction thickness then increased to also become very similar for M3-5 and M3-6 which, again, had very similar gloss values.

The above suggests that there could be a relationship between the thickness of the interaction zone and resulting glaze gloss. If the matte appearance was provided

by the barium silicoaluminate and anorthite crystalline phases (large crystals) respectively, it would appear reasonable to consider gloss to possibly be a function of the thickness of the interaction zones in which dissolution of these phases occurred. Therefore, it was decided to measure the thickness of the interaction zones, manually delimiting the outline of these zones, determining their surface area by image analysis and calculating their average thickness by dividing the surface area by the length of the object in microns. The average thickness was measured in 10 images for each piece and the result was calculated as the average of these ten measurements.









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Figure 5. Cross section of fired glaze M3 without ink application (M2-0) and with different ink grammage. 1200x.



Figure 6 shows the interaction zone of micrographs of samples M1-5 and M2-5.

Figure 6. Selected example of the interaction zone in two micrographs, corresponding to pieces M1-5 and M2-5, respectively.

The measured thicknesses are plotted against the amount of applied ink, in Figure 7 (a). It is observed that the curves drawn joining the points show the same trend as the curves of gloss development with amount of applied ink shown in Figure 1. Therefore, this suggests that there could be a practically linear relationship between the gloss of the pieces and the thickness of the ink-base glaze interaction layer.

The dashed straight line represents the approximate thickness that the ink application would be expected to have as a function of the deposited grammage, taking into account a 50% solids content by weight, density of 2.6 g/cm³ for the molten solid and zero porosity in the layer.

The interaction layer thicknesses were observed to be considerably greater than what would generally correspond to the applied ink thickness, except for sample M1-2, whose interaction layer thickness was smaller, indicating that for this small grammage, the character of base glaze M1 had predominated over that of the ink.



Figure 7. (a) Thickness of the interaction layer of the base glaze with the ink as a function of the amount of ink applied to the three porcelain stoneware tile base glazes. Curves have been drawn to facilitate tracking of the experimental points. The dashed straight line indicates the expected approximate thickness of the applied ink layer. (b) Variation of gloss with interaction layer thickness.

4.2.3. RELATIONSHIP BETWEEN GLOSS AND INTERACTION LAYER THICKNESS

The development of gloss versus interaction layer thickness is shown in Figure 7 (b). A very similar trend is now seen for all pieces obtained with base glazes M1 to M3, although the gloss obtained with base glaze M1 was always slightly lower. These results confirm that, for these pieces, in which the nature of the interaction layer seemed very similar, since it was a homogeneous glass, gloss was directly determined by interaction layer thickness.

4.3. RED BODY TILES: GLAZES OBTAINED WITH BASES GLAZES M4 AND M5

The M4 glaze was a calcium and barium matte that devitrified barium silicoaluminates, though not in a high amount, together with alumina, nepheline, zirconium silicate and quartz additions. M5 was a barium and zinc matte with quartz, nepheline, alumina and zirconium silicate additions. The appearance may be seen in Figures 8 and 9 (glazes M4-0 and M5-0, respectively).

Base glazes M4 and M5 differed in the amount of devitrified barium aluminosilicate crystals (higher in M5) and in the glassy phase composition, which in M4 contained more calcium and in M5 more zinc. A gahnite $(ZnAl_2O_4)$ shell formed on the alumina particles of the glaze, through interaction with the zinc-rich melt. The shell protected the alumina and prevented its dissolution.

Figures 8 and 9 show the development of glaze microstructure with increased ink application. As in the previous cases, the ink created interaction zones that inhibited

M4-5

the formation of the phases responsible for the matte effect of the base glazes. In the fired glazes, only the pieces with 26.6 and 66.5 g/m^2 ink application were observed.







Figure 8. Cross section of fired glaze M4 without ink application (M4-0) and with 26.6 and 66.5 g/m² ink (M4-2 and M4-5). 1000x. W: wollastonite.







Figure 9. Cross section of fired glaze M5 without ink application (M5-0) and with 26.6 and 66.5 g/m² ink (M5-2 and M5-5). 1000x. W: wollastonite: wollastonite.

It is observed that the thickness of the interaction zone of the ink with glaze M4 was notably greater than that with glaze M5, with which it apparently reacted less. This may be due to the nature of M4, which contained more glassy phase and fewer devitrified crystals than M5.

It should be noted that, in the case of M4-2, M4-5 and M5-5, the ink did not generate a homogeneous glass at the surface of the piece, as wollastonite devitrified, as may be seen in Figure 8 for M4-5 and in Figure 9 in the case of M5-5.

Figure 10 shows the gloss of the pieces obtained using base glazes M4 and M5 as a function of the interaction thickness. The gloss values from the previous base glazes are also included.



Figure 10. Gloss development of all glazed pieces with interaction layer thickness. The points have been joined with lines to facilitate observation.

All base glazes except M4 were observed to follow approximately the same trend and M4 gloss was much lower than that which would normally have corresponded to its interaction thickness, which was considerable.

These results could be related to wollastonite devitrification at the glaze surface. This phase, characteristic of traditional calcium mattes, forms large crystals. Its presence at the outer surface of the fired glaze predominated over the influence of the underlying interaction layer, so that M4-5 and M5-5 (both with surface wollastonite) attained the same gloss value despite the difference in size of their respective interaction areas.

5. CONCLUSIONS

The studied gloss ink behaved differently when used for porcelain stoneware tile and for red-body tile.

In the case of the porcelain stoneware tile, the ink created interaction areas in which the phases that devitrified in the base glaze were eliminated, providing a matte appearance. For the porcelain stoneware tile, crystalline phases did not devitrify in the interaction layer and there seemed to be a direct correlation between the thickness of the interaction layer and increased gloss.

For a grammage of 40 g/m^2 , this being the average studied grammage, base glaze M2, a calcium matte, had a higher gloss value and thicker interaction layer. It was therefore this particular base glaze structure of those studied that most favoured the formation of a glass layer for this grammage. Subsequently, at greater application grammages, it was observed that gloss gradually approached a maximum value, which appeared to be about 84.

The thickness of the interaction layer was always much greater than the thickness that would normally have corresponded to each ink application, except in the case of samples M1-1 and M1-2, in which interaction layer thickness was less than the theoretical thickness. This may be due to the fact that M1 was a barium matte with a high tendency to form crystals and a greater amount of gloss ink was required to inhibit crystallization and form a clear glassy interaction layer. As a result, both M1-1 and M1-2 had very low gloss values compared to those of the other mattes to which the same amount of ink was applied. It should be noted that in plotting gloss versus the interaction zone, these glazes followed the same trend.

In the case of the red-body tile, there was a big difference in the interaction zones with the ink. The gloss of these glazes was affected by the presence of wollastonite crystals at the surface. The presence of these crystals reduced the gloss of the pieces, this being lower than that which would normally have corresponded to the interaction area.

6. **REFERENCES**

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