KAOLIN FOR DIGITAL CERAMIC DECORATION

Cédric Poilly, Luc Bourgy

Imerys Ceramics

1. ABSTRACT

An initial study presented for Qualicer 2014 has shown that the digital ink behaviour and colour development can be affected and controlled by characteristics of the kaolin used in the glaze substrate. In particular the kaolin amount in the substrate composition, its particle size distribution and its shape factor have an influence on the dot spread size and the absorption time of the inks. It was also shown that the particle shape is key to obtaining a homogeneous surface to control suction. After this first part of the work, a further step was done by using Scanning Electron Microscopy to measure the ink penetration into the substrate. The results were put in perspective with the pore structure of the substrate layer measured by mercury porosimetry. Finally kaolin samples have been treated by either physical or chemical processes in order to modify the wettability of the surface and the ink suction into the substrate layer. The treated kaolins were characterized in terms of chemical analysis, particle size distribution, span, top cut and shape factor. After being incorporated in glaze compositions, they were used as substrate layer on which ink was digitally printed. Depending on the process routes of the kaolin, it was possible to modify such parameters as contact angle, dot spread, and ink penetration depth in the substrate. As a result after firing, the printed dots had more or less width and depth. The visual effect on the colours was an increase of the pigment yield and colour strength for a given ink pattern. Also in relation with the ink pigment refractoriness, the coloured surface had more or less tendency to render a mat or glossy surface aspect depending on the ink spread and penetration.

2. INTRODUCTION

Previous studies (Sanz, Bautista, Belda, Coll, Pato, & Gonzalez, 2014) have shown that the digital ink behaviour and colour development can be affected by the substrate on which the ink is printed. In particular the kaolin amount in the substrate composition, its particle size distribution and its shape factor have an influence on the dot spread size and on the absorption time of the inks (Bourgy, Barreau, & Poilly, 2014). It was also shown that the particle shape is key to obtaining a homogeneous surface to control suction. In the present work, samples were subjected to optical microscopy and SEM to measure the ink depth penetration, and to mercury porosimetry to determine the pore structure of the glaze layer. The ink contact angle was also determined. Various kaolin samples were tried and the kaolin particle surface was treated chemically to modify its surface properties. Finally some additives were used to modify the ink penetration into the substrate.

3. TESTING CONDITIONS

A standard opaque glaze substrate recipe was prepared with the different kaolins. The substrate is composed by weight of 90% opaque frit and 10% kaolin. In addition 0.3% sodium carboxymethylcellulose (CMC) and 0.3% Sodium Tripolyphosphate (Na-TPP) were introduced by weight relative to the solid.

The suspensions were prepared by wet milling in a fast laboratory mill using alumina grinding media. The glazes were characterized and presented similar particle size distribution.

Each suspension was applied on a fired wall tile on top of engobe, using a glaze applicator with an aperture of 600µm to obtain a homogeneous layer.

Commercial ceramic inks were then applied on the substrate either by an Efi – Cretaprint printer or by a Ceradrop custom printer.

4. INK PENETRATION

This was studied firstly with 10% ink coverage on the glaze to be able to analyse single dots. But it appeared too difficult to observe single dots either in optical microscopy or with SEM due to the very low amount of pigment which was not sufficient to be detected. Increasing up to 100% ink coverage enabled the pictures below to be obtained.

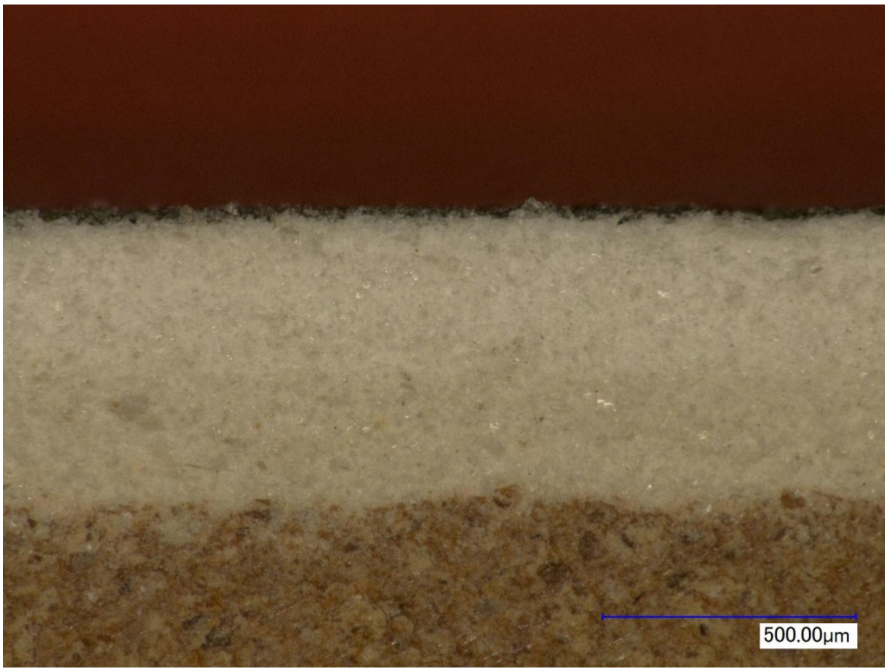


Figure 1. *Printed Tile 'FJK58' (x200)*

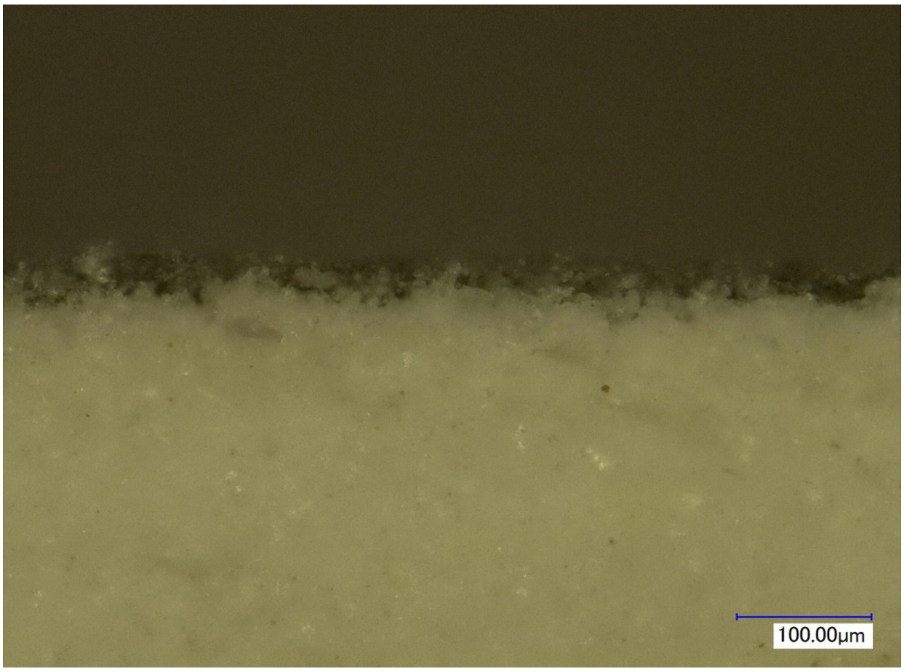


Figure 2. *Printed Tile 'FJK58' (x500)*

The black ink layer was observed by optical microscopy which gave an approximate depth of penetration. It was difficult to determine a precise limit for the ink penetration. To achieve a better field depth and more accurate measurement, the samples were subjected to SEM with EDS analysis.

Cobalt (Co) and Chromium (Cr) were analysed as major components of the black ink pigment.

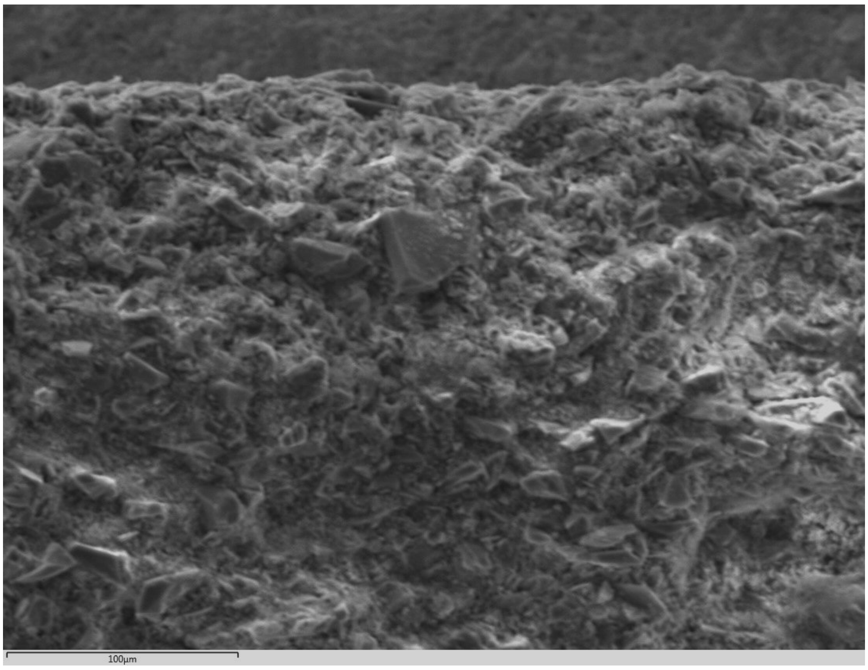


Figure 3. *Unfired glaze with 100% black ink coverage (x300)*

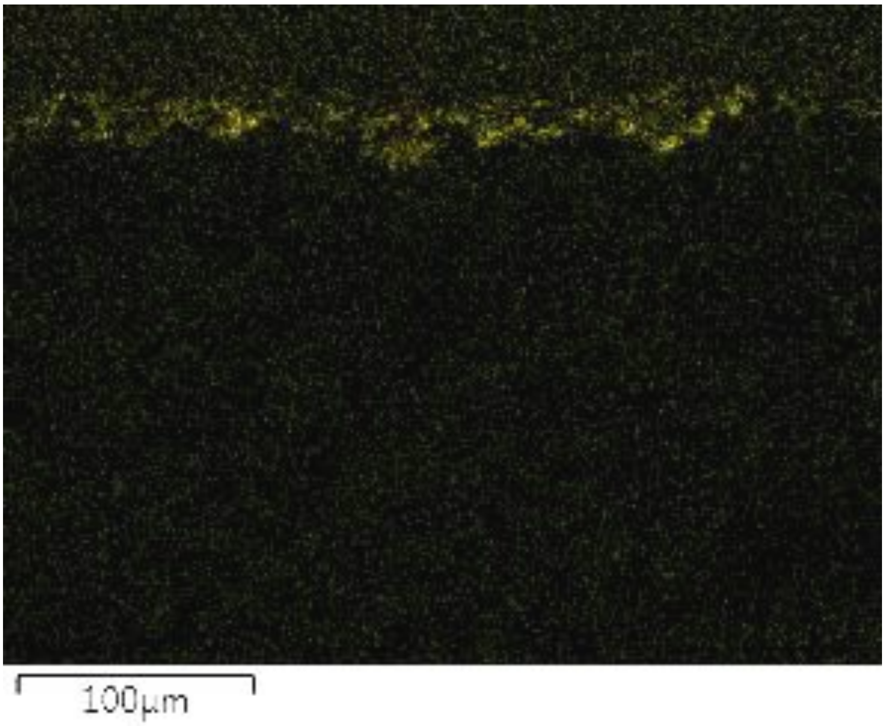


Figure 4. *Cobalt (Co) distribution in the unfired glaze (x300)*

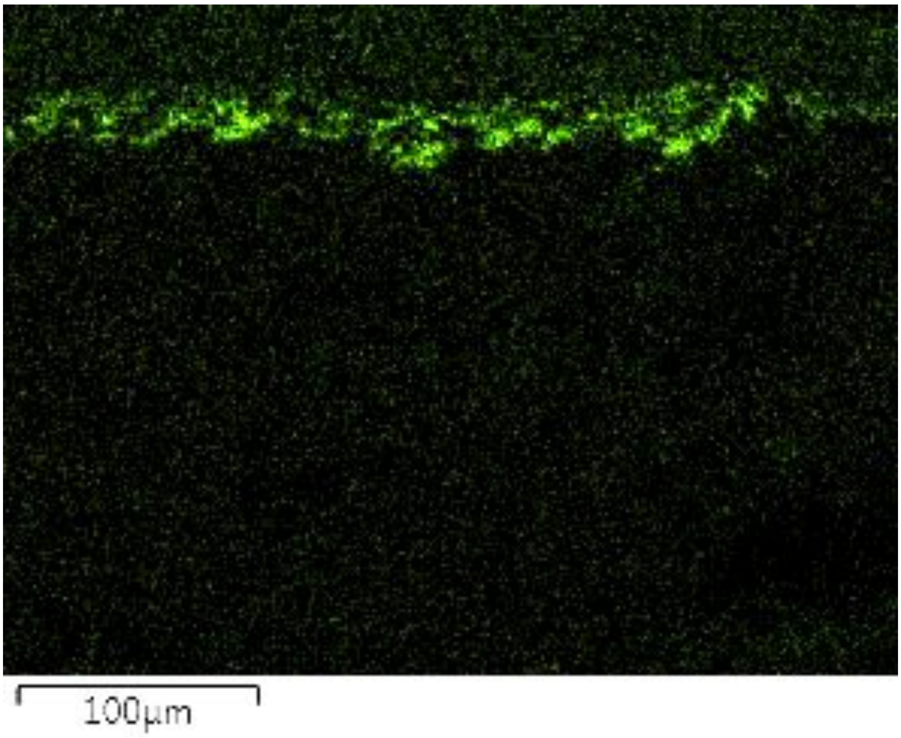
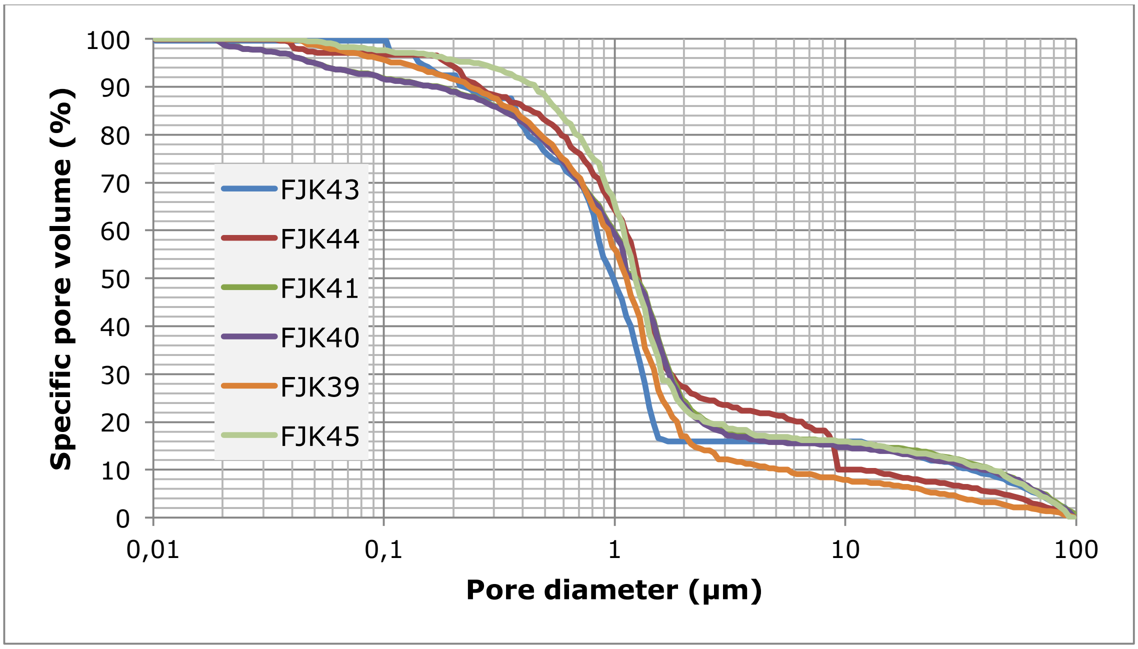


Figure 5. *Chromium (Cr) distribution in the unfired glaze layer (x300)*

It was possible to confirm the penetration depth of the black ink pigments (25µm in the above.)

5. PORE STRUCTURE

Porosity was characterized by mercury porosimetry.



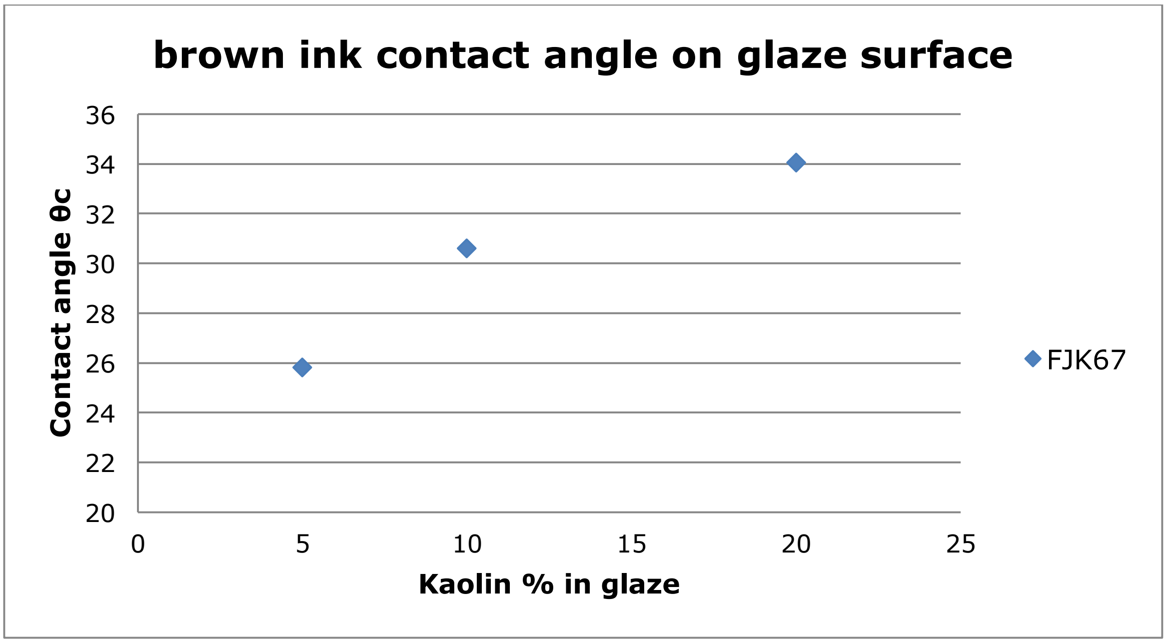
The main fraction of pores can be observed to lie between 0.2 and 2 µm. There is also a smaller fraction of macro pores above 30 µm.

The composition prepared with kaolin FJK 40 presents a wider pore size distribution while the formulation made with the kaolin FJK45 presents a much narrower pore distribution.

6. CONTACT ANGLE

The contact angles of ink on the raw glaze surface were studied for brown ink. Several raw kaolins were evaluated in the glaze composition as well as some chemically processed kaolins to observe whether any significant difference could be observed. Also some additives were used in the glaze recipe to modify the contact angle obtained with the raw kaolins.

First to evaluate the importance of the kaolin, the percentage of kaolin in the glaze was increased from 5 to 20%.



The contact angle is affected by the quantity of kaolin in the glaze.

On the raw kaolins the contact angle ranged between 26 and 31 degrees (see FJK63 below for example)

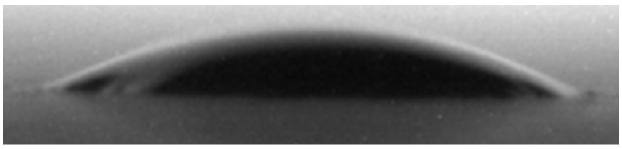


Figure 6. *Standard kaolin FJK63, (θc: 26.9 deg)*

With a specific chemical treatment on the surface of the kaolin particles, with the same kaolin it was possible to obtain an increase of the contact angle up to 37 deg.

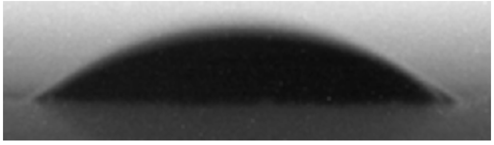
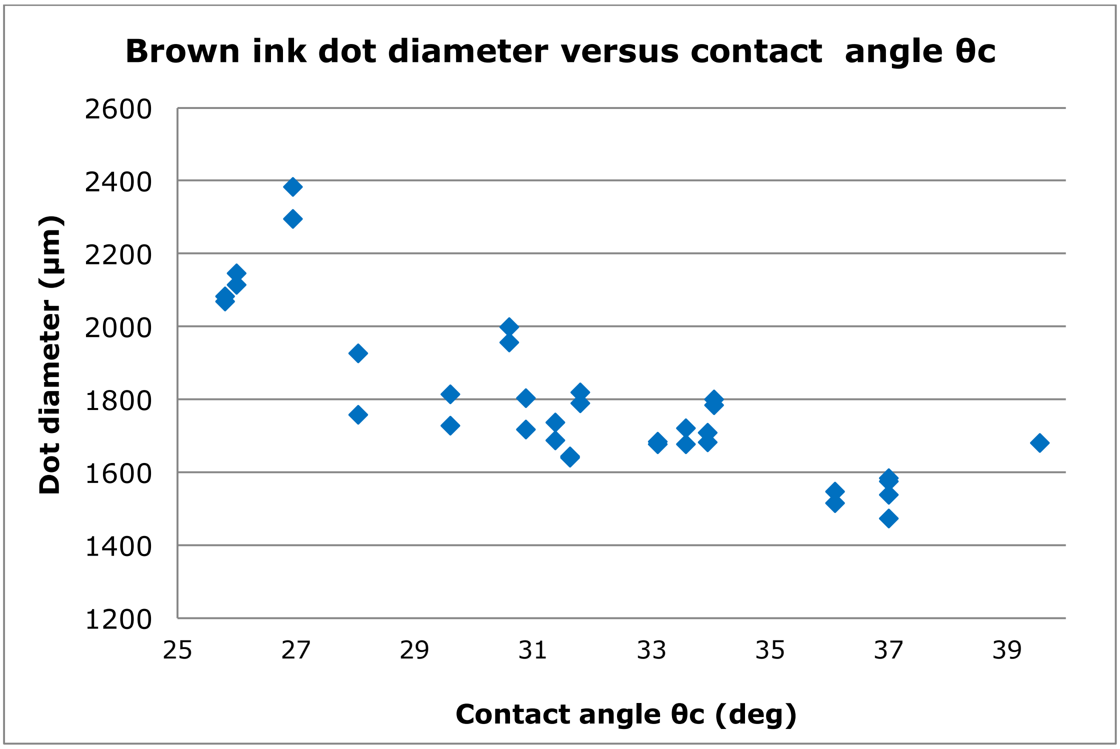


Figure 7. *Chemically treated FJK63 kaolin (θc: 37.0 deg)*

After the ink was fully absorbed by the glaze and dried, the diameter of the resulting dot was measured by optical microscope.



The dot diameter could then be related to the contact angle. As the volume of each ink drop was adjusted at a given value, it is then probable that the ink penetrated deeper into the substrate for the smaller diameter, i.e. higher contact angles.

7. INK DOT SIZE BEFORE AND AFTER FIRING

Single dots were printed onto the raw glaze surface with the brown ink with a spacing of 150µm. The volume of each drop of ink was on average 25 pl.

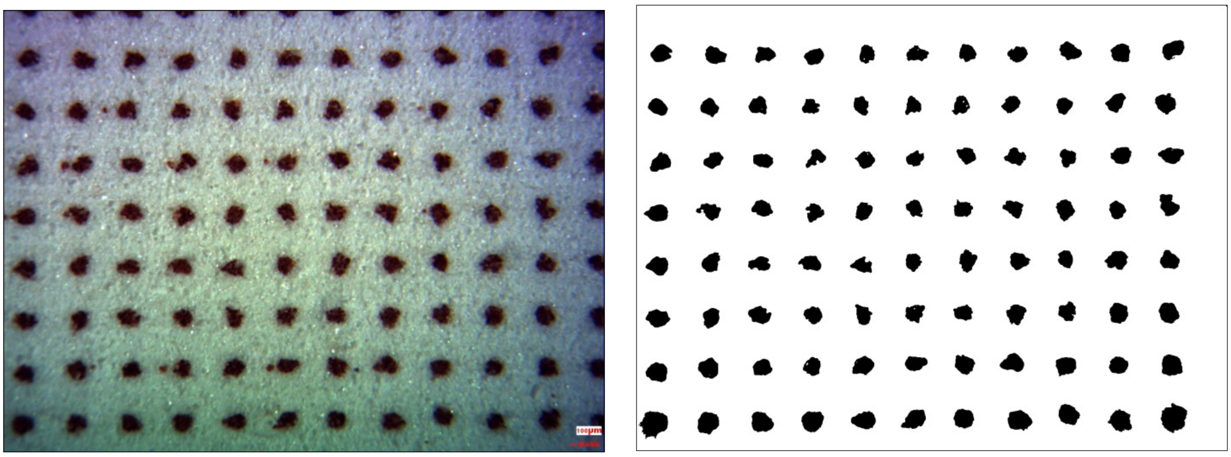


Figure 8. *Brown ink dots on unfired glaze (x40)*

It could be observed that the dots do not have a very regular surface. They are far from a perfect circle shape, thus it is likely that the absorption of the ink is anisotropic. This is mostly due to the roughness and heterogeneity of the glaze surface with some coarser frit particles between 20 and 50 µm in diameter and pores as shown above.

The average surface and diameter measured for a given composition was measured as below.

	Area (µm²)	Equivalent circular diameter (µm)
MEDIA	6090	87.9
SD	795	5.7
MAX	7800	99.7
MIN	4573	76.3

After firing the same sample gave the pictures and values below.

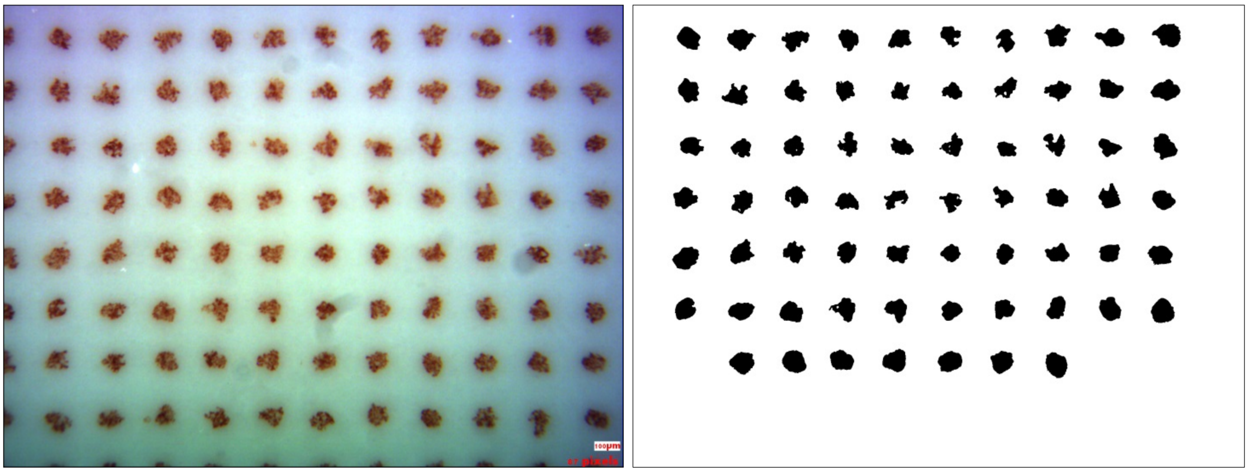


Figure 9. *Brown ink dots on fired glaze (x40)*

	Area (µm²)	Equivalent circular diameter (µm)
MEDIA	6050	87.5
SD	937	6.9
MAX	7968	100.7
MIN	3974	71.1

In this case for 10% kaolin in the glaze, the results obtained after firing were very close to the results before firing

The surface aspect of the substrate was also measured to detect the presence of defects. The influence of the depth penetration of the ink on glossiness will be explored in further studies.

8. CONCLUSIONS

The characteristics of the substrate for ink jet printing can be modified by adjusting the type and properties of the kaolin used in the substrate. By modifying the Particle Size Distribution, the shape and the surface charges of the kaolin particles, it is possible to modify the contact angle of the ink with the substrate layer and thus to change the ink penetration depth into the substrate layer before firing.

REFERENCES

[1] *Influence of printing conditions.* **Sanz V. et al.,** Castellón: s.n., 2014. Qualicer.

[2] *Influence of the kaolin in the substrate on the quality of inkjet printing.* **Bourgy, L., Barreau, A. and Poilly, C.** Castellón: s.n., 2014. Qualicer.