PIGMENTED AQUEOUS SYSTEMS FOR DIGITAL DECORATION

Gülşen L. Güngör [1-2], Alpagut Kara [1-2], Davide Gardini [3], Magda Blosi [3], Michele Dondi [3], Chiara Zanelli [3]

[1] SAM, Ceramic Research Center, Eskişehir, Turkey

[2] Department of Materials Science and Engineering, Anadolu University, Eskişehir, Turkey

[3] CNR-ISTEC, Institute of Science and Technology for Ceramics, Faenza, Italy

ABSTRACT

Ceramic pigments are important materials for digital decoration of ceramic tiles and are preferred as colouring agents in solvent-based inks. On the other hand, due to environmental problems associated with these inks, water-based systems are envisaged as a green alternative for ceramic tile decoration. Controlling the rheology of water-based systems is an important factor to achieve a better product performance; however, there is little knowledge about the effect of grinding and pigment type on the stability of sub-micrometric aqueous pigmented suspensions. Therefore, this study was aimed at defining the rheological behaviour and stability of three different pigments in water: i.e., zircon ($ZrSiO_4$:V), rutile ($(Cr,Sb)TiO_2$) and spinel ($(Co,Mn)(Fe,Cr)_2O_4$). The pigments were ground to submicron level in water using circulation type agitator mill (Netzsch Labstar LS1) by varying parameters (rotation speed, type and amount of dispersants and bead size). An attempt was made to understand the jettability behaviour with the help of physical and rheological properties, i.e. viscosity change at different shear rates, surface tension and density and the rheological properties were measured with a rotational rheometer. Stability of aqueous suspensions of the pigments was studied by dynamic light scattering method for the determination of zeta potential and isoelectric point (zeta potential as a function of pH) and sedimentation tests. Polycarboxylic acid-sodium salt and ammonium polymethacrylate were chosen as two different dispersants for the determination of effective stabilization mechanism. The interval of pH where zeta potential is out of the typical stability range (-30; 30 mV) and, correspondingly, the most stable conditions, according to the pH values, were determined. All three types of ground pigments showed high stability due to having zeta potential below -30 mV and the starting pH values were measured as 7.7, 7.2 and 10. When acid was added to the system, zeta potential value reached close to zero. When surface tension and density values were considered in terms of jettability, it was observed that the ground aqueous systems were in the optimum jettability range.

1. INTRODUCTION

Inkjet printing is an emerging technology with many applications being explored[1]. The growth of digital ceramic tile decoration is proceeding at breakneck speed and shows no sign of slackening[2]. The drop on demand method is most commonly used method for modern industrial applications[1]. It deposits precise quantities of functional inks in the form of droplets on an arbitrary surface by applying a short pressure pulse through a nozzle which is typically 20-50 µm in diameter. Under suitable conditions, the ejected fluid develops into a single droplet for quality ink-jetting[1].

The ceramic inks are normally dispersed in non-aqueous media; however, the preparation of suspensions of ceramic powders in aqueous media represents a desirable advancement in terms of environmental and personal safety[3]. There are two primary routes of entry for inkjet inks in the human body: inhalation and skin/eye contact. Water makes up the bulk of water-based inkjet ink, leaving few volatile constituents. In fact, the minimal odours released during printing are only detectable in the immediate vicinity of the printer. No residual odours are released from dry prints[4].

All solvent and water-based inks have basically the same components: colorant (pigment for ceramic decoration), vehicle, additives and co-solvent. The difference between two systems lies in the resolubility mechanisms and the working conditions of the systems. When the ink is applied on the substrate, it begins to dry on the contact surface. The ink left behind is called ink split. The resolubility mechanisms of solvent-based inks are quite forgiving, easily reversible and controlled with solvent blends. The ink balance is also maintained by using the proper viscosity range as provided by the supplier. With water inks, the resolubility mechanisms are quite different. The resin systems that are not dissolved also need to remain suspended to help the pigments reach the substrate. Surface drying and rewetting are not reversible or as forgiving as the alcohol system[5].

Appropriate functional ink materials are limited in availability[1]. Inkjet technology imposes many constraints on the inks, which must fulfil requirements such as suspension stability, viscosity, surface tension, pigment particle size and colour strength[6]. For viscosity, the requirement is in the range of 4-40 mPa s, while for surface tension, it is

20 to 45 mN/m. For preventing the nozzle corrosion, pH should be in the range of 5-10 and the pigment solubility should be very low[7]. With respect to water-based inks, it is difficult to fulfil the requirements. Surface tension and viscosity are the farthest from the recommended values for drop-on-demand ink-jet printing (DOD-IJP) among solvents commonly addressed to ink making. Furthermore, sedimentation rates are higher in water than in more viscous carriers.

The purpose of this study was to define the physical properties of ground aqueous pigmented systems to submicronic scale and to understand the jettability and stability of the samples. Water-based formulations for DOD-IJP were developed by investigating the rheological behaviour and the electrochemical characteristics of three different systems i.e. spinel (black), zircon (turquoise) and rutile (orange). Jettability was also assessed with reference to a current model for inkjet printers, based on ink physical properties (surface tension, viscosity, density) while attempting to develop an understanding of the ink stability with the help of zeta potential and sedimentation measurements.

2. EXPERIMENTAL

The pathway followed in the development of pigmented aqueous systems was:

i) Micronizing conventional pigments to a target around 0.3 µm in terms of median particle size (d_{50});

ii) Determining density, surface tension and viscosity of aqueous suspensions, checking the effect of solids loading on physical properties and jettability;

iii) Investigating the suspension stability over time in terms of both electrostatic and steric stabilization (measuring pH and zeta potential, sedimentation behaviour and effect of different surfactants).

Industrial pigments i.e. black spinel (Co-Cr-Fe-Mn-Ni), turquoise zircon (V-Zr-Si) and orange rutile (Cr-Sb-Ti) were ground under certain conditions (2000-3000 rpm rotation speed, grinding time, 0.3 mm bead size, 30% solids load and two different types of additive usage) using a circulation type bead mill (Netzsch Labstar LS1). The grinding operation was performed in aqueous medium and the two types of dispersants named as Darvan C-N and Dolopix G10 were chosen for certain trials. The amount of dispersant was kept constant.

3. RESULTS AND DISCUSSION

INK JETTABILITY

For inks, it is crucial to tailor properties to the specific demands of the printer system and substrate. These properties include: pH, viscosity, storage stability, printing reliability, drying behaviour, decap time, transparency, chroma, optical density and gloss. An issue that has to be addressed for both water-based pigment preparations and resulting inks is the proper adjustment of the interfacial tension[8]. For the water-based ink systems in three colours, surface tension, viscosity and density values were given in Table 1. For turquoise and orange samples, the viscosity changed with shear rate showing a Newtonian behaviour, while black sample had pseudoplastic flow behaviour due to gellation. Surface tension values were measured as 21.3, 17.2 and 29.3 mN/m for turquoise, black and orange, respectively. These values were also considered (Figure 1) with respect to jettability with the help of Reynolds and Ohnesorge numbers.

Pigment-grinding conditions	mN/m	mPa s (200 s^{-1})	kg/m^3
TZ-3000-0.3MM-2H	21.3	8	1160
BS-3000-0.3MM-2H	17.2	10	1200
OR-3000-0.3MM-2H	29.3	12	1100

Table 1. Surface tension, viscosity and density values of the inks for three colours.

A flow curve plots viscosity as a function of shear. The viscosity of a Newtonian fluid is independent of shear rate, while the viscosity of a shear thinning material (many paints, inks and coatings) reduces as shear rate increases. Metal oxide suspensions, involving sub-micrometre particles, can display very different rheological phenomena, including shear thinning, shear thickening, yielding and thixotropy. The nature and magnitude of forces acting in those systems and the resulting microstructure are responsible for these complicated rheological responses[9].

The jettability of ink can be predicted through fluid mechanics dimensionless numbers like Reynolds and Ohnesorge[10]. The Reynolds (Re) number is the ratio of inertial to the viscous forces:

$$Re = \frac{\rho v d}{\eta}$$

The Ohnesorge number (Oh) is the ratio of viscous forces to surface tension and inertial forces:

$$Oh = \frac{\eta}{\sqrt{\rho \gamma d}}$$

where ρ, η, γ, d y v are the density, viscosity, surface tension, nozzle diameter and droplet velocity, respectively. These dimensionless numbers were calculated for common values of nozzle diameter (50 μm) and droplet velocity (6 m/s) in digital printers (Fig. 1). The pigmented aqueous systems under investigation have physical properties that allow them to be placed in the field of printable fluid with DOD-IJP technology (squares in Figure 1).

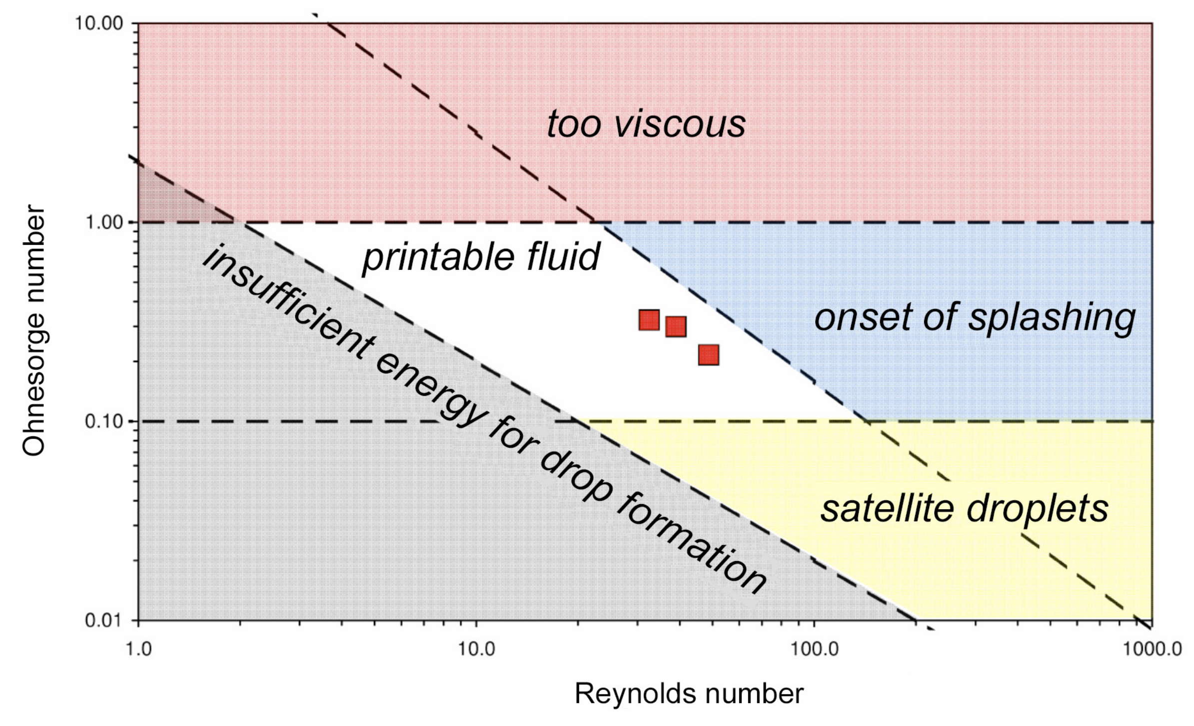

Figure 1. Behaviour during the jetting cycle of the pigmented aqueous systems with reference to jettability of DOD-IJP inks according to McKinley and Renardy[10].

INK STABILITY OVER TIME

As the particle size range is in the colloidal size range, i.e. sub-micronic, the particles will aggregate together due to the attractive Van der Waals force[11]. When a particle moves (e.g. due to gravity), the solvent and the ions in the layer adjacent to the particle move along with it, while the liquid far from the particle will be not affected by the motion. A boundary delimiting those two regions will exist (surface of hydrodynamic shear) and the electrical potential at that boundary is the so-called zeta potential. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there will be no tendency for the particles to come together. The general dividing line between stable and unstable suspensions is generally taken at either +30 or -30 mV. Particles with zeta potentials more positive than +30 mV or more negative than -30 mV are normally considered stable. However, if the particles have a density different from the one of the dispersing liquid, as usually happens, they will sediment forming a close packed bed (i.e. a hard cake)[12]. In Fig. 2, the change of zeta potential is illustrated for black, orange and turquoise inks that were ground under 2000 rpm with 0.5% DC for one hour. As a general trend, the zeta potential decreases with further milling. This could be due to the creation of new particles with an increase of the total surface area and the need of more dispersant, to the dissolution of ions or the phase changes during grinding due to plastic deformation of the particles.

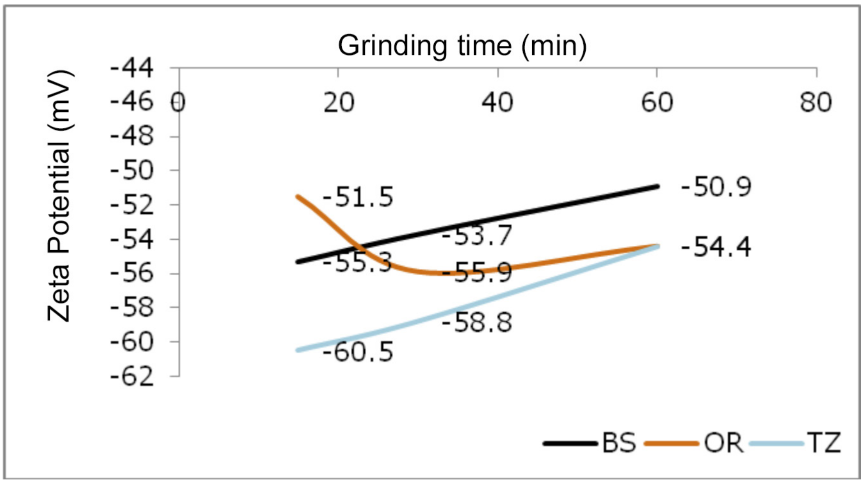

Figure 2. Change of zeta potential during further milling.

In aqueous media, the pH of the sample is one of the most important factors that affect its zeta potential. A zeta potential value on its own without defining the solution conditions is a virtually meaningless number. For a particle in suspension with a negative zeta potential, if more alkali is added to this suspension then the particles tend to acquire a more negative charge. If acid is added, then a point will be reached where the charge will be neutralized. Further addition of acid will cause an inversion of the charge with the build-up of positive charge. Therefore, a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH. The point where the plot passes through zero zeta potential is called isoelectric point and is very important from a practical consideration. It is normally the point where the colloidal system is less stable[12]. For the samples in three colours ground under 3000 rpm rotation speed for two hours and without an additive, the zeta potential change with pH is illustrated in Fig. 3. The initial pH values of the suspensions were in basic site and the starting zeta potential values were in the stability range (<-30 mV). When the pH shifted through the acidic site, the stability of the system deteriorated, but the zeta potential was in the stability range until pH 6.

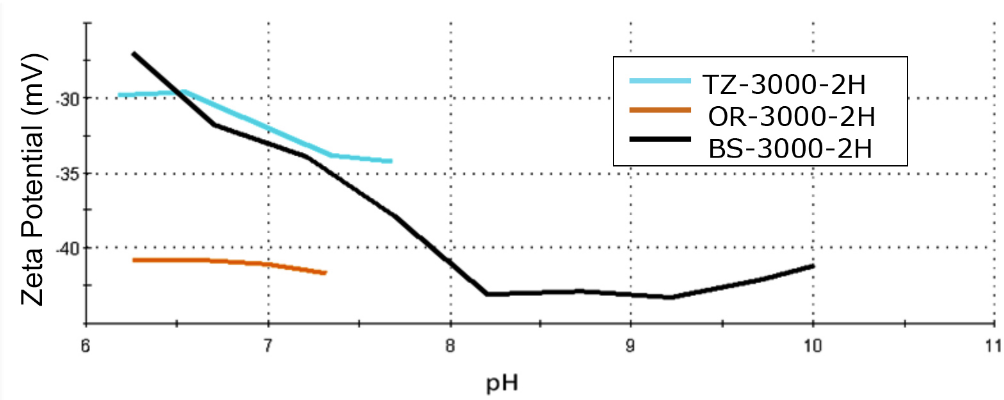

Figure 3. Zeta potential change according to pH of the samples ground under 3000 rpm for 2 hours with no additives.

In order to see the effect of dispersant type, two different dispersants were used: DC (Darvan C-N) which is a type of ammonium polymethacrylate polymeric dispersant and the other one is DOL (Dolopix G10) which is a sodium salt of a polycarboxylic acid. The zeta potential values of three different colours are given in Table 2. No significant change was observed with dispersant type but their presence increased the zeta potential and therefore stability of the system.

Pigment-grinding conditions	0.5% wt% DC	0.5% wt% DOL
TZ-2000-1H	-54.4	-50.7
OR-2000-1H	-54.4	-54.3
BS-2000-1H	-50.9	-49.1

Table 2. Effect of dispersant type on zeta potential of three coloured inks.

Similar to the effect of grinding time, the zeta potential decreased with the increase of rotation speed due to the new surface creation and the need of more dispersant, dissolution of the ions or the phase changes during grinding due to plastic deformation of the particles.

Pigment-grinding conditions	2000 rpm	3000 rpm
TZ-1H-no disp	-58.6	-44.4
OR-1H-no disp	-49.4	-35.7
BS-1H-no disp	-43.9	-22.0

Table 3. Effect of rotation speed on zeta potential of three coloured inks.

SEDIMENTATION TESTS

Understood in terms of colloidal stability and stability over time (with reference to sedimentation rates, etc.) the sedimentation test for the TZ ink ground at 1000 rpm for 0.5 h in absence of dispersant (vial 2) showed a dense sediment at the bottom of the vial and a clear liquid on the top. By increasing the grinding time up to 1 and 1.5 hours, the height of the sediment increased (vials 2, 4 and 5) (Figure 4). This can be explained by the fact that a longer grinding makes the particles finer enhancing the flocculation phenomena. The increase of the rotation speed to 2000 rpm (vials 3 and 6) improved the pigments micronization, therefore the sediment height was further increased with respect to the pigments micronized at 1000 rpm with the same grinding time. In all these cases, the formation of packed sediment showed that the stability over time is quite limited.

The introduction of a dispersant (Darvan C) (vial 1) still gave compact sediment, but with respect to the other samples, more particles were kept in suspension, in fact the supernatant was coloured and not clear.

The fact that the sediment was close packed together with a coloured supernatant means that the dispersant screened well both the large and the small particles, which due to their small sizes remain suspended, improving the stability over time.

In order to match the requirements to have a sufficient stability over time, a compromise between a good colloidal stability preventing large agglomerates and easy redispersibility of the sediment has to be found. Sample 1 possibly represents a good choice since it is less colloidally stable than the others, but it allows the particles to be kept in suspension for a longer time and the sediment to be easily redispersed. Similar tests were performed, resulting in similar conclusions, for the orange inks but the black inks had an irregular sedimentation behaviour due to problems of gellation, and a regular relationship could not be found (Figures 5 and 6).

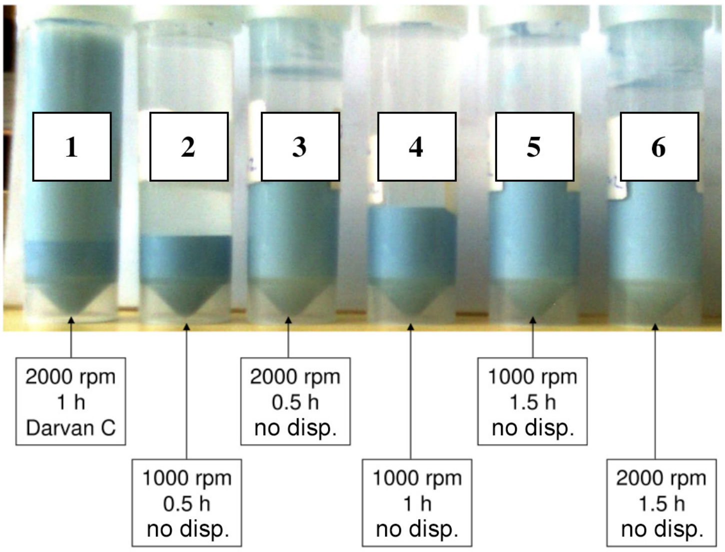

Figure 4. Sedimentation test for the samples containing turquoise pigment.

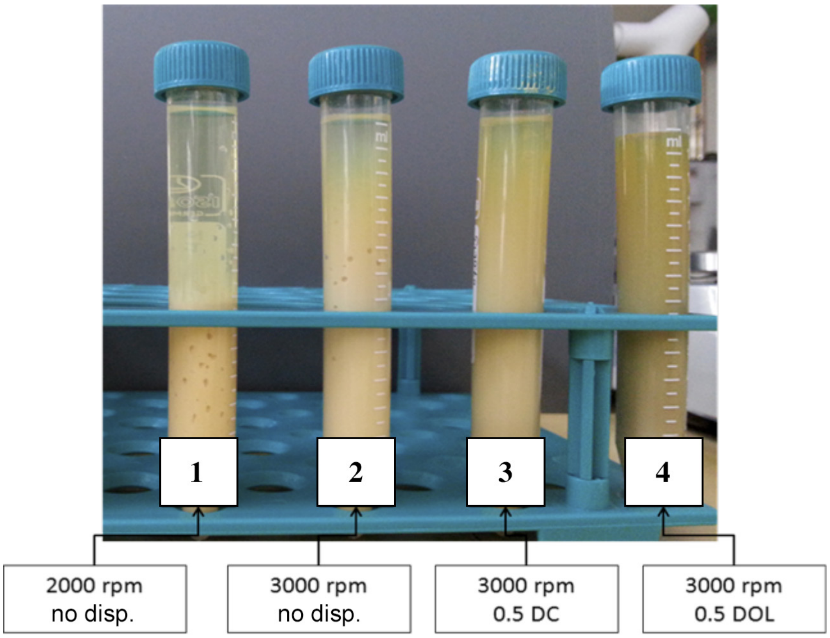

Figure 5. Sedimentation test for the samples containing orange pigment.

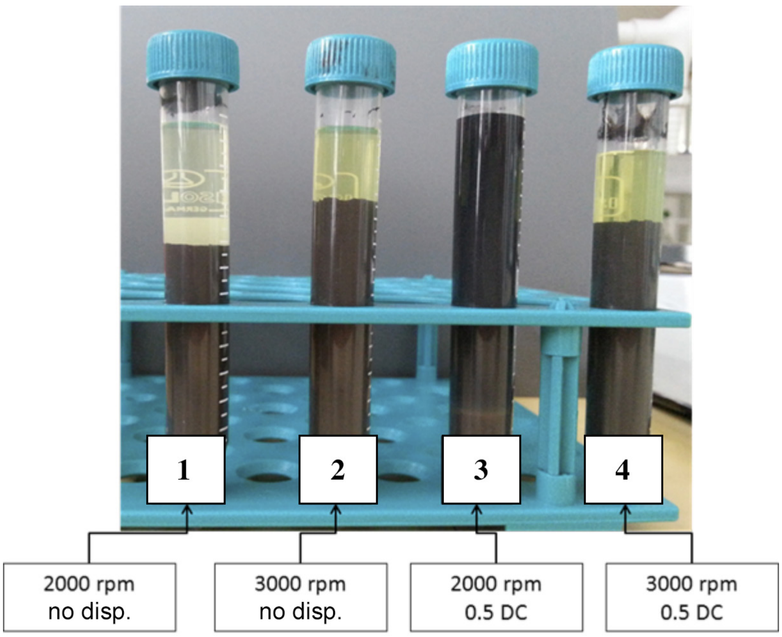

Figure 6. Sedimentation test for the samples containing black pigment.

4. CONCLUSIONS

This work describes the requirements of aqueous pigmented systems for digital decoration of ceramic tiles in terms of rheological, physical and electrochemical properties. According to the results, ground sub-micronic systems in three different colours were involved in the jettability ranges having zeta potential below -30 mV in basic site. When pH went through acidic site, zeta potential increased. Further milling deteriorated the stability and the increase of dispersant ratio was thought to be helpful to keep zeta potential below -30 mV during milling. Use of dispersant increased stability, while changing the dispersant type did not have a significant difference on zeta potential.

According to viscosity determination studies it was observed that the turquoise and rutile samples displayed Newtonian flow, while the black sample displayed pseudoplastic flow due to gellation, and the final viscosity values were low similar to water. Similarly, the surface tension of the three systems was not high, like that of pigmented systems for digital decoration which were developed with respect to jettability and stability range.

REFERENCES

[1] D. Jang, D. Kim, J. Moon, "Influence of fluid physical properties on inkjet printability" Langmuir, 2009, 25, 2629-2635.

[2] G. P. Crasta, "Boom in digital technology" Ceramic World Review No: 92/2012, pp. 64

[3] S. OBATA, H. YOKOYAMA, T. OISHI, M. USUI, "Preparation of aqueous pigment slurry for decorating whiteware by ink jet printing" Journal of Materials Science 39 (2004) 258–2584.

[4] Photo marketing Association, "Digital Imaging: Water Based Inks and HSE".

[5] S. Utschig, "Question: Why can the transition from alcohol to water based inks be so difficult?" Converting Magazine, Sept. 1998, 16, 9, pg. 40.

[6] F. Matteucci, G. Baldi, D. Gardini, M. Blosi, E. Cinotti, M. Dondi, A.L. Costa, C. Galassi, "New nano-sized ceramic inks can provide good reproducibility and high color saturation on ceramic tile" Ceramic Industry, Oct. 2006, 156, 10, pp. 20-21.

[7] M. Dondi, M. Blosi, D. Gardini, C. Zanelli, "Ceramic Pigments For Digital Decoration Inks: An Overview", Qualicer 2012.

[8] K. H. Schweikart, B. Fechner, H. T. Macholt, "Dynamic surface tension measurements" Ink Maker, July-August 2005, pp. 21.

[9] Z. Zhou, P. J. Scales, D. V. Boger, "Chemical and physical control of the rheology of concentrated metal oxide suspensions" Chemical Engineering Science 56 (2001) 2901-2920.

[10] M. Dondi, M. Blosi, D. Gardini, C. Zanelli, P. Zannini, Ink technology for digital decoration of ceramic tiles: an overview. Proceedings of the 14th World Congress on Ceramic Tile Quality, QUALICER 2014, Castellón (Spain).

[11] R. Greenwood, "Review of the measurement of zeta potentials in concentrated aqueous suspensions using electroacoustics" Advances in Colloid and Interface Science 106 (2003) 55–81.

[12] http://www.nbtc.cornell.edu/facilities/downloads/Zeta%20potential%20-%20An%20introduction%20in%2030%20minutes.pdf