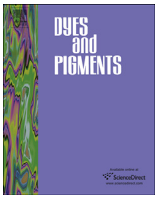
Dyes and Pigments 127 (2016) 148–154

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



# Ink-jet printability of aqueous ceramic inks for digital decoration of ceramic tiles

Gülşen L. Güngör [a, b, *], Alpagut Kara [a, b], Davide Gardini [c], Magda Blosi [c], Michele Dondi [c], Chiara Zanelli [c]

[a] SAM, Ceramic Research Center, Anadolu University, Yunusemre Campus, ETGB Anadolu Sciencepark, No: 107-103, 26470 Eskişehir, Turkey
[b] Department of Materials Science and Engineering, Anadolu University, Iki Eylül Campus, Eskişehir 26555, Turkey
[c] CNR-ISTEC, Institute of Science and Technology for Ceramics, Via Granarolo, 64, 48018 Faenza, Italy

## ARTICLE INFO

*Article history:*
Received 30 July 2015
Received in revised form
11 December 2015
Accepted 22 December 2015
Available online 31 December 2015

*Keywords:*
Aqueous inks
Ceramic pigments
Digital decoration
Ink stability
Printability
Rheology

## ABSTRACT

Digital decoration of ceramic tiles has turned to be a prevalent and dynamic technology in the last decade. Current printers use drop-on-demand (DOD) ink-jet print heads (IJP) fed with solvent-based inks containing ceramic pigments as coloring agents. However, due to environmental constraints, water-based systems are envisaged as a green alternative for ceramic tiles decoration. Nevertheless, aqueous suspensions are difficult to be managed because physical properties of water are far away from the DOD-IJP operating window. Thus, the control on the stability, homogeneity and rheology of such water-based systems is an important factor to achieve better product performances. This study was aimed at exploring both the rheological behavior and stability of three inks based on micronized pigments dispersed in water and water-MEG solutions: $(V,Zr)SiO_4$ (turquoise zircon, TZ), $(Cr,Sb)TiO_2$ (orange rutile, OR) and $(Co,Mn)(Fe,Cr)_2O_4$ (black spinel, BS). The pigments were ground to submicronic size in water using a circulation type agitator mill and by changing the main parameters affecting the particle-size distribution (rotation speed, type and amount of dispersants). The stability of aqueous pigment suspensions was studied by measuring the zeta potential as function of pH and by sedimentation tests. The zeta potential was sufficiently strong (lower than −30 mV) to render the inks stable in the 7–10 pH range. Rheological measurements of the suspensions showed a Newtonian flow behavior for zircon and rutile inks and slightly pseudoplastic for the spinel one. An attempt was also made to evaluate the inks printability with the help of dimensionless numbers based on the relevant physical and rheological properties affecting the jetting, i.e. viscosity, surface tension and density. It was observed that the ground aqueous systems fall in the printable fluid region obtained with semi-empirical models.

## 1. Introduction

Ink-jet printing is an emerging technology with many applications being explored [1]. The growth of digital decoration in ceramic tile production is proceeding at breakneck speed towards a saturation of manufacturing lines [2]. Ceramic tiles are printed by the drop-on-demand method, which is the most commonly used technique in modern industrial applications. It deposits precise quantities of functional inks (in the form of 6–80 pL droplets) on the green tile surface by applying a short pressure pulse through a nozzle which is typically 20–50 μm in diameter. Under suitable conditions, the fluid is ejected into a single droplet for high 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 for handling, safety and the environment [3]. In addition, the legislation in many countries is forcing the ink-making industry to reduce the level of volatile organic solvents as well as solvent-borne additives used to adjust the chemical and physical properties of ceramic inks [4].

Both solvent and water-based inks have basically the same components: colorant (pigment for ceramic decoration), vehicles (the so called “solvent” and “co-solvent”), and additives. The difference between the two systems lies mainly in the pigment

---

* Corresponding author. SAM, Ceramic Research Center, Anadolu University, Yunusemre Campus, ETGB Anadolu Sciencepark, No: 107-103, 26470 Eskişehir, Turkey. Tel.: +90 222 323 82 76; fax: +90 222 322 29 43.
*E-mail address:* glgungor@anadolu.edu.tr (G.L. Güngör).

http://dx.doi.org/10.1016/j.dyepig.2015.12.018
0143-7208/

dispersion mechanism, as all these inks are designed to work in the DOD-IJP operating conditions. Solvent-based systems can show a wide range of physical properties (being shear viscosity and surface tension the most important) and dispersion mechanisms, which are easily reversible and controlled by vehicle blends and proper additives designed to achieve a steric stabilization of the colloidal system (using in particular block co-polymers) [5]. The ink formulations are set up for modulating the proper viscosity and surface tension as requested by DOD ink-jet printers. The dispersion mechanisms are quite different with water-based inks, whose colloidal stability is firstly pursued by an electrostatic approach (achieving a sufficiently high zeta potential acting on the pH and using proper additives) [6]. In addition, hybrid systems are also used in ceramic tile decoration: these inks contain water (usually from 5% to 60% of the total amount of carrier) together with water-soluble or easily miscible solvents (e.g., alcohols and glycols) [5].

Ceramic pigments are currently micronized down to a mean particle diameter around 0.3 μm in order to prevent clogging of print heads [7,8]. However, micronization causes a strong increase in the specific surface area of pigments, with the drawback of a high tendency of particles to agglomerate. Therefore, the main concern is to ensure the colloidal stability of inks after grinding. For this purpose, the pigment dispersion is stabilized by proper additives, besides micronized pigment particles, once dispersed in the vehicle, are in continuous random movement due to collisions with the solvent molecules in thermal agitation (Brownian motion). As the particles collide or come very close, attractive forces pull the particles closer together. These intermolecular forces come from attractive dipole–dipole interactions known as van der Waals forces, or, in particular, London forces [9]. This is very often the cause of flocculation. In order to overcome the flocculation, the steric hindrance effect by polymer adsorption to the pigment has been usually studied [10]. The presence of the polymer dispersant allows avoiding anomalies susceptible to generate flocculation, sedimentation, fall of gloss etc. [11].

The knowledge of the rheological behavior of suspensions is important to control their flow and to increase the solid volume content, keeping the desired fluidity, avoiding sedimentation and agglomeration phenomena [12]. The DOD-IJP technology imposes many constraints on the inks, which must fulfill requirements about viscosity and surface tension (to ensure the printability), suspension stability and pigment particle size (to avoid sedimentation and nozzle clogging), and solid load (to achieve the desired color strength) [13,14]. The requirements are 4–40 mPa s for viscosity (best 4–10 mPa s) and 20–45 mN/m for surface tension (best 25–35 mN/m). The pH has to be in the 5–10 range to prevent nozzle corrosion and the pigment solubility should be very low [14]. However, the physical characteristics of water (especially shear viscosity ~1 mPa s and surface tension ~73 mN/m at room temperature) are far away from the above-mentioned DOD-IJP operating window [15].

The objective of this study is to explore the ink-jet printability and stability (colloidal and over time) of water-based ceramic inks containing different types of micronized pigments dispersed only in pure water with addition of MEG in order to adjust the viscosity. The inks performance was assessed by measuring their physical and rheological properties (particle size, viscosity and surface tension) and testing their zeta potential and sedimentation rate in order to answer to the main questions about the potential use of water-based ceramic inks in place of solvent-based commercial counterparts.

## 2. Experimental

The pathway followed in the development of pigmented aqueous systems was firstly to micronize conventional pigments dispersed in pure water and secondly to assess the physical and rheological properties of aqueous suspensions (pigment particle size, density, surface tension and viscosity) at room temperature. Instead of being an important parameter, temperature was kept constant in order to limit the experimental matrix. Three industrial ceramic pigments were selected: turquoise zircon (TZ, V-doped $ZrSiO_4$), orange rutile (OR, Cr,Sb-doped $TiO_2$), and black spinel (BS, a Co–Cr–Fe–Mn oxide).

The pigment micronization process was carried out by a circulation type agitator bead mill (Labstar LS1, Netzsch, Germany) with a 30 wt.% solid loading of pigments in water and 0.3 mm bead size. The milling conditions were varied between 1000 and 3000 rpm for the rotation speed and between 15 and 120 min for the grinding time, in order to reach the target of around 0.3 μm in terms of median particle size ($d_{50}$). Two types of dispersants, added in the same amount (0.5 wt %), were used: Darvan C–N (DC), an ammonium salt of polymethacrylic acid (Vanderbilt, USA), and Dolapix G10 (DX) a sodium salt of a polycarboxylic acid (Zschimmer and Schwarz, Germany). Particle size distribution was determined by laser diffraction (Mastersizer 2000, Malvern, UK).

Rheological properties were measured at 25 °C with a rotational rheometer (Gemini 2000, Malvern Bohlin, UK), the surface tension was measured with a tensiometer (K100, Krüss, Germany), and the density with a liquid picnometer. Suspension stability over time was studied by measuring the zeta potential dependence on pH, by observing the sedimentation behavior for different grinding times (15, 30, 60, 90, and 120 min) and by evaluating the effect of different dispersants on such behavior. Zeta potential was measured with Zetasizer Nano ZS (Malvern, UK).

In order to increase the viscosity of inks, with the aim to improve the ink performances, 10 wt.% and 20 wt.% of monoethylene glycol (MEG) were added to the water-pigment systems and the viscosity and zeta potentials were measured.

## 3. Results and discussion

### 3.1. Grinding effect

The particle size distribution of micronized pigments varies according to both intrinsic properties of each pigment and milling conditions. Fig. 1 shows the particle size distribution assessed for the inks obtained grinding at 3000 rpm for 2 h in presence of 0.5 wt. % of DC dispersant. The grinding process gave rise to a monomodal particle size distribution for TZ and OR inks and bimodal particle size distribution with a coarser tail for BS ink in the case of more intensive milling conditions. Bimodal distribution is probably due to agglomeration phenomena. The new surface area created by comminution increases linearly with milling time, but different trends in the increase in specific surface area were seen as a function of median particle size, indicative of complex changes in particle size and shape as confirmed by the pigments' microstructure, that were illustrated in the first two parts of this study [7,8].

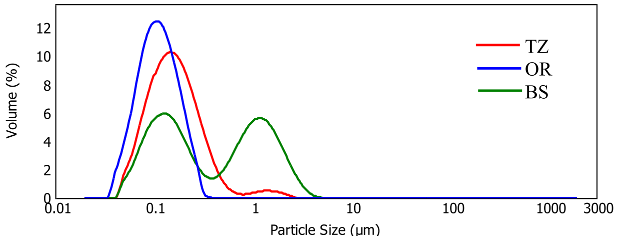


**Fig. 1.** Particle size distribution of the investigated inks prepared under grinding conditions of 3000 rpm, 2 h grinding, 0.5 wt. % DC.