INK TECHNOLOGY FOR DIGITAL DECORATION OF CERAMIC TILES: AN OVERVIEW

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ABSTRACT

The rapid and widespread diffusion of digital printers is turning inkjet printing into the leading technology in ceramic tile decoration. The purpose of this overview is to outline the evolution of ink technology in the last decade and to highlight its role in the development of successful digital printing of ceramic tiles. Indeed, the quality and reliability of inkjet printing on ceramic surfaces largely depend on ink performance. For this reason, the technological requirements of inks extend well beyond the prescriptions of DOD printhead manufacturers, encompassing the storage, interaction with substrate and firing stages. Ink behaviour is theoretically governed by its density, rheological and surface properties in a wide and dynamic range of stress regimes: from the very high stress rates during jetting, drop flight and impact on the tile; moderate-low stress during drop spreading and penetration into the porous substrate; to minimal stress during footprint drying or ink storage. However, the peculiar conditions occurring in ceramic

tile application have gradually led to specific fields for ink properties and performances, where particle size distribution, sedimentation rate, agglomeration phenomena and colour strength are particularly highlighted. This situation has generated original pathways in the criteria of ink formulation and pigment processing, entailing different technological solutions concerning colorants, solvent/carriers and additives, which will be briefly reviewed. Relevant parameters (e.g., viscosity, surface tension, Zeta potential, solids load, fluid mechanics dimensionless numbers: Reynolds, Weber, Ohnesorge) acting on stability over time, jettability, footprint formation and colouring performance will be outlined and discussed to focus on the peculiarities of ceramic ink technology and the challenges for the near future.

1. INTRODUCTION

Drop on Demand Ink-Jet Printing (DOD-IJP) is turning into the leading technology in ceramic tile decoration. The reason for such a rapid and widespread dissemination of inkjet printers stems from several advantages of digital technology: e.g., non-contact decoration, rational ink management, possibility to print textured surfaces and high quality images, more efficient management of the decoration department and greater control on the production line, saving space and cutting costs (shorter time-to-market, elimination of screens, reduction of ink and additive wastes, etc)[1-2].

In this framework, the development of suspensions with appropriate characteristics and behaviours for inkjet printers had a critical role and ink technology has become the key to the success of digital printing[3-4].

The purpose of this overview is to highlight the role of ink technology in the development of successful digital printing of ceramic tiles, by outlining the evolution of DOD-IJP inks in the last decade and reviewing their physical and chemical properties in relation to the technological behaviour during the main stages of ink lifetime (storage, jetting, impact and spreading, drying and firing).

2. EVOLUTION OF INK TECHNOLOGY FOR CERAMIC TILE DECORATION

The first digital printer was launched on the market in 2000, as a result of several years of attempts to print ceramic tiles by continuous and drop-on-demand ink-jet machines. The initial challenge was matching the strict requirements of available printheads, essentially addressed to desktop applications, starting from the existing formulations of pastes for screen and silicon roller printing, which proved to be unsuitable for DOD-IJP, particularly ceramic pigments due to their too coarse particle size distribution. It was soon clear that further ink properties must be kept under control beyond those usually considered in the production of ceramic tiles[5-6].

This step implied a remarkable paradigm shift, moving from simple measurements of particle size (residue on a 40 μm sieve), density (by a pycnometer) and time of flow (by a Ford cup) of suspensions towards a global approach to account for the many phenomena occurring during DOD-IJP on ceramic substrates[7]. Therefore, the past decade was to a large extent spent on making sense of "ceramic" ink: identifying the relationship between ink properties and printhead performance in order to develop appropriate ink formulations encompassing a colorant (dye or pigment), a solvent/carrier and a wide range of possible additives[3].Thus, the most important chemical, physical and technological variables were eventually established and the ink requirements were gradually defined (Table 1). The range of properties to be determined was considerably widened to include: pH, particle size distribution (10 to 0.1 μm), viscosity (by rheometer), surface tension (by pendant drop), stability over time (sedimentation test and Z-potential), electrical conductivity, and behaviour during DOD jetting (high resolution camera). The colouring performance became a major concern, as the chromatic palette of ceramic inks is much narrower than that achievable with conventional pigments[7]. As the amount of ink is constrained by printhead type and tile velocity along the decoration line, the solids loading was stressed from the beginning, with feedback on physical properties (e.g. viscosity) and technological behaviours (e.g. particle agglomeration).

This development was assisted little by the existing know-how on DOD-IJP: no useful information existed on suitable ink batches, as commercial inks used in other sectors were based on organic dyes and solvents, so not directly transferable to ceramic production. On the other hand, the scientific literature was focused on ceramic inks almost exclusively designed for 3D shaping of miniaturized objects by continuous inkjet printing[8-10].

In order to overcome the hindrances coming from the severe constraints posed by printhead manufacturers, an easier approach was pursued to prevent nozzle clogging. The early ink formulations were based on solvent naphtha and dyes, e.g. transition metals octanoates or 2-ethylhexanoates[11]. Other routes proposed pigment suspension in ethanol-methyl ethyl ketone-resin solutions[12] or metal nitrates aqueous solutions corrected by diols, triols and lactams[13].

Phenomenon	Ink property	Ink requirement
Nozzle clogging	pigment particle size	diameter <1 μm
Ink dripping	surface tension	20-45 $mN \cdot m^{-1}$
Ink spreading over the nozzle		
Ink spreading over the tile		
Ink drop size and shape	viscosity	4-30 mPa·s
Ink penetration into the tile		
Ink addressability	density	1.1-1.5 $g \cdot cm^{-3}$
Corrosion of nozzles	pH	5 < pH < 10
Pigment sedimentation	Zeta potential (electrostatic stabilization)	best larger than ±20 mV (water-based inks)

Table 1. Ink properties as required by manufacturers of DOD inkjet printers for ceramic tiles.

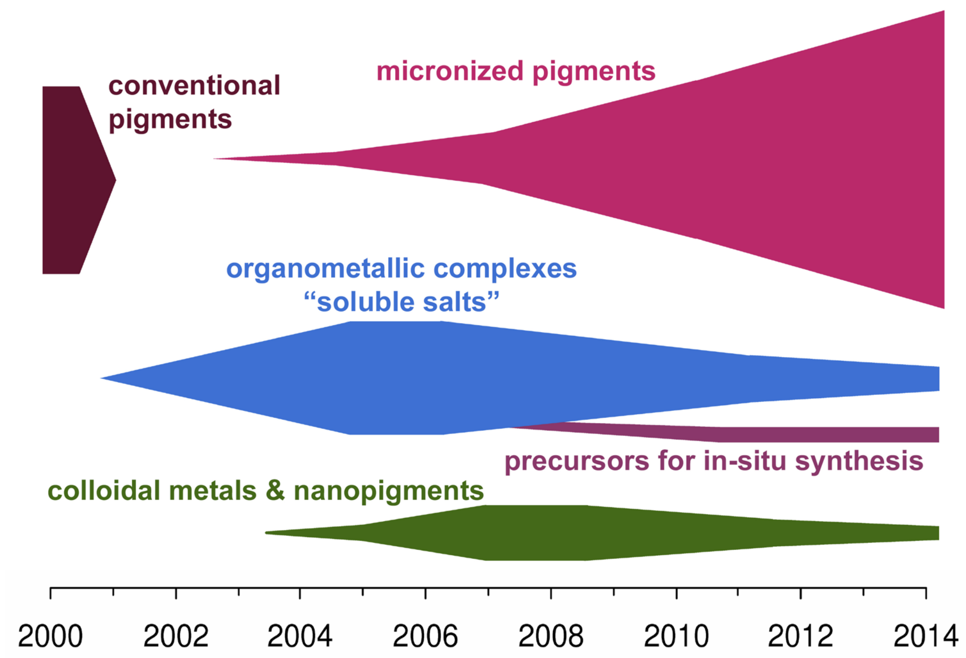

Figure 1. Evolution of DOD-IJP ink technologies for ceramic tile decoration.

The ghost of nozzle clogging and the need to improve ink stability over time promoted the search for technological solutions to get small-sized particles, i.e. submicrometric colorants. These technological trends are summarized in Figure 1, where in reality there is a moving target: at the beginning, the ink-making industry wanted colorants that were able to reproduce as faithfully as possible the pure colours for quadrichromy (cyan, magenta, yellow and black). However, the tile-making industry expectations in terms of colour purity have relaxed remarkably over the last few years, to the point that current inks mostly reproduce pastel colours (i.e. brownish hues approaching magenta, yellow and black, plus a cobalt-based colorant for blue instead of cyan)[7].

Dye-based inks, i.e. containing organometallic complexes (so-called "soluble salts"), were the early choice, leading to several patents[11,13-14], though requiring a great effort to improve their relatively poor colour strength and widen their limited colour palette. A side effect of research in this field has been the development of improved soluble salts able to foster the in-situ formation during firing of small-sized pigments, as in the case of yellow-orange rutile[14-15].

The use of pigmented inks appeared to be the best route to improve colour strength and reproducibility on ceramic substrates[16-17]. However, one issue involved how to obtain suitable ceramic pigments with a submicrometric size: top-down (i.e. milling conventional pigments down to the submicronic range) versus bottom-up approach (i.e. synthesizing pigments directly at the nanometric scale). Indeed, the introduction of micronization technologies was not straightforward: micronizing ceramic pigments is the most energy consuming among grinding processes. Technological transfer of high-energy ball milling from other sectors (e.g., catalyst industry) took years to be accomplished, as a brand new department had to be scaled up (finding the best solutions for the plant, machinery, pre-milling treatments, ink storage and transportation, etc). Processing conditions had to be set up too, overcoming complications stemming from specific requirements that were hard to meet, e.g. working with a target set on the 90th or 99th percentile of particle size curves (to avoid micrometric particles, thus preventing nozzle clogging) instead of the mean size as usual in milling processes.

During the upgrading of the top-down approach, nano-inks based on oxides and colloidal metals were developed[5,17-18]. Although the scientific interest in these inks is still growing[19-20], their diffusion was constrained by manufacturing costs that were too high with respect to micronized inks. In fact, once the high-energy ball milling technology had been successfully transferred to the colorant factories, the production of micronized inks boomed, leading to a global rush to slow down manufacturing costs and ink prices. Nowadays, almost the entire production of DOD-IJP inks for ceramic tile decoration comes from micronization plants.

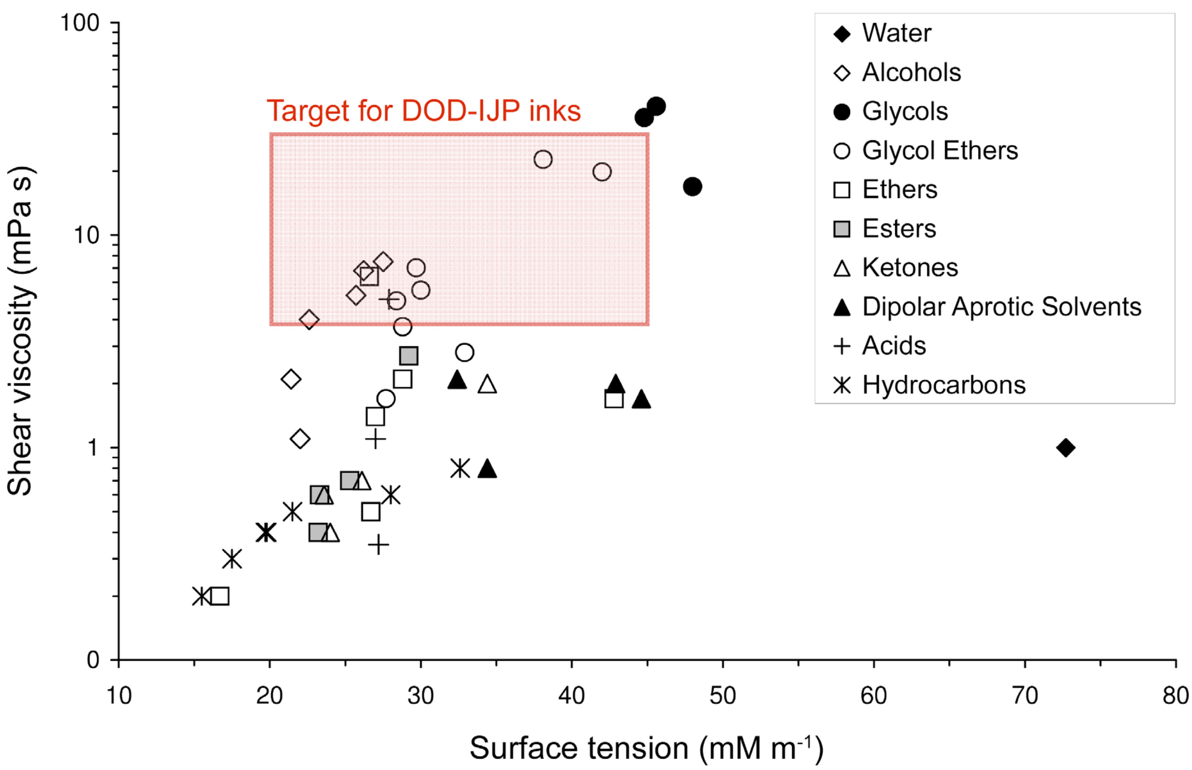

Figure 2. Physical properties (at 25°C) of potential carriers/solvents and the target for DOD-IJP inks for ceramic tile decoration (from Table 1).

3. INK TECHNOLOGY FOR CERAMIC TILES

Ceramic inks must satisfy a wide range of requirements, regarding not only their behaviour during the jetting cycle of the DOD printhead (so-called jettability) but also their performance before and after the printing stage. A suitable behaviour is required during ink storage and transportation (when sedimentation and agglomeration phenomena should be avoided) and particularly in contact with the unfired ceramic substrate, where drop impact, spreading, penetration and drying occur in a very rapid succession, to some extent contemporaneously[21-22]. Ink performance during firing is obviously a key point: colour saturation is pursued by increasing solids loading, while preventing reactions at high temperature between pigments and glaze or body becomes fundamental to keep final colour under control.

At each of these steps, phenomena that may happen are governed by physical and chemical variables that can be used to predict ink performances and to design suitable ink batches. The most important parameters are viscosity, density and surface tension, which in principle dictate the jettability of a given ink:

- a sufficiently low viscosity is necessary to enable the refill of the piezoelectric device reservoir in a very short time (usually around 100 ms) so as to allow the drop ejection out of the nozzle by the pressure pulse imparted by the piezoelectric element;

- surface tension must be low enough to let the drop break away from the nozzle, but high enough to avoid any unwanted dripping from the nozzle;

- density must be high enough to fulfil the requirements in terms of addressability, i.e. amount of ink to ensure the desired colour strength.

The same physical parameters also govern ink behaviour during impact, spreading and penetration.

The recommended values for DOD-IJP inks for ceramic tile decoration are listed in Table 1. These constraints define a window of surface tension versus shear viscosity that represents the first step in ink formulation. The physical properties of the carrier – which usually represents 60% to 70% of the ink mass – act as the starting point: examples of a wide set of different solvents are given in Figure 2. According to this picture, it appears to be easier to fit the DOD-IJP window by using glycol ethers or alcohols with respect to other compounds, for which the use of additives is fundamental, e.g. to boost viscosity using hydrocarbons or dipolar aprotic solvents, or to correct both viscosity and surface tension in the case of glycols or particularly water.

Characteristics	Unit	Type D	Type X
Drop velocity	m s^{-1}	8	6
Nozzle diameter	µm	50	50
Operational frequency	kHz	65	6
Droplet volume	pL	12	6

Table 2. Technological characteristics of archetype printheads considered in the calculation of fluid mechanics dimensionless numbers.

3.1. JETTABILITY

The jettability of ink and its behaviour during impact and spreading over the unfired ceramic substrate can be predicted through the fluid mechanics dimensionless numbers: Reynolds (Re), Weber (We) and Ohnesorge (Oh). The Reynolds number is the ratio of inertial to the viscous forces:

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

the Weber number is the ratio of inertial to surface tension forces:

$$We = \frac{\rho v^2 d}{\gamma}$$

the Ohnesorge number is the ratio of viscous forces to surface tension and inertial forces:

$$Oh = \frac{We^{1/2}}{Re} = \frac{\eta}{\sqrt{\rho \gamma d}}$$

where ρ, η, γ, d and v are the density, viscosity, surface tension, nozzle diameter and droplet velocity, respectively. In order to calculate these dimensionless numbers for digital printers actually used to decorate ceramic tiles, two archetype printheads with different characteristics were considered, taking into account that jettability is characterized by responses such as drop volume, shape, velocity and directionality, which are affected by fire frequency and nozzle geometry (Table 2). In short, type D fires with frequency, droplet speed and volume that are at the upper limit of the industrial practice, while type X operates close to the lower limit.

Jettability can be predicted by a model developed by Stow and Hadfield[23], Duineveld[24] and Derby[25] on the basis of the following equations. An ink drop is formed if the kinetic energy imparted by the piezoelectric element (inducing a pressure wave) is enough to overcome the surface tension: therefore, the ratio of inertial to surface tension forces, i.e. the Weber number, must be We>4. If this kinetic energy is too high ($We^{0.5}Re^{0.25} > 50$) the drop splashes at the impact with the target. On the other hand, drops with desired size and shape are formed if the correct balance of viscosity to surface tension is ensured. This is made possible if the Ohnesorge number is between 0.1 and 1: inks with Oh > 1 are too viscous, resulting unprintable; in contrast, inks with Oh < 0.1 give rise to the formation of satellite droplets and long tails, with detrimental effect on the image quality. Graphic representations of the model are given in two diagrams (Fig. 3): Re-We, modified after Derby[25] and Re-Oh, after McKinley & Renardy[26].

Current industrial inks used to decorate ceramic tiles plot into the field of printable fluids in both models, irrespectively of printhead type, though more or less close to the limit Oh = 1. It would mean that ceramic inks need to be rather viscous, to the point that in some cases they fall outside the recommended field. However, the viscosity and surface tension data of the inks plotted in Figure 3 were determined at 25°C, while the temperatures on the decoration line of a tile-making factory are always significantly higher and often in the 40-50°C range. This increase in temperature affects ink viscosity much more than its surface tension or density, so the Reynolds number will be higher and the Ohnesorge number will be lower than in Figure 3. Therefore, the ceramic inks will likely shift to the centre of the "printable fluid" field of both diagrams once in operation.

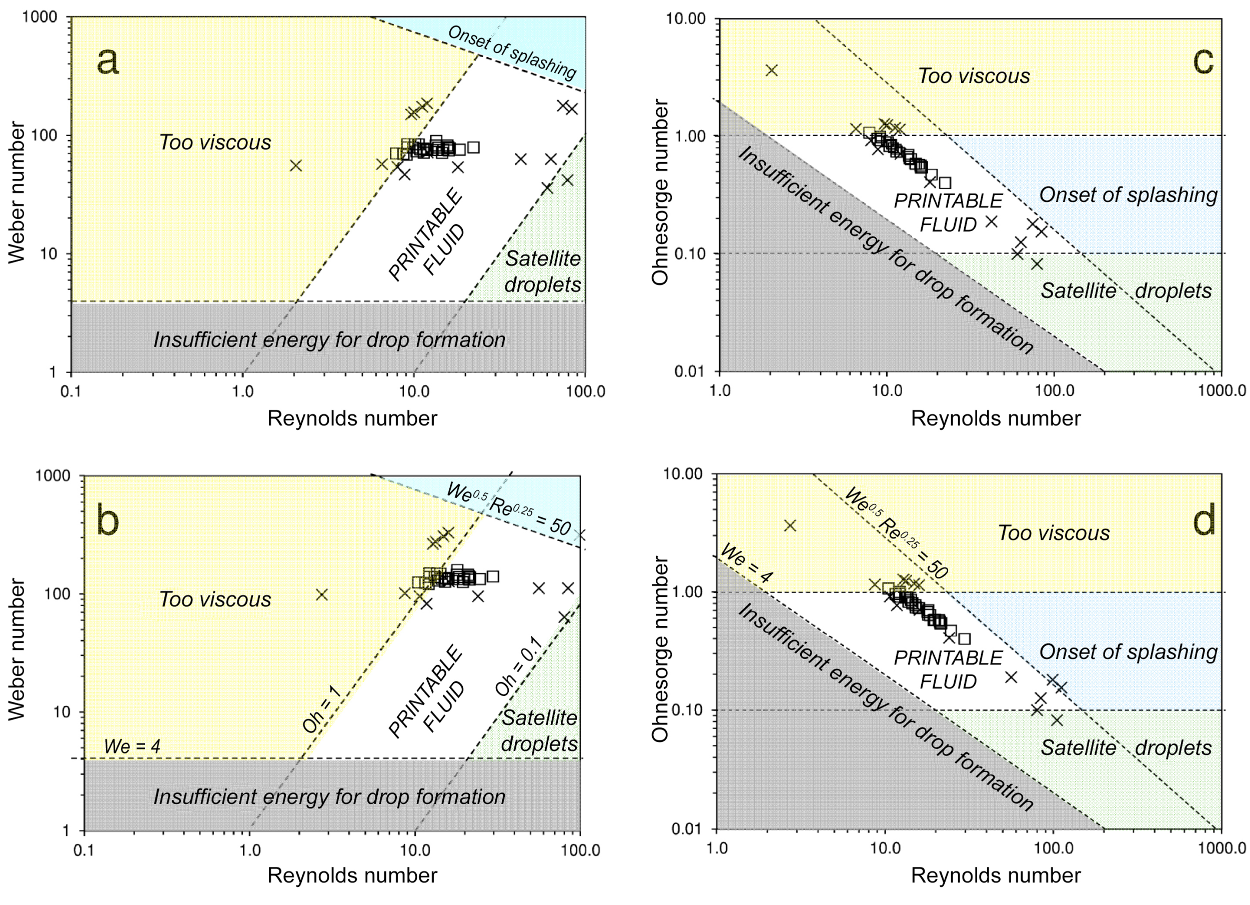

Figure 3. Physical properties of the inks for DOD-IJP of ceramic tiles compared with the jettability as predicted on the basis of the Re-We diagram (modified after Derby[25]) for printhead types X (a) and D (b) or the Re-Oh diagram (after McKinley & Renardy[26]) for printhead types X (c) and D (d). Squares = current industrial inks (2011-2013); crosses = early inks (2003-2008).

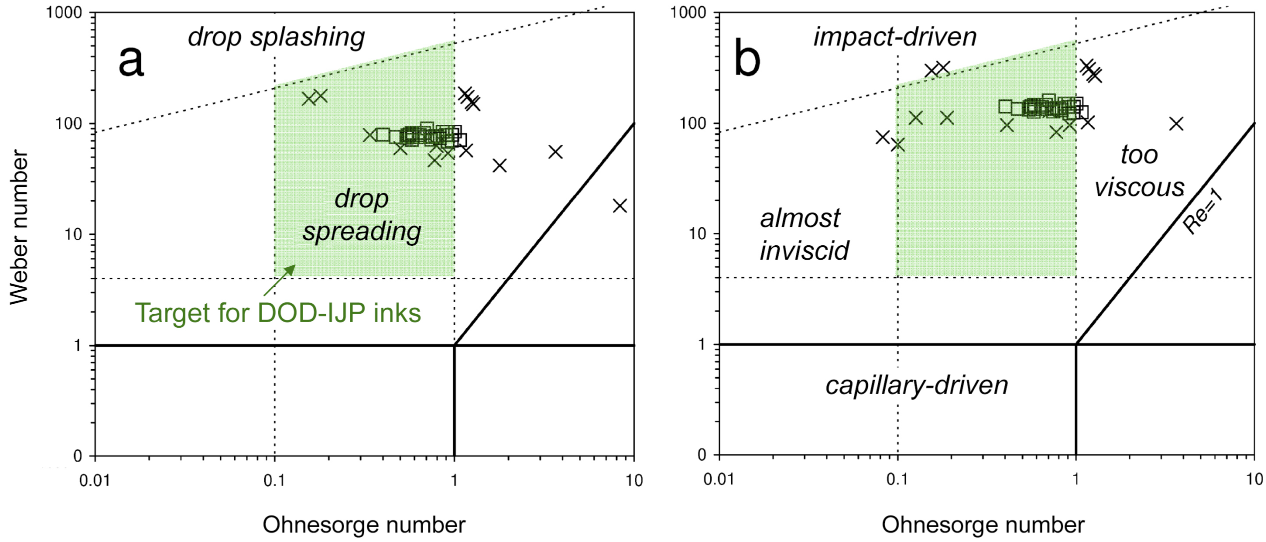

Figure 4. Physical properties of the inks for DOD-IJP of ceramic tiles compared with the behaviour during impact and spreading as predicted on the basis of the Oh-We diagram (modified after Derby[25]) for printhead types X (a) and D (b). Squares = current industrial inks (2011-2013); crosses = early inks (2003-2008).

Interestingly, the points representing "early" inks, i.e. those developed in the period between 2003 and 2008, sometimes fall outside the target field for both printhead types (Fig. 3).

3.2. DROP SPREADING ON THE SUBSTRATE

The behaviour during drop spreading onto the substrate can be outlined by the Oh-We diagram (Fig. 4) modified after Derby[25]. Here the Ohnesorge number is again used to define the field where a proper balance of viscous forces to surface tension and inertial forces occurs ($0.1 < Oh < 1$) while the Weber number is utilized to discriminate the regions where spreading is capillary-driven or impact-driven, according to Schiaffino and Sonin[27], the limit to have drop splashing being $We = 50^{8/5}Oh^{2/5}$. DOD-IJP inks are always in the region of impact-driven phenomena that may range from the desired drop spreading to a drop splashing (Fig. 4). Current industrial inks fit well the target, although some differences can be appreciated between the two printhead types. As in the case of jettability, in some cases the early inks do not satisfy the prescriptions of the model.

The higher temperatures on the decoration line will translate into lower Ohnesorge numbers with minor changes to the Weber numbers. This trend is not expected to affect significantly the drop behaviour during spreading, as the points of current inks will move leftward, thus remaining in the field of drop spreading for both printheads (Fig. 4).

3.3. INK STABILITY OVER TIME

The DOD-IJP inks may have a limited stability over time, just a few weeks in some cases; so, stability became a major concern for the ink-making industry. Overall, the ink stability is mainly affected by particle sedimentation and/or agglomeration phenomena[28]. The velocity of sedimentation (v_s) depends on density (ρ_p) and particle diameter (d) of the pigment as well as on the density (ρ_c) and viscosity (η_c) of the carrier, according to Stokes' law:

$$v_s = \frac{(\rho_p - \rho_c)\, g\, d^2}{18\,\eta_c}$$

where g is the gravitational acceleration. It can be appreciated, by a simulation for current inks and nano-inks (Fig. 5), how the sedimentation rate of particles in the 0.2-0.3 µm range is much lower (about 1/6) than that of particles with size around 0.5-0.6 µm. Furthermore, settling is expected to be contested by the onset of Brownian motion for particle size below 0.5 µm. These arguments strongly support the emphasis on pigment micronization demonstrated by the ink-making industry.

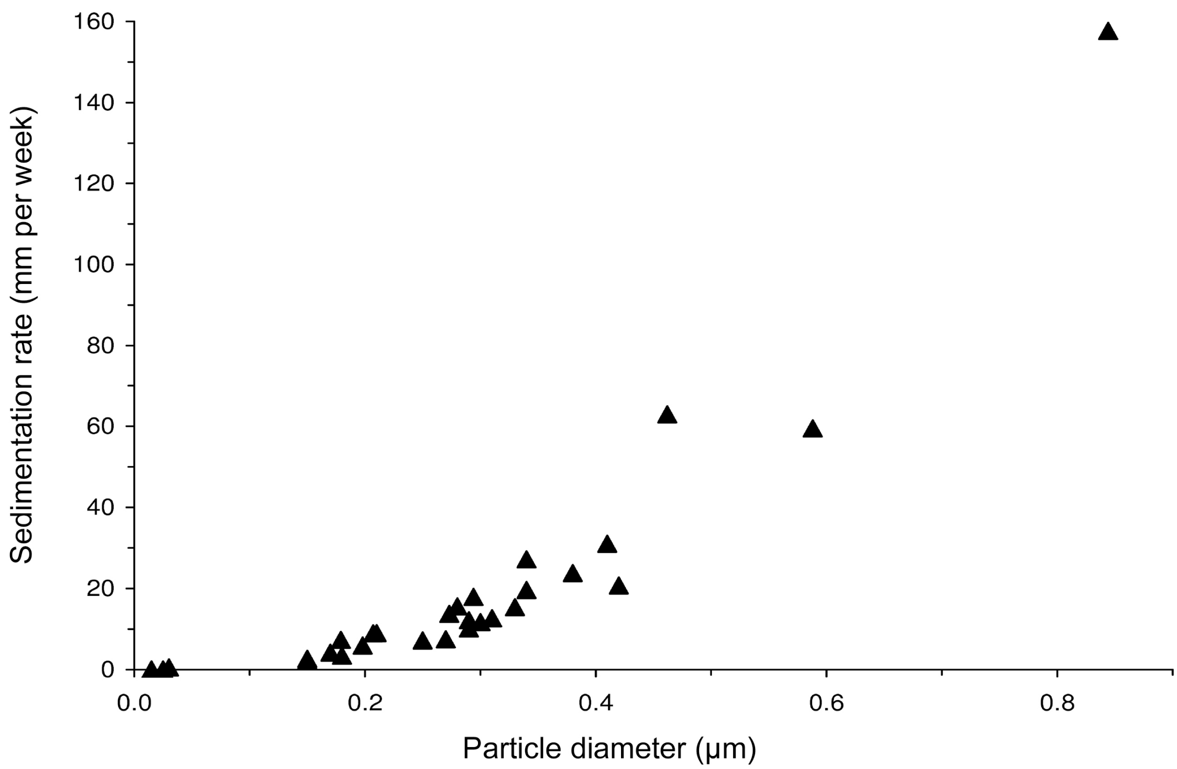

Figure 5. Sedimentation rate as a function of the median particle diameter of pigments, as calculated for current inks and nano-inks[5].

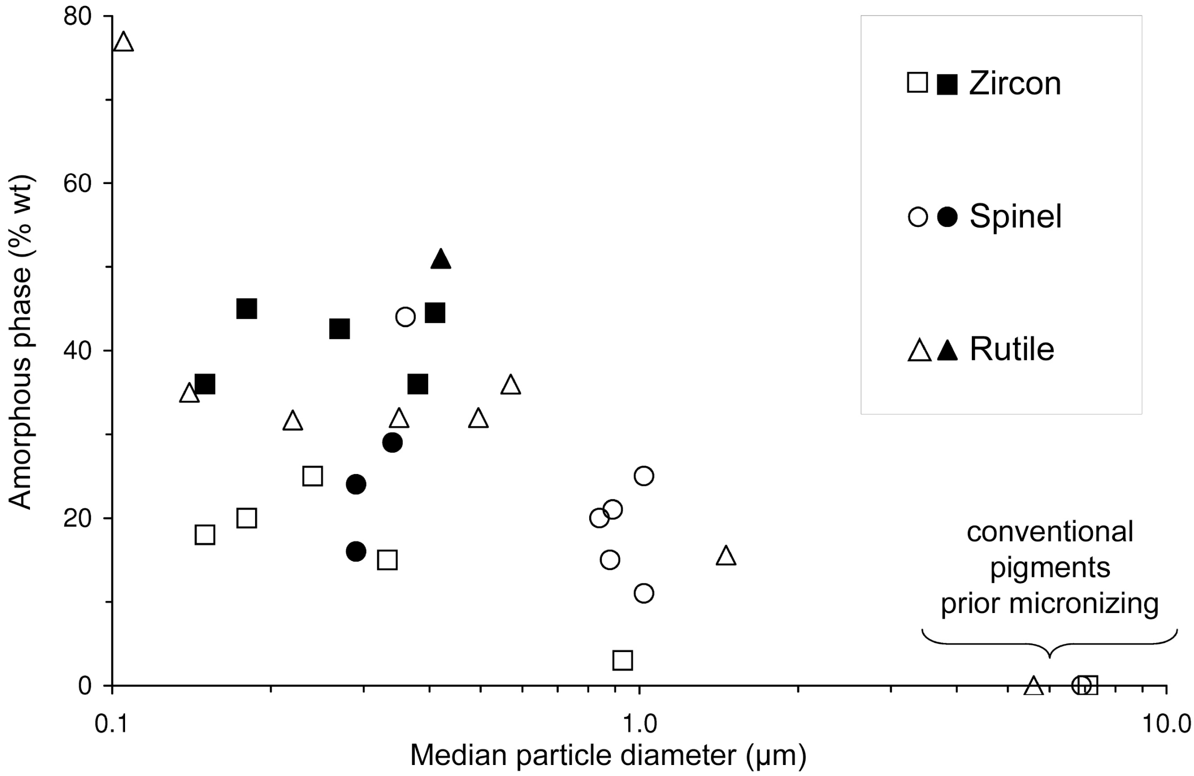

Figure 6. Amount of amorphous phase formed at the expense of the pigment during micronizing as a function of particle size in DOD-IJP inks for ceramic tile decoration. Black symbols: industrial inks; empty symbols: laboratory trials[31].

In principle, as the ink particle size (often <0.5 µm) is much finer than the nozzle diameter (typically 50 µm), no problems of nozzle clogging should occur. However, current inks exhibit a solids concentration in the 5-13% volume range and agglomeration may occur, if attractive forces between particles in suspension overcome the repulsive forces[29-30]. Particle agglomeration and sedimentation are usually countered by improving the stability of suspensions through different strategies aimed at: electrostatic stabilization, steric stabilization or both[16]. A detailed description of these strategies goes beyond the scope of this contribution.

3.4. COLOUR STRENGTH

Overall, DOD-IJP inks are able to reproduce a limited colour space[7]. This is largely the result of faster kinetics of pigment-glaze reactions during firing that originate from the small size and the large specific surface area of micronized pigments.

The chance for widening the chromatic palette by enhancing the colour saturation have already been noted, by increasing the solids load up to 30-40% by weight (pigmented inks) and 10-15% of residue for soluble salts. Therefore, the ink-making industry is following two different approaches to improve the colouring performance:

- searching for new pigment formulations tailored for DOD-IJP, including mixes of colorants (e.g., pigments and dyes) and protective coatings;

- developing technological solutions to reduce the extent of pigment-glaze reactions during firing by utilizing primers, new glaze formulations, and additives.

De todas formas, el pobre poder colorante de las tintas digitales está asociado a fenómenos que todavía se descuidan o no se conocen a fondo, especialmente las modificaciones que experimentan los pigmentos cerámicos durante la micronización y la cocción.

In any event, the poor colour strength of digital inks is related to phenomena that are still neglected or not fully understood, particularly the changes that ceramic pigments undergo during micronizing and firing.

The emphasis on the small particle size to gain advantages in terms of ink stability over time is leading in industrial practice to "overmilling" ceramic pigments, reaching mean diameters down to 200-300 nm (Fig. 5). However, it is not perceived how this processing may induce a conspicuous amorphization with a loss of colorant, generally between 20% and 50% by weight (Fig. 6) as recently outlined[31]. Although the intentional presence of some glassy phase (i.e. frit added to foster pigment adhesion to ceramic surfaces) cannot be ruled out, the amount of pigment in current industrial inks is 70-80% (spinel) or around 50% (zircon) or even less for rutile (i.e. the complementary of the amorphous phase in Figure 6).

Reactions occurring at high temperature during firing may lead to: a) pigment breakdown or melting; b) phase transformation from the crystal structure of pigment to another compound stable in the glaze; c) change in the crystal chemistry of pigment that retains its structure[32]. These reactions are all detrimental to the quality of DOD-IJP, as they change the final colour remarkably.

4. CONCLUSIONS

The outstanding development of ink technology has allowed the widespread diffusion of DOD-IJP to decorate ceramic tiles. However, the rapidity of changes in this field has left behind several open questions that need answering to achieve a better comprehension of the technological behaviours observed in industrial practice. This knowledge is essential to designing new materials and establishing technical solutions for further innovation in the digital decoration of ceramic substrates.

A key point is the setup of models able to predict ink jettability and ink behaviour during impact, spreading and penetration in the green tile on the basis of physical and chemical properties. In this sense, the specific characteristics of ceramic inks must be determined and properly accounted for.

Further investigations are necessary to understand in-depth what happens during pigment micronization, long-term storage of ink, and firing of ceramic tiles. In fact, the extent of phenomena like amorphization and damage of the pigment crystal structure, particle agglomeration over time or pigment-glaze reactions are largely unknown in DOD-IJP inks. This knowledge is fundamental in order to establish appropriate solutions and further develop ink technology for the digital decoration of ceramic tiles.

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