CERAMIC PIGMENTS FOR DIGITAL DECORATION INKS: AN OVERVIEW

M. Dondi, M. Blosi, D. Gardini, C. Zanelli

ISTEC-CNR, Institute of Science and Technology for Ceramics, Faenza (Italy)

ABSTRACT

The field of ceramic colorants is one of the most conservative in tile making. Reduction of cost and impact on health and the environment have been the driving force for innovation in pigment manufacturing, where the main technological goals were fast synthesis routes and minimizing hazardous components and additives. The advent of digital decoration is overviewed with its paradigm shift from colorant to ink. The requirements for ink-jet printing are reviewed: rheological properties, surface tension, zeta potential, sedimentation, drop size and shape, kinetics of penetration, particle size, control of electrical and magnetic properties, stability in organic media, improved colorant strength. As conventional pigments and dyes proved to be unsuitable for digital decoration, colorant manufacturers were forced to upgrade processing (micronizing step for pigments) and to become involved in ink design (improving colorant strength for dyes). By this way, different classes of colorants for digital ink have been developed: organo-metallic complexes, micronized pigments, colloidal metals, nanopigments and reactive sol precursors for in-situ synthesis. The main challenges for ink manufacturers are still the stability over time (sometimes limited to a few weeks) and the gamut (much narrower than that of conventional ceramic colorants). As a matter of fact, typical quadrichromy or hexachromy is still a hard task to be achieved with ceramic colorants and tile makers are often choosing unconventional colour sets based on brown shades. This circumstance is revitalizing the industrial interest towards alternative routes for pigment synthesis (*chimie douce* or bottom-up approach) and technological solutions to improve the colour performance (pigment coating, core-shell structures, use of primers and buffers). Physico-chemical properties of inks, which affect the stability over time, are turning critical with increasing diffusion of digital decoration. From this standpoint, technologies able to control colloidal suspensions and to design hybrid organic-inorganic composites are rapidly gaining interest and application potential.

1. INTRODUCTION

The field of ceramic colorants is probably the most conservative in tile making: almost every pigment and dye have been known for decades (Table I). Pigments are coloured crystals dispersed in glazes or bodies; they must withstand physical and chemical attack from the liquid phase formed during firing. Dyes are substances that during firing dissolve in the liquid phase; they impart colour by diffusing transition elements into glazes and bodies [1-2].

Ceramic colorants passed practically unchanged through technological revolutions, like development of fast firing [3] or through-body decoration of porcelain stoneware [4] despite their drastic variation of firing schedules (particularly higher temperatures) and composition of ceramic matrices (glazes and porcelain stoneware bodies).

In pigment manufacturing, innovation has been essentially driven by the pressure to reduce cost and impact on health and the environment. The main technological advancements have concerned the introduction of fast synthesis routes, e.g. rotary furnaces and roller kilns [5], as well as jet milling [6], to keep manufacturing costs competitive. In order to fulfil the ever stricter requirements about the environmental impact, the number and amount of hazardous components and additives have been minimized [7-8].

This overall trend committed to large-scale production of ceramic colorants has been shaken by the advent of digital decoration. Its rapid spread in tile making is bringing about new requisites for performance of colorants that are changing their criteria of design [9]. The aim of this paper is to overview the impact that ink-jet printing has on current situation and prospect of ceramic pigments and dyes.

Structure	Colour	Formula	Known since (at least)
Bindheimite	yellow	$Pb_2Sb_2O_7$	Babylonia, 6th century BC
Olivine	blue	Co_2SiO_4	Ullmann's Enzyklopaedie der technischen Chemie, 1929
Spinel	blue	$CoAl_2O_4$	
Spinel	black	$(Co,Ni,Fe,Cr,Mn)_3O_4$	
Cassiterite	pink	$(Sn,Cr)O_2$	
Corundum	green	$(Cr,Al)_2O_3$	
Uvarovite	green	$Ca_3Cr_2Si_3O_{12}$	
Malayaite	burgundy	$Ca(Sn,Cr)SiO_5$	
Greenockite	orange-red	$Cd(S,Se)$	Stuckert, Farbenzeit. 1934
Rutile	orange	$(Ti,Cr,Sb)O_2$	Harbert, US Patent 1934
Rutile	tobacco	$(Ti,Cr,W)O_2$	Harbert, US Patent 1941
Zircon	yellow	$(Zr,Pr)SiO_4$	Seabright, US Patent 1947
Zircon	turquoise	$(Zr,V)(Si,V)O_4$	
Zircon	red	Fe_2O_3-$ZrSiO_4$	
Baddeleyite	yellow	$(Zr,V)O_2$	Viehweger, Sprechsaal 1956
Cerianite	red	$(Ce,Pr)O_2$	Olazcuaga, CR Ac Sci 1986
Perovskite	red	$Y(Al,Cr)O_3$	Baldi & Dolen, Patent 1995

Table I. Early industrial application of the main ceramic colorants.

Phenomenon	Ink property	Ink requirement
Nozzle clogging	pigment particle size	diameter <1 μm
Pigment sedimentation	Zeta potential (electrostatic stabilization)	(water-based inks)
Ink dripping Ink spreading over the nozzle Ink spreading over the tile	surface tension	20-45 $mN \times m^{-1}$
Ink drop size and shape Ink penetration into the tile	viscosity	4-40 mPa×s
Ink addressability	density	1.1-1.5 $g \times cm^{-3}$
Corrosion of nozzles	pH	5 < pH < 10
Pigment dissolution	insolubility in organic media	very low
Conduction of electricity	electric conductivity	[1] >1000 $\mu S \times cm^{-1}$ [2] <100 $\mu S \times cm^{-1}$

[1] water-based inks, [2] inks based on organic solvents.

Table II. Phenomena possibly occurring during ink-jet printing, related ink chemical and physical properties and ink requirements for digital decoration.

2. FROM COLORANT TO INK

The growing diffusion of ink-jet printing in ceramic tile making implies for colorant manufacturers a paradigm shift: the emphasis is forced to move from pigment (or dye) to ink, as a consequence of digital production constraints [9]. In fact, digital printers impose very strict requirements for inks, which may be hardly controlled and adjusted on the decoration line, as it happens with conventional technologies, like screen printing or silicon roller printing. Therefore, colorant manufacturers have to be involved in ink design and preparation: the finished product is no longer a pigment or a dye to be added to the ink formulation by the customer, but rather an "engineered ink" encompassing colorant, solvent and usually a lot of additives used to keep chemical and physical properties within the window of values acceptable by ink-jet printers [10-12].

The inks for digital printing must fulfil both:

- stricter requirements for parameters already controlled in conventional decoration (e.g. viscosity, density, sedimentation);
- specific needs of ink-jet printers, such as surface tension, drop size and shape, kinetics of penetration, electrical and magnetic properties.

Every variable is somehow connected with phenomena that occur or may happen during ink-jet printing (see Table II).

These properties can be changed by means of additives or by modifying printing conditions (such as ink temperature). In particular, viscosity and surface tension should be carefully controlled because they strongly affect the fluid dynamics of ink jets. Too viscous inks slow down the flow in printhead channels, the droplet ejection and re-filling of shot-chambers, while high surface tension makes the drop formation hard and may cause the generation of satellite droplets instead of one of the proper size. On the other hand, inks with too low surface tension could give rise to wetting phenomena at the surfaces around the nozzles, dripping effects by gravity from orifices, and do not ensure sufficient stability of droplets during their flight towards the substrate. A useful dimensionless parameter summarizing the effects of the viscous and surface forces on the droplets is the Z number, defined as the ratio between the Reynolds number and the square root of the Weber number [13]:

$$Z = \frac{Re}{We^{1/2}} = \frac{\sqrt{\gamma\, \rho\, a}}{\eta} \qquad (1)$$

where $Re = \frac{\rho\, v\, a}{\eta}$ and $We = \frac{\rho\, v^2 a}{\gamma}$ (2)

where γ , η and ρ are the surface tension, the viscosity and the density of ink, respectively; v is a characteristic velocity of the fluid and a is a characteristic dimension (e.g., the nozzle diameter). It was found that ink-jet printing is effective when the parameter Z has values ranging between 1 and 10 [14].

Depending on the nature of the carrier medium (water or organic solvent) the main physical parameters of inks can be quite different. Typically, the water-based inks have lower viscosities, higher surface tension and higher electrical conductivity than the corresponding solvent-based systems. The solid loadings depend strongly on the size of the dispersed pigment particles, being lower for nanoinks with respect to the micronized ones, on their interactions with the carrier medium and on the chromatic yield of the pigments. However, it should be taken into account that on increasing the solid loading, the viscosity increases and the surface tension decreases; thus, in order to fulfil the aforementioned requirements on fluid dynamics, its value cannot be too high. A suitable colloidal stabilization of the pigment particles allows the solid loading to increase without compromising the performance of ink-jet printers.

As a consequence, the ink for digital printing became a complex system, whose properties are set up for a specific printer, which cannot be adjusted on the decoration line, e.g. by solvent dilution, use of additives or mixing with other ink.

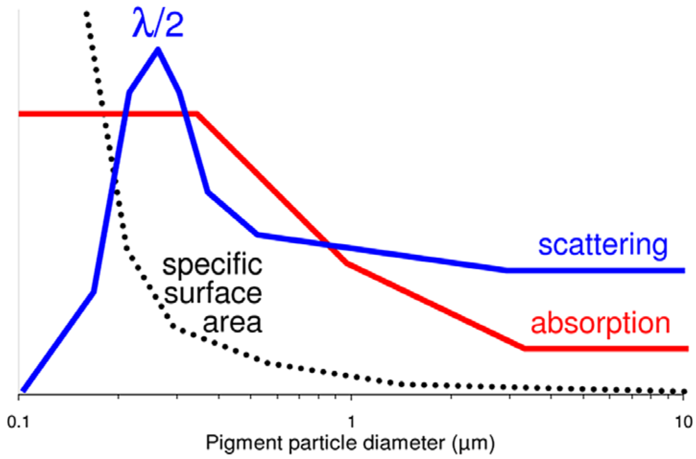

Figure 1. Optical properties (absorption and scattering of visible light) in function of particle size and specific surface area of pigments.

3. COLORANTS FOR DIGITAL INKS

Conventional pigments or dyes have soon proved to be unsuitable for digital decoration, due to occlusion of nozzles or insufficient stability over time and colorant strength. In order to overcome these drawbacks, colorant manufacturers have developed various strategies for pigments (e.g. upgrading the manufacturing process by an expensive micronizing step) and dyes (increasing concentration and introducing primers). Such operations have opened questions like: how do optical properties and colouring performance change in submicronic pigments? Or how to manage complex systems ensuring improved colorant strength?

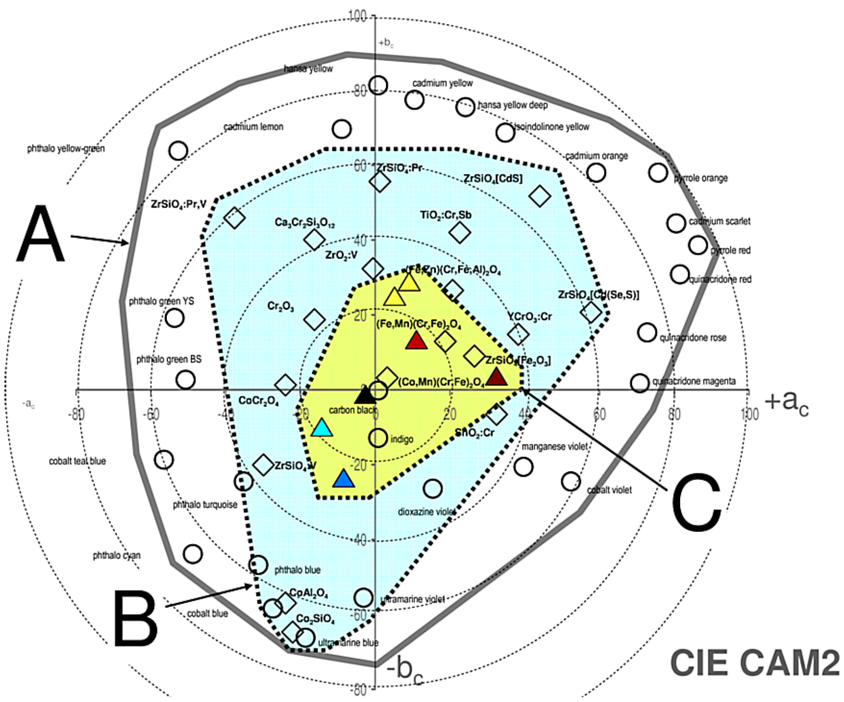

Figure 2. Complete set of colours (gamut) obtainable with organic dyes and pigments (A), conventional ceramic colorants (B), colorants for digital printing (C).

Optical properties change in function of particle size of pigments (Fig. 1). Light absorption increases when pigment dimension decreases until a critical value, as in very small particles absorption is practically constant with size. Light scattering grows as particles turn smaller, until a maximum approximately corresponding to half wavelength: as the visible region is 400-780 nm, best scattering occurs in the 200-400 nm range.

However, the colouring performance cannot be determined on as-synthesized (or as-micronized) pigments, but after the firing process, during which the colorant is involved in a series of chemical and physical reactions, including dissolution in the liquid phase (glaze or body), phase transformation (in another crystalline compound) and change of crystal chemistry (due to diffusion of elements from the glaze). All these phenomena are strongly dependent on the specific surface area of pigments, which rapidly increases when particle size turns submicrometric (Fig. 1). Therefore, looking at the chromatic performance (Fig. 2), it is not surprising if the set of colours (or *gamut*) achievable with colorants for digital printing is much narrower than that obtained by conventional ceramic colorants (which in turn is restricted when compared with the gamut given by organic pigments and dyes).

Along the path from conventional to digital decoration, several colorants have demonstrated to be unsuitable, depending on various factors, especially the effect of particle size on colouring mechanism and interaction with glazes and bodies.

A reduction of particle size has a different effect on colouring mechanisms depending on the colorant type:

- <u>Occluded pigments</u>, e.g. pink $ZrSiO_4[Fe_2O_3]$ and red $ZrSiO_4[Cd(S,Se)]$, cannot be ground, as their core-shell structuring would be destroyed, making the heat-liable pigment enter into contact with the liquid phase of glazes and bodies.
- <u>Idiochromatic pigments</u>, i.e. those where chromophores are main constituents – like in blue spinel $CoAl_2O_4$, green uvarovite $Ca_3Cr_2Si_3O_{12}$ or black spinels – can be micronized as they keep a high concentration of colour centres per unit volume, which can be estimated by frequency of chromophore ions and pigment unit cell volume. Taking the minimum volume accommodating a $Co^{2+}O_4$ centre in $CoAl_2O_4$ equal to 1, it turns to ~2.5 in the case of a $Cr^{3+}O_6$ centre in uvarovite pigments, which therefore are less effective once reduced to submicrometric size.
- <u>Allochromatic pigments</u> – where colour is imparted by dopant ions into an otherwise colourless structure, like yellow zircon $ZrSiO_4$:Pr, turquoise zircon $ZrSiO_4$:V or burgundy malayaite $CaSnSiO_5$:Cr – cannot be micronized without a significant loss of colour strength, as their concentration of colour centres per unit volume is much lower than in idiochromatic pigments. If the minimum volume to accommodate a $Co^{2+}O_4$ centre in $CoAl_2O_4$ is 1, in the case of zircon pigments it turns to ~50 for Pr^{3+} or V^{4+} centres and ~80 for the $Cr^{4+}O_6$ centre in the malayaite pigment.

Another important aspect in digital decoration, involving especially dye-based inks, is the need of colours much stronger than in conventional application of soluble salts. In order to ensure the ink addressability, in terms of colour saturation, two tactics are simultaneously applied: increasing the concentration of transition metal ions in the dye solution on the one side and a stricter control on surface substrate composition, by application of primers, on the other side. While the former is pursuing a larger number of colour centres per unit volume, the latter is aimed at controlling both the ink drop spreading on the substrate and the local chemical environment around metal ions [15-16].

As a matter of fact, colorants for digital printing are less efficient than conventional ceramic ones due to increased liquid phase-pigment interactions. As a consequence, typical quadrichromy or hexachromy is still a hard task to be achieved with ceramic colorants; hence tile makers are often choosing unconventional colour sets based on brown shades. Typical colours (and colorant used) on the market now are: Cyan ($CoAl_2O_4$); Blue (Co_2SiO_4); Magenta (Au); Brown (Zn-Fe-Cr-Al spinels); Pink ($CaSnSiO_5$:Cr); Yellow (TiO_2:CrSb, $ZrSiO_4$:Pr); Black (Co-Cr-Fe-Mn spinels); Green ($CoCr_2O_4$).

There are five routes to obtain colorants for digital printing:

- <u>Soluble salts</u> are solutions of metallo-organic complexes, which behave as dyes diffusing transition elements into the vitreous phase [10-11, 17].
- <u>Micronized pigments</u> are conventional ceramic pigments milled down to submicrometric size (mean diameter between 0.6 and 0.2 µm, i.e. 200 to 600 nm) [18].
- <u>Colloidal metals</u> are suspensions of very fine-grained crystals of noble metals (typically below 50 nm) which impart colour by surface plasmon resonance [12,19].
- <u>Nanopigments</u> are crystalline compounds, which bestow colour analogously to conventional pigments, but directly synthesized at the nanoscale (usually 10-50 nm) [12, 19].
- <u>Precursors for synthesis in situ</u> of nanopigments or colloidal metals are solutions of metallo-organic complexes, analogue to soluble salts, which form coloured crystals directly in the ceramic matrix during firing [20-21].

4. ALTERNATIVE ROUTES FOR DIGITAL PIGMENTS

The limited gamut achievable with digital inks is revitalizing the industrial interest towards alternative routes for pigment synthesis (*chimie douce* or bottom-up approach) and technological solutions to improve the colour performance (protective coatings, core-shell structures, use of primers and buffers, etc.). Moreover, since ink-jet printing technology requires very strict physico-chemical properties of inks, the search for new syntheses, enabling the effective control over colloidal stability, particles size and phase composition, is rapidly gaining interest and application potential.

Actually the bottom-up methods, starting from the compounds at the molecular level, allow a good control on the main synthesis steps, like nucleation and growth, so enabling the achievement of engineered structures. As a result, particle size, shape and composition can be properly tuned in order to fulfil the ink requirements. This approach, involving particle nucleation directly into the solvent, is particularly useful for obtaining nanosized particles in form of suspensions (no need of particle separation and subsequent re-dispersion) avoiding all the disadvantages of grinding. From this standpoint, the fact of dealing constantly with suspensions represents an essential process goal for the development of large-scale productions. Moreover this way is very suitable for increasing the colloidal stability and for promoting the design of hybrid organic-inorganic composites with the addition of organic dispersants or chelating agents. This is a key point, because stability over time is turning critical with increasing diffusion of digital decoration.

In several cases, nanoparticles prepared by bottom-up routes require further reaction during firing to obtain the desired colour, so overlapping the in-situ formation approach. Some syntheses provide already formed particles, but they can be produced only by firing the expected phase or the desired doping.

Nowadays, the main challenge is not only the development of inks with suitable properties, but also the achievement of easily transferable and eco-friendly methods. For this purpose, most researchers and industries are focussing towards green processes, versatile syntheses and *chimie douce* approaches. Very often the alternative routes provide nanopigments in form of colloidal suspensions [22] or thin gel layer [23]. This class of materials has been developed to overcome the typical problems observed with soluble salts or micronized pigments: the former suffer from a limited colour palette, while the latter is frequently affected by dispersion instability, possibly causing sedimentation and nozzle clogging. As a matter of fact, pigment micronizing is an energy-consuming process, during which it is difficult to control the particle size distribution to the extent demanded. Furthermore, grinding introduces contamination and damages the crystal structure, and both adversely affect colour quality. Finally, ground particles tend to have angular shapes; as a result, their suspension rheology is complicated and they may be abrasive [23].

Among bottom-up approaches, polyol synthesis represents a strategic and versatile route for producing nanoinks, enabling the improvement of colloidal stability, the obtainment of several coloured oxides and an easy scale-up of the process [24]. By using the polyol method both metals and oxides can be prepared in a wide and controlled dimension range. The high chelating power of the polyol used as solvent promotes the stability of inks, its reducing power is useful for the production of metals, while its high boiling point allows the obtainment of crystalline structures. A lot of materials can be synthesized by the polyol approach (Table III and Fig. 3) and many of them are usable in ceramic ink-jet printing [12]. Thanks to the high stability offered by polyol suspensions, the solid content of inks can be as high as 20% by weight, so ensuring optimal colour performance.

Although the chelating power of polyol is fundamental in order to improve inks stability, polyol syntheses are frequently added with organic additives both for further increasing the stability over time and for tuning the rheology as needed by the requirements. In this manner, hybrid inorganic-organic core-shell particles can be easily achieved [25].

Material	Ink colour	Mean particle size (nm)
$CoFe_2O_4$	Black	22
$CoAl_2O_4$	Blue	35
$Ti(Cr, Sb)O_2$	Yellow	20
Au	Magenta	15
Cu	Magenta	50

Table III. Some pigments synthesized by polyol method suitable for ceramic inks.

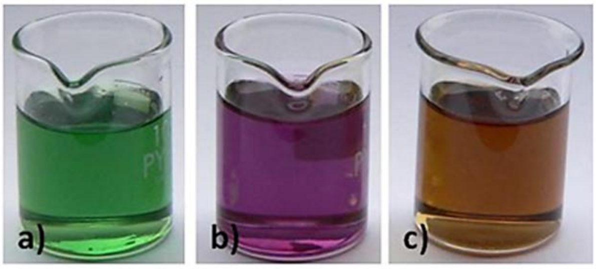

Figure 3. Inks prepared by polyol synthesis: a) TiO_2:Sb,Cr, b) $CoAl_2O_4$, c) $CoFe_2O_4$.

A different route frequently used for the synthesis of ceramic nanoparticles is the sol-gel method [23]. The application of the so-prepared materials as inks in jet printing technology is particularly interesting for water-based formulations, due to the reduced environmental impact and high stability of sols with respect to alcohol-based methods. In this case the sol droplets will form a solid gel on the substrate when some of the water has been lost through evaporation as the drop dries. The gel stage tends to prevent segregation of the different ceramic-forming components in the ink (as is likely to happen when mixed salt solutions dry). The sol-gel inks contain the constituents (precursors), consequently the sol inks do not exhibit the final colour at the printing stage. These precursors react with each other during firing and pigments are formed in situ at that stage.

In addition to the oxides, another class of materials suitable for making inks are metals. Although noble metal nanoparticles have been used to colour glass and lustre glassy coatings for centuries, today they represent an efficient way to bestow yellow to red coloration on glass and transparent glazes [26]. In these materials colour is developed through the mechanism of surface plasmon resonance (SPR) [27] typical of nanoparticles and they have been recently exploited by the ceramic industry through digital decoration techniques [11-12, 19]. Noble metal nanoparticles can be synthesized through different wet chemical methods; in any event, it can be very interesting to focus on aqueous methods. Recently, a green synthesis concerning the production of noble metal nanoparticles in water media, involving low hazardous reagents, has been patented [28]. In this case, the reduction of precursors salt by glucose provides metal nanosuspensions with high solid concentration and excellent stability over time. In addition, the high versatility of the process enables the easy production of inorganic core-shell or alloy nanostructures, e.g. AuAg and AuCu, with the chance of tuning the colour shade (Figs. 4 and 5).

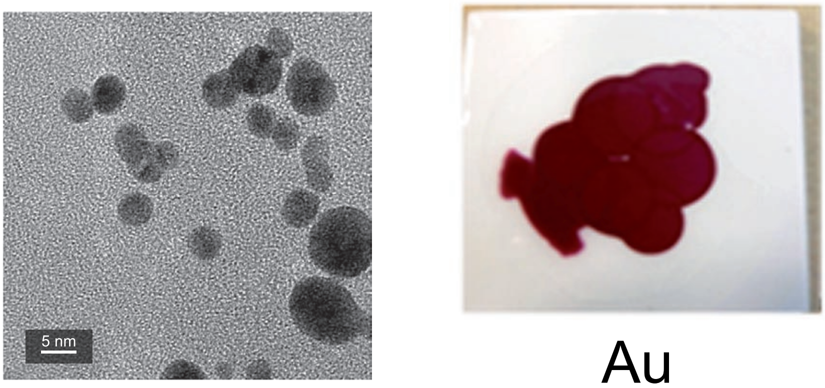

Figure 4. TEM analysis of gold nanoparticles synthesized by a water-based green method (a); gold inks applied on a glazed porcelain stoneware (b).

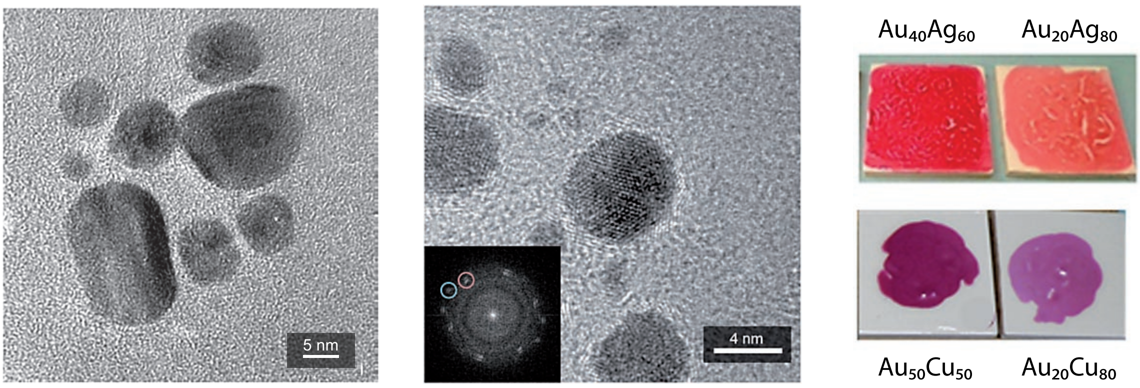

Figure 5. TEM analysis of a) sample $Au_{40}Ag_{60}$ core-shell; b) sample $Au_{20}Cu_{80}$ alloy; c) bimetallic inks applied on glazed porcelain stoneware.

Other suitable methods for ink-jet printing involve the use of primers dropped before the chromophore agents; in this case, the primers are fluid glazing materials followed by the injection of hydroalcoholic solutions of metal salts. The colour is observed only after firing for reaction of salts and glaze at high temperature [29].

5. CONCLUSIONS

The process innovation from conventional to digital techniques in ceramic tiles decoration is driving new chances also to achieve product innovation. The pressure coming from higher expectations for colorant performance and stricter controls on both materials properties and synthesis mechanisms is turning ceramic pigments and dyes for digital printing into engineered products. This circumstance is opening the way for further innovation focussing on functionalized tiles with improved surface performance.

REFERENCES

[1] Eppler RA. Colorants for ceramics. En: Kirk RE, Othmer DF, editores. Encyclopedia of chemical technology, Wiley, New York, 1998, 8, 877–892.

[2] Italian Ceramic Society, Colour, Pigments and Colouring in Ceramics. SALA, Módena, 2003.

[3] Dondi M., Clay materials for ceramic tiles from the Sassuolo District (northern Apennines, Italy). Geology, composition and technological properties. Appl. Clay Sci., 1999, 15, 337-366.

[4] Ferrari, A.M., Leonelli C., Manfredini T., Miselli P., Monari G., Pellacani G.C., Colouring effects of synthetic inorganic cobalt-pigments in fast-fired porcelainised stoneware tiles, Ind. Ceram., 1998, 18, 1, 7-11.

[5] Janz H., Rodi F., Soppe A., Rademachers J., US Patent, 1987, 4629500.

[6] Polke R., The relevance of particle measurement technology to process engineering. Part. Part. Syst. Charact., 1993, 10, 86-91.

[7] Llusar M., Vicent J.B., Badenes J., Tena M.A., Monrós G., Environmental optimisation of blue vanadium zircon ceramic pigment. J. Eur. Ceram. Soc., 1999, 19, 2647-2657.

[8] Muñoz R., Masó N., Julián B., Márquez F., Beltrán H., Escribano P., Cordoncillo E., Environmental study of Cr_2O_3–Al_2O_3 green ceramic pigment synthesis. J. Eur. Ceram. Soc., 2004, 24, 2087-2094.

[9] Hutchings I., Ink-jet printing for the decoration of ceramic tiles: technology and opportunities. Actas de QUALICER, 2010, 1-16.

[10] Loria A.M., Tai L., US Patent, 1995, 5443628.

[11] Garcia Sainz J., Benet Garcia C., Fenollosa Romero J.L., Querol Villaba A.M., Secrest, P.C., US Patent, 2002, 6402823 B1.

[12] Gardini D., Dondi M., Costa A.L., Matteucci F., Blosi M., Galassi C., Baldi G., Cinotti E., Nano-sized ceramic inks for drop-on-demand ink-jet printing in quadrichromy. Journal of Nanoscience and Nanotechnology, 2008, 8, 1979-1988.

[13] Fromm J.E., Numerical calculation of the fluid dynamics of drop-on-demand jets. IBM J. Res. Develop., 1984, 28, 322-333.

[14] Derby B., Reis N., Seerden K.A.M., Grant P.S., Evans J.R.G., Freeform fabrication of ceramics by hot-melt ink-jet printing. Mater. Res. Soc. Symp., 2000, 195-201, San Francisco, USA.

[15] Savorani B., Tomasi C., Influence of mineralisers on the development of colours in porcelain stoneware. Ceram. Inf., 1992, 312, 152-159.

[16] .S.R. Krishna Prasad a, A. Venumadhav Reddya, P.K. Rajesh b,P. Ponnambalamc, K. Prakasan, Studies on rheology of ceramic inks and spread of ink droplets for direct ceramic ink jet printing. J. Mater. Process. Technol., 2006, 176, 222–229.

[17] Vignali G., Guizzardi F., Canto E., Bernardi I., Giorgi M., EU Patent 2009, EP 2 231 794 B1.

[18] Verucchi D., Cavedoni M., Pigmented ceramic inks. World Ceram. Rev., 2011, 91.

[19] Cavalcante P.M.T., Dondi M., Guarini G., Raimondo M., Baldi G., Colour performance of ceramic nano-pigments. Dyes and Pigments, 2009, 80, 226-232.

[20] Hohemberger J.M., Nebot-Diaz I., Escribano P., Carda J.B., Development of a black pigment without cobalt "in situ", with a spinel structure. Brit. Ceram. Proc., 1999, 60, 377-378.

[21] Gargori C., Cerro S., Galindo R., Monrós G., In situ synthesis of orange rutile ceramic pigments by non-conventional methods. Ceram. Int., 2010, 36, 23-31.

[22] Blosi M., Albonetti S., Gatti F., Dondi M., Migliori A., Ortolani L., Morandi V., Baldi G., Au, Ag and Au-Ag nanoparticles: microwave-assisted synthesis in water and applications in ceramic and catalysis. NANOTECH 2010, 1, Chapter, 352-355, Anaheim, USA.

[23] Atkinson A., Doorbar J., Hudd A., Segal D.L., White, A., Continuous ink-jet printing using sol-gel "Ceramic" inks. J. Sol-Gel Sci. Technol., 1997, 8, 1093-1097.

[24] Blosi M., Albonetti S., Dondi M., Martelli C., Baldi G., Microwave-assisted polyol synthesis of Cu nanoparticles. J. Nanoparticle Res., 2011, 13, 127-138.

[25] Izu N., Shen R., Shin W., Itoh T., Nishibori M., Matsubara I., Preparation of core-shell type cerium oxide/polymer hybrid nanoparticles for ink-jet printing. J. Ceram. Soc. Japan, 2009, 117, 769-772

[26] Colomban P., The Use of Metal Nanoparticles to Produce Yellow, Red and Iridescent Colour, from Bronze Age to Present Times in Lustre Pottery and Glass: Solid State Chemistry, Spectroscopy and Nanostructure. J. Nano Res., 2009, 8, 109-132.

[27] Moores A., Goetmanns F., The plasmon band in noble metal nanoparticles: an introduction to theory and applications. New J, Chem., 2006, 30, 1121-1132.

[28] Blosi M., Albonetti S., Dondi M., Baldi G., Barzanti A., Patent WO, 2010, 100107 PCT/EP2010/052534.

[29] Kabalnov A.S., Johnson L.E., Wenzel D.E., US Patent, 2001, 7270407 B2.