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NANO-SIZED CERAMIC INKS FOR INK-JET PRINTING

Nano-sized ceramic inks, suitable for ink-jet printing, have been developed for the four-colours process. Stable sols of different pigment composition have been prepared and their chemico-physical properties were tailored for the ink-jet application. The nano-sized inks investigated behave satisfactorily in preliminary printing tests on several unfired industrial ceramic tiles, developing saturated colours in a wide range of firing temperatures.

Increasing the aesthetic value of consumer products turned to be pivotal, especially in ceramic manufacturing. Ink-jet printing is a non-impact method based on projecting ink droplets onto a surface [1]. In the drop-on-demand (DOD) printers, ink droplets are ejected, only when required, by the application of an electrical signal on a piezoelectric actuator that squeezes out the droplets [1-2].

Many features of ink-jet printing technology make it interesting for decoration of ceramic products. As increasing image resolution is requested, the fact that ink-jet printing involves the smallest droplet volume amongst the decorating technologies allows both a better control of image quality and to get customized products at admissible costs. This is especially true when the quadrichromy process is used, implying four basic colours: cyan, magenta, yellow and black. In fact, the change of the image is simply obtained by changing the software input, without any substitution of mechanical parts, as it happens in the other decoration technologies.

Besides ink-jet printing has been applied to ceramic decoration since a few years, it does not turned to be yet a common technology in tilemaking [3]. This delay time is due to the severe requirements of both ceramic pigments and inks. In particular, colorants for ceramics must be highly refractory, withstanding the chemical corrosion of liquid phases during firing of bodies or glazes, and exhibit suitable optical characteristics. On the other hand, the quality of the ink-jet image depends on the ink properties (viscosity, surface tension) and substrates (composition, porosity) as well as their interaction (wettability, spreading, penetration) [4]. In any case, the control and optimisation of the ink physical properties, such as viscosity and surface tension, are crucial points [2, 4]. Ink viscosity must be low enough to allow a fast flow through the nozzles, under the pressure gradient of piezoelectric actuator, and to ensure the penetration in the porous substrate. Surface tension must be in the 35-45 $mN \cdot m^{-1}$ range to avoid ink spreading over the nozzle or any spilling out of the orifice by gravity [1]. At present, ink-jet printing on ceramic tiles is carried out by using either organometallic dyes (the so-called *soluble salts*) or conventional ceramic pigments ground down to submicrometric sizes. Soluble salts suffer for a limited colour palette and insufficient chromatic saturation; furthermore, their use brings about both health and environmental attention. Micronized pigments cause nozzle clogging and dispersion settling; moreover, a loss of colour strength occurs in respect of the starting pigments. These problems are overcome by using nano-sized ceramic inks (*nano-inks*) i.e. dispersions of nanometric particles in a liquid organic vehicle, that increase both image quality and reliability of ink-jet printing systems.

Experimental

Nano-inks were prepared by Cericol in the form of suspensions of ceramic oxides or metals synthesized in an organic medium. The syntheses were pursued by a specifically modified polyol procedure in which the metal precursors are dispersed in glycol and the batch heated over 150 °C [5]. The particle size distribution of pigment dispersed in the ink was appraised by dynamic light scattering (DLS), transmission electron microscopy (TEM) and scanning electron microscopy equipped with a field emission gun (SEM-FEG and STEM). The pigment phase composition was determined through high temperature X-ray powder diffraction (HTXRPD). The shear viscosity of nano-inks was measured by a stress-controlled rotational rheometer equipped with a plate-plate geometry increasing the temperature from 25 to 85 °C.

The surface tension of nano-inks was determined with an optical device provided with a CCD video camera. Pendant drop method was used to determine the dependence of surface tension of nano-inks on temperature, it was measured in a thermal chamber from 25 to 70 °C.

The ζ-potential of pigments was measured by an electroacoustic technique based on the measure of the Electrokinetic Sonic Amplitude (ESA) signal generated in the colloidal systems.

The electrical conductivity of nano-inks was measured with a dip conductivity probe. The optical absorption spectra were recorded using a UV-visible-NIR spectro-photometer on inks diluted with glycol. The technological behaviour was assessed by applying the nano-inks on several unfired substrates for ceramic tiles and firing in industrial roller kilns at the temperatures from 1,100 to 1,200 °C and measuring the colour of ceramics by diffuse reflectance spectroscopy (DRS).

Results and discussion

Particle size distribution

The pigments contained in the nano-inks have sizes in between 20 and 80 nm, as measured by dynamic light scattering (DLS) or in the 10-40 nm range according to microscopic observations (Fig. 1 and Table).

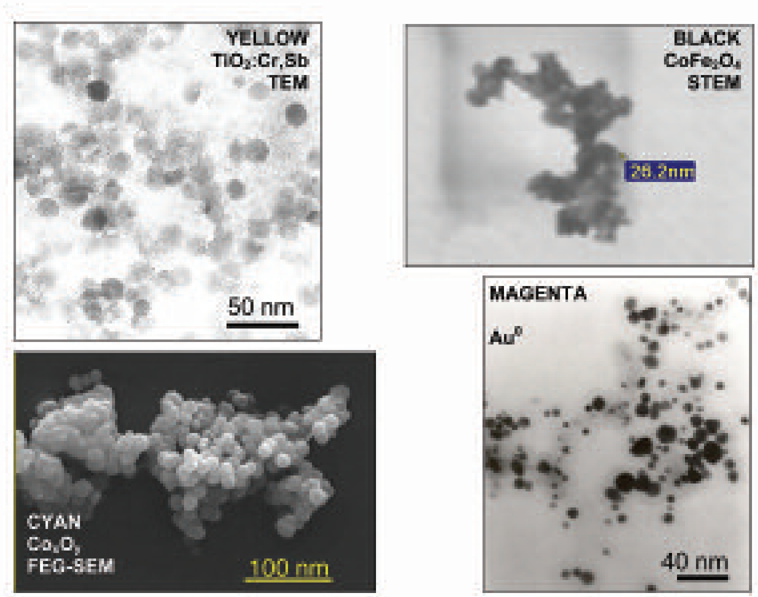

Fig. 1 - Photomicrographs of the pigments dispersed in nano-inks

Table - Physical and chemical properties of nano-inks					
Property	**Unit**	**Nano-ink**			
		Cyan	**Magenta**	**Yellow**	**Black**
Pigment stoichiometry		$Co_{1-x}O$	Au^0	TiO_2:Sb,Cr	$CoFe_2O_4$
Ink density	$g \cdot cm^{-3}$	1.14	1.12	1.26	1.23
Solid loading	vol.%	0.74	0.06	3.47	3.05
Particle size (DLS)	nm	n.d.	74	19	22
Particle size (microscopy)	nm	10÷20	20÷40	10÷20	20÷30
Viscosity (25 °C)	mPa·s	38.8	42.0	185	56.7
Temperature for optimal viscosity (35 mPa·s)	°C	30	30	72	36
Surface tension (25 °C)	$mN \cdot m^{-1}$	44.0	37.3	40.8	38.8
ζ-potential	mV	4.4	91.1	20.3	47.5
Electric conductivity	$\mu S \cdot cm^{-1}$	10	1,420	88	15

Phase composition

The Black ink consists of spinel-like cobalt ferrite ($CoFe_2O_4$). The Magenta ink contains metallic gold. The pigment in the Cyan ink is a mixture of cobalt oxides with different oxidation states. The Yellow ink is peculiar, bearing anatase at room temperature, that during heating transforms in rutile in between 500 and 600 °C.

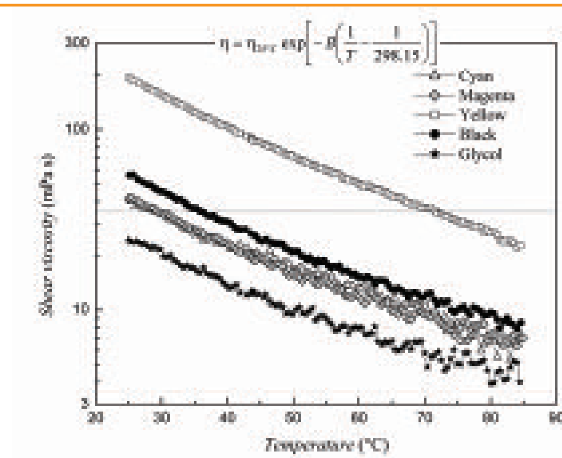

Fig. 2 - Dependence of viscosity on temperature for nano-inks and glycol. In the inset, γ 25°C is the ink viscosity at 25 °C, B is a parameter characteristic of each ink and T is the absolute temperature

Shear viscosity

The ink flow in the printhead channels must be very fast to permit a quick ejection of droplets from nozzles as well as the subsequent filling of shot-chambers. Both high flow velocity - about 20 $m \cdot s^{-1}$ [2] - and small diameters of nozzles (typically 20-120 μm) give shear rates around $10^5 \div 10^6$ s^{-1}. In such flow conditions, the ink viscosity must be as low as possible. Nano-inks have shown a Newtonian behaviour with viscosities ranging from about 40 to 200 mPa·s (at 25 °C). As the cutoff value for viscosity is about 35 mPa·s, the nano-inks are heated in the printing device prior ejection, as the viscosity roughly decreases with the same exponential decay for all the inks, following, in first approximation, an Arrhenius-like exponential law (Fig. 2). It is necessary to heat the Cyan and Magenta inks to 30 °C, the Black ink to 36 °C and the Yellow ink to 72 °C.

Surface tension

The surface tension is the other physical parameter to control in order to obtain printable inks. In particular values lower than 35 $mN \cdot m^{-1}$ are not advisable to avoid ink wetting of the surfaces around nozzles or dripping effect by gravity and to ensure a sufficient stability of droplets during their flight towards the substrates [1]. On the other hand, the surface tension has to be low enough

Riassunto

Inchiostri ceramici nanometrici per applicazioni in stampa a getto d'inchiostro

Nel corso di questo studio sono stati sviluppati inchiostri ceramici nanoparticellari utilizzabili per la stampa a getto di inchiostro in quadricromia. Sols stabili a diverso contenuto di pigmento sono stati preparati mediante sintesi in polioli e ne sono state ottimizzate le proprietà chimico-fisiche in funzione dell'applicazione ink-jet. Gli inchiostri studiati hanno mostrato un comportamento soddisfacente in test preliminari di stampa, sviluppando colori saturi in un ampio intervallo di temperatura.

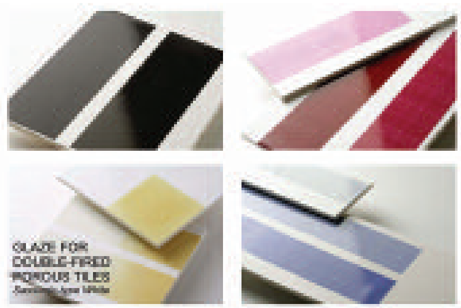

Fig. 3 - Preliminary tests of ink-jet printing of ceramic tiles

to permit the droplets formation under the deformation of the piezoelectric actuator [4]. The surface tension slightly decreases for increasing temperature in every inks, so that values over 35 mN·m^{-1} are retained at the temperatures needed to achieve the optimal viscosity for ink-jet printing.

Printability

The fluid dynamics of DOD jets is controlled by both viscous and surface forces acting on the droplets, which can be grouped in a dimensionless number, *Z*, defined as the ratio between the Reynolds number and the square root of the Weber number:

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

where γ, η and ρ are surface tension, viscosity and density of ink, respectively; *a* is a characteristic dimension, e.g. the diameter of nozzles [6]. On the basis of numerical simulations, it was found that the ink-jet printing is effective when the parameter *Z* is in between 1 and 10 [7] as, when *Z* is lower than 1, the viscosity is too high for droplets ejection while, when *Z* is higher than 10, the droplets formation is hindered and a large number of small-sized droplets are produced instead of the designed size. On this simple criterion, assuming a nozzle diameter of 50 µm and neglecting the dependence of density on temperature, it is found that, at the cutoff temperatures for optimal viscosity, all inks are printable (having $1<Z<10$).

Stability

The nano-inks are characterized by positive values of ζ-potential that ensure an excellent electrostatic stabilization (e.g. Magenta and Black inks). Otherwise, a steric stabilization mechanism is claimed for the Cyan ink, whose low ζ-potential does not match its good colloidal stability, as the dynamic mobility argument (phase angle) increases with frequency, implying the presence of organic units or polymers adsorbed on the surface. The ζ-potential value depends also on the occurrence of other species, that may come from the synthesis (*e.g.* water, surfactants).

Electrical conductivity

Electrical conductivity values are in the 10-100 µS·cm^{-1} range but for the Magenta ink, whose high conductivity is typical of a metal dispersion when the particle size is over 10 nm.

Ink-jet printing tests

Preliminary testing was performed applying the four nano-inks on unfired ceramic substrates: bright glaze for double-fire tiles and body for porcelain stoneware unglazed tiles. After firing in industrial roller kilns, at temperatures as high as 1,100 °C (bright glaze) and 1,200 °C (porcelain stoneware) the decorated tiles exhibit vivid and saturated colours reasonably corresponding to the quadrichromy requirements (Fig. 3).

Conclusions

Highly stable ceramic inks were synthesized by the polyol technique obtaining metallic or oxide pigments, actually nano-sized (20-80 nm), which develop vivid colours approaching the yellow, cyan, magenta and black required for the quadrichromy printing process. Particle size distribution, phase composition, shear viscosity, surface tension, and ζ-potentials proved these inks to fulfil the requirements for the DOD ink-jet printing, at most adjusting the ink temperature prior ejection. Preliminary testing demonstrates that these nano-inks are fully suitable for the four-colours ink-jet printing on ceramic tiles. Further work will attempt to optimise the ink-jet application, trying to understand which phenomena occur and mostly influence the penetration kinetics.

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