Ink-jet printing of micro-emulsion TiO₂ nano-particles ink on the surface of glass

Maryam Hosseini Zori a, Atashe Soleimani-Gorgani b,∗

a Department of Inorganic Pigment and Glazes, Institute for Colour Science and Technology, PO Box 16765654, Tehran, Iran
b Department of Printing Science and Technology, Institute for Colour Science and Technology, PO Box 16765654, Tehran, Iran

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Abstract
A self-cleaning ceramic ink that contains nano-titanium dioxide was formulated. The nano-titanium dioxide was generated through the micro-emulsion process. The physical properties such as surface tension and viscosity of the prepared ink were evaluated. The ink-jet printing was carried out with an Epson Stylus Photo P50 printer on microscope glass slides. The print was set to 1, 3 and 5 runs in order to evaluate variations in wettability and resulting self-cleaning properties with varying thicknesses of the printed film. Following initial drying of the printed self-cleaning microscope glass slides; they were heat-treated at 400 °C. The SEM analysis and contact angle measurements of the printed microscope glass slides were carried out. The thicknesses of the raw printed self-cleaning ceramic inks were increased linearly with the number of printing runs. Ultimately, the results demonstrated that the direct ceramic ink-jet printing method can be used to produce a self-cleaning film on the glass.

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Keywords: Ink-jet printing; Nano-TiO₂; Self-cleaning; Micro-emulsion; Ink

1. Introduction
Solid freeform fabrication (SFF) is an important developing technology that enables the fabrication of custom objects directly from computer data. Since the 1990s, this technology has been used in rapid forming processes, which can also be used in fabrication of glass and ceramics. A variety of processing operations such as stereo-lithography,1 selective laser sintering,2,3 laminated object manufacture,4,5 3-D printing6–8 and ink-jet printing9–11 have been modified for compatibility with this process.

Ink-jet printing has evolved from printing text and graphics where it started originally, to a tool for rapid manufacturing as well as other uses. It is a non-contact printing technique that is able to deposit droplets of a variety of materials, such as ceramic, on pre-determined points on a substrate; this is normally controlled via a computer program. There are two types of ink-jet printers, continuous and drop on demand, which have different ink requirements. The drop-on-demand direct ceramic ink-jet printing (DCIJP) is often fully automated from design to the output stage with minimal human interference and can be used to fabricate components with unique characteristics.12 These features are difficult to realize using conventional methods. Furthermore, in direct ceramic ink-jet printing, unlike conventional methods, chemical waste is significantly reduced as ink-jet printers can print exclusively on the desired location.

Recently, this technique has been developed for the fabrication of small ceramic components,13,14 thin ceramic walls,15,16 thick ceramic films17–19 and ceramic microdot arrays.20,21

In drop-on-demand direct ceramic ink-jet printing (DCIJP) ceramic ink, which contains well dispersed ceramic powder in a liquid carrier, passes through the printer nozzles (40–100 μm in diameter) at high speed.22,23 Droplets of ceramic ink are forced towards the substrate where they spread on impact to produce a layer with a thickness not greater than 1 mm.2 The size and shape of the image can be easily controlled by the computer.

The aim of this study is to prepare a self-cleaning ceramic ink to reduce the cleaning costs of window glass. Self-cleaning
Table 1
Percentage by weight and chemical formulation of materials used.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formulation</th>
<th>Weight percent</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-titanium dioxide (anatase) TiO₂</td>
<td>40</td>
<td>Photocatalyst</td>
<td></td>
</tr>
<tr>
<td>Dioctylsulphosuccinate sodium salt C₂₀H₃₇NaO₇S</td>
<td>8</td>
<td>Surfactant</td>
<td></td>
</tr>
<tr>
<td>Cyclo-hexane</td>
<td>C₆H₁₂</td>
<td>26</td>
<td>Immiscible phase 1</td>
</tr>
<tr>
<td>Propanol</td>
<td>C₃H₈O</td>
<td>14</td>
<td>Co-surfactant</td>
</tr>
<tr>
<td>De-ionised water</td>
<td>H₂O</td>
<td>12</td>
<td>Immiscible phase 2</td>
</tr>
</tbody>
</table>

Glass is a specific type of glass that possesses a surface which is kept free of organic contaminants such as dirt and grime through natural processes. The self-cleaning ability of the glass is based on the photocatalytic property of a thin nano-structured titanium dioxide film, which coats the surface of a glass.

Titanium dioxide is the material of choice as it possesses the required characteristics: high photocatalytic properties, low price, non-toxic, chemically inert when there is no light present, easy to handle and already well-known in household chemicals (pigment in cosmetic and paint). The strong oxidation power and super hydrophilic properties of titanium dioxide make it an appropriate material for use as a self-cleaning coating for outdoor purposes. When titanium dioxide is exposed to sunlight, it reacts with the oxygen and water molecules present in the atmosphere to produce free radicals leading to the formation of oxidative species. These are later able to breakdown organic compounds present on the surface producing volatile molecules, leaving the surface of the glass more hydrophilic than ordinary un-coated glass. The photocatalytic and hydrophilic properties of titanium dioxide-coated glass then allows the rain to easily wash away the deposited surface particles.

Preparing the ceramic inks is still very challenging to ceramic researchers. However, it is fallible in that agglomerates, and debris present in the ink could block the nozzles and bring the printing process to a halt rather than entering the product as imperfections. Well-formulated inks fitted with adequate filtration, aim to prevent agglomeration. Consequently, the stability, and homogeneity of ceramic inks are key requirements, and the physicochemical properties of the ceramic inks are further needed to meet the requirements of the commercially available printers. Therefore, the properties of the inks are critical in ensuring high quality direct ink-jet printing results.

Various methods such as homogeneous precipitation method, dispersion method, sol–gel method and micro-emulsion method, which have their own advantages and disadvantages, have been used to prepare ceramic inks previously. In this study, the self-cleaning ceramic ink was prepared through the use of the micro-emulsion method. Micro-emulsion is a homogeneous and thermodynamically stable system consisting of a surfactant, co-surfactant and two immiscible liquid such as water and oil. Micro-emulsions appear clear or translucent and not cream because of the smaller droplet sizes. The water droplets provide reaction spaces for the formation of ceramic nano-particles, on account of its stability and homogenous dispersion in nano-meter sizes. The use of micro-emulsion formed ceramic ink was intended to overcome the problems related to ink stability and the quality of the printed patterns. In a previous study self-cleaning ceramic ink that contained micro-crystalline titanium dioxide was applied to glass and ceramic by chemical vapour deposition, magnetron sputtering and screen printing.

In the present work, a self-cleaning ceramic ink that has been prepared by the micro-emulsion process was used to coat glass by ink-jet printing. The rheological behaviour of ink and self-cleaning property of the printed glass was also examined and documented.

2. Experimental

2.1. Materials and preparation of self-cleaning ceramic ink by micro-emulsion method

The self-cleaning ceramic ink was formulated using the micro-emulsion method. The preparation details for the synthesis of nano-titanium dioxide particles via the micro-emulsion method have been published previously. The substrate used was microscope glass slides, which were supplied by Pearl, China. Dioctylsulphosuccinate sodium salt as the surfactant and cyclohexane as oil phase were provided by Acros Organic and Sigma–Aldrich Company, respectively. All other chemicals used in this work were laboratory grade as received from Merck Company, UK. Table 1 shows the percentage by weight and chemical formulation of materials used.

2.2. Equipment and instrumentation

The microscope glass slides were ink-jet printed using an Epson Stylus Photo P50 printer in 1, 3 and 5 printing runs. Subsequently the printed glass slides were dried and heat-treated in an Azar 1250 furnace at 400 °C. The equilibrium contact angle θ of each ink/substrate combination was measured using CCD camera and image analysis software (LB-ADSA mode). The pH, surface tension and viscosity of the ink were obtained using 827 pH Metrohm meters, Tensiometer K100MK2 and Rheometer MCR 300 respectively. The surface morphology and cross-sectional view of printed self-cleaning ceramic ink on the glass slides was determined through the use of a scanning electron microscope (SEM) and TEM.

2.3. Printing of self-cleaning ceramic ink

The ink-jet printing was carried out with Epson Stylus Photo P50 printer at 1200 dpi using the ink formulation as shown in Table 1 onto microscope glass slides. This printer operates by
use of a piezoelectric squeeze mode print head that squirts ink droplets through a nozzle with a 65 μm opening. Prior to each run, the printer was flushed through with self-cleaning ceramic ink to remove any contamination from previous printing runs. All substrates were cleaned with acetone before deposition of droplets. The pH of ink was adjusted to 7–7.5 by buffer solution to prevent打印头和墨囊受到破坏。打印图像

2.4. Heat-treating of printed self-cleaning ceramic ink

Subsequent to drying the self-cleaning ceramic ink coated slides were heat-treated. The printed glass slides were heat-treated at 400 °C at a rate of 10 °C per minute the total soaking time was one hour after which it was cooled from 400 °C to room temperature. The thickness of the heat-treated samples was measured by emission scanning electron microscope (SEM).

3. Results and discussion

3.1. Rheological behaviour

The viscosity of self-cleaning ceramic ink mainly affected the rheological performances through the capillary of the printer’s nozzle. High viscosity could lead to an insufficient jet of ink, conversely too low a viscosity could lower the inner resistance of the ink, which makes the ink drop become crescent shaped, resulting in damped oscillation the result being that the ink-jet velocity decreases.

Fig. 1 shows the variation of viscosities with shear rate for the self-cleaning ceramic ink on a logarithmic scale. It is evident that when the viscosity of the self-cleaning ceramic ink was reduced to 5mpas by increasing the shear rate to 1000 S⁻¹ the prepared ink behaved as non-Newtonian fluids. This observation is in consistent with the shear thinning behaviour represented by several other ceramic inks.²³,⁴⁰,⁴¹

3.2. Surface tension

The surface tension of the ceramic ink mainly affected two parts of the printing process. Firstly, the decomposition into fine drops of ceramic ink efflux through the capillary tube of the printer nozzle, and secondly wettability of the self-cleaning ceramic ink onto the forming carrier. The oil phase, as a major phase in the ink formulation, had a predominant role in controlling the surface tension. Cyclohexane was chosen as the oil phase due to its suitable surface tension. The existence of surfactants made a further contribution to lowering the surface tension. The surface tension of self-cleaning ceramic ink was found to be 31 mN m⁻¹, placing it within the normal range of values of commercial ink-jet inks for ceramic printing.³⁴,⁴¹

3.3. Self-cleaning study by measurement of water contact angle

The hydrophilic self-cleaning coatings are dependent on photocatalysis; when exposed to light they are able to break down impurities. These kinds of coatings act in two ways to clean the surface. The organic material (dirt) absorbed on the glass is broken down chemically by photocatalysis and water washes the dirt away by forming sheets in the presence of a low contact angle.

In this experiment, the association, between the joint effects of the photocatalytic mechanism and hydrophilic effect, is cleared although dependent on the photo-induced change in the contact angle of the printed film as is shown in Figs. 2–4 following 4 h UV irradiation. Fig. 2 shows the water contact angle of the microscope glass slide without printing; this was comparable to the printed microscope glass slide not activated by UV.

This dependence on UV activation is seen again in photo-induced hydrophilicity, which suggests that the photo-induced hydrophilicity of the film is closely related to the photocatalytic activity for removal of organic substances from the printed glass slides (Fig. 4).

The synergetic effect of photocatalysis and hydrophilicity can be explained as follows: subsequent to heat-treating the surface area of the nano-titanium dioxide increases following evaporation of material from the ink. Consequently, the photocatalytic activity and hydrophilicity are enhanced due to increased OH groups that can be adsorbed on the enlarged print surface. This observation complements previous research carried out.⁴²

On the other hand, the greater surface of the printed microscope glass slide can adsorb contaminants which tend to transform the hydrophilic surface to a hydrophobic surface. Photocatalysis may aid decompose the organic compounds on the surface resulting in the restoration of a hydrophilic surface. Therefore, photocatalysis can improve hydrophilicity of the surface and maintain this characteristic overtime.⁴²

Table 2 shows the average water contact angle results obtained from the raw and heat-treated printed glass slides after 1, 3 and 5 printing runs followed by 4 h of UV irradiation as explained previously. The self-cleaning property improved due to the increase in surface area of the nano-titanium dioxide following heat-treatment in all samples. Water contact angles in all of the samples after heat-treating are lower than the raw samples due to the increased number of absorbed OH groups on the treated surface. Raw printed microscope glass after 3 and 5 runs had analogous water contact angles (28.22–37.99°). After
Table 2
Summary of water contact angles for raw and heat-treated printed microscope glass slides after 1, 3 and 5 runs following 4 h UV irradiation.

<table>
<thead>
<tr>
<th>Printing runs</th>
<th>Raw average water contact angles</th>
<th>Heat-treated average water contact angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.2245</td>
<td>23.02375</td>
</tr>
<tr>
<td>3</td>
<td>37.5335</td>
<td>27.23667</td>
</tr>
<tr>
<td>5</td>
<td>37.9995</td>
<td>19.35775</td>
</tr>
</tbody>
</table>

3.4. Morphology observation of printed self-cleaning ceramic ink on microscope glass slides

The SEM photographs of the raw and heat-treated printed microscope glass slides by the self-cleaning ink are shown in Figs. 5–8 that visibly demonstrate the cross-sectional uniformity in the thickness of the print layer on the microscope glass slides. Fig. 5 depicts the single run print of raw printed microscope glass slides, were the self-cleaning print layer had about 120–150 nm thicknesses, which demonstrated a lower water contact angle when compared to the triple run print having a greater thickness of 400 nm. The lower water contact angle and resulting increase in self-cleaning ability perhaps are the consequential effects of the titanium dioxide nano-layer on the microscope glass slides.

Fig. 6 shows some micro-emulsion nano-particles on the heat-treated microscope glass slide surface of the single run sample. In all of the samples, following heat-treatment, water contact
angles were being reduced due to release of organic materials from the ink formulation and an increase in the surface area of nano-titanium dioxide particles.

Based on Figs. 7 and 8, it can be concluded that the thickness of the raw printed microscope glass slides after 3 and 5 runs is between 400–500 nm and 800 nm−1 μm respectively. These results demonstrate that the direct ink-jet method of solid free-forming can also be used to control the thickness throughout a component.

### 3.5. Morphology observation of the self-cleaning ceramic ink by TEM

The TEM photograph of the particles in the self-cleaning ceramic ink is shown in Fig. 9 which visibly demonstrates well-dispersed particles with minimal size variation (20–30 nm) in the ink. No agglomerate was found and the particles were almost
completely spherical. The surfactant and co-surfactant formed a shell around the particle surfaces protecting them from collision, hence they exist stably in isolation equally distributed in the ink.

4. Conclusion

Prepared micro-emulsion titanium dioxide nano-particle ink was printed using an Epson Stylus Photo P50 printer onto micro-scope glass slides. The printing was carried out by a computer program to 1, 3, and 5 print runs. The surface tension of prepared inks at pH = 7.5 was 37.5 mN m−1. The viscosities of prepared ink were reduced to 5 mPas by increasing shear rate to 1000 s−1, therefore, the prepared ink behaved as non-Newtonian fluids. The surface tension and viscosity of self-cleaning ceramic ink fell into the range required by “drop on demand” ink jet printers making the inks compatible with commercially available printers.

The contact angle results indicate that all heat-treated printed microscope glass slides were able to be hydrophil and therefore have self-cleaning properties. Using a single print run, the raw printed microscope glass slide had about 130 nm thicknesses. The thicknesses of raw printed self-cleaning ceramic ink were approximately increased linearly with the number of printing runs. The lowest water contact angle and therefore most effective self-cleaning glass sample were achieved by using 5 print runs and subsequently heat treating the 800 nm to 1 μm thick print before activation with UV. In conclusion the results of this work show that the direct ceramic ink-jet printing (DCIJJP) method can be used to produce self-cleaning glasses using a micro-emulsion titanium dioxide nano-particle ceramic ink.

References