Ceramics International 29 (2003) 887–892

CERAMICS INTERNATIONAL

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Formulation of a ceramic ink for a wide-array drop-on-demand ink-jet printer

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Received 19 December 2002; accepted 28 December 2002

Abstract

This paper describes the methodology for simulating a reprographic ink with a ceramic ink based on a commercially available zirconia powder for direct ceramic ink-jet printing. Of over-riding importance was matching viscosity and this was tested systematically by using a mineral oil–hexane binary system. Of secondary importance was adjustment of the pressure defect behind the nozzle to compensate for small differences in surface tension. The inks tested in the wide array print-head were based on low electrical conductivity liquids to avoid damage to the electroding system. The organic binder for the zirconia ink was paraffin wax and the dispersant was a hydroxystearic acid based polyester.

Keywords: D. Zirconia; Ink-jet printing; Solid freeforming

1. Introduction

Solid freeform fabrication is a computer controlled manufacturing operation in which components are made by adding material to, rather than abstracting material from the component. Various processing operations have been adapted for this purpose. They include stereolithography [1], selective laser sintering [2], laminated object manufacture [3] and ink-jet printing. In the last of these, either binder is sprayed onto layers of compacted [4] or sprayed powder [5] at selected sites to build a three dimensional sinterable shape or ceramic suspensions are printed directly [6–10]. In direct ceramic ink jet printing (DCIJP), ink with ceramic 'pigment' passes through the nozzle to build up a multilayered 3-dimensional structure.

Direct ceramic ink jet printing has the advantage that composition is spatially programmable down to the resolution of an ink droplet throughout a component. By placing different materials throughout a component, a complete shape with any compositional distribution can be realised. It is 'fail-safe' in that agglomerates and debris present in the ink would block the nozzles and bring the printing process to a halt rather than entering the product. Well-formulated inks used in sophisticated ink management systems fitted with adequate filtration, aim to prevent this. Unlike compaction processes, this method of manufacture does not rely on the use of deliberately agglomerated powders. Agglomeration and entrained debris are considered to provide the main sources of strength-limiting defects in ceramics [11].

Multi-nozzle printers can print complex graphics at high speed. A multi-nozzle, 70 mm wide array drop-on-demand ink jet printer similar to the one used in this work can print colour graphics of width 70 mm at 500 mm/s. Such devices would be suitable for mass production of sophisticated delicate components such as circuit tracks, miniature capacitors and micro-engineered and functionally graded materials.

Making highly loaded ceramic inks suitable for long residence times in 3-dimensional ink-jet printers suitable for mass production is a challenge. In the work carried out here, the ink properties that determine the suitability for printing in a modern wide array print head are explored. Liquids with a similar but wider range of properties to those of the proprietary ink were explored. A ceramic ink was formulated and successfully tested based on this approach.

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doi:10.1016/S0272-8842(03)00032-4

2. Experimental details

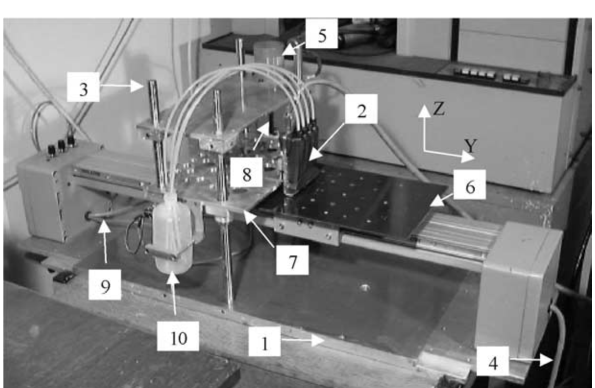
2.1. Materials

The ceramic powder was grade HSY3 (ex Daiichi Kigenso, Japan), a non-spray dried 5.4 wt.% yttria grade with ultimate particles in the 200 nm region as deduced by TEM. The solvents included octane, hexane and isopropyl alcohol (reagent grades). The wax was Shellwax 130/135 (Shell Chemicals, UK). The dispersants were from the Solsperse range (ex Avecia, Manchester, UK) and are based on polyesters of hydroxystearic acid. The oil was white heavy mineral oil (grade 33 076 ex Sigma-Aldrich, Dorset, UK).

2.2. Printing station

The printing station consisted of a printing table (Fig. 1) that prints with a piezoelectric XJ500 monochromatic print head (kindly donated by Xaarjet Ltd. Cambridge, UK). A MC202 controller (supplied *ibidem)* for the sliding table and print-head movement and a Xaarjet PCI Interface Adapter for print head operation were incorporated. The control program was written in C^{++} and operated from the Visual C^{++} workspace.

The XJ500 print head is capable of printing a two dimensional image of width 70 mm so no X-direction translation was needed. The image files, in device-independent bitmap (.DIB) format, were sent to the print head by means of a stroke engine, a shaft encoder and a product detector, which co-ordinate and control the firing of the ink from the nozzle and the movement of the sliding table for each pass of printing. The sliding table was moved to the end of the track behind the print head after each pass where it re-registered its initial position ready for the next pass. The gap between the nozzle plate and the printing surface was maintained at ~1 mm by z displacement.



1	chassis	2	print head
3	guiding pillar	4	cable to Y-step motor
5	Z-step motor	6	sliding table
7	mounting plate	8	lead screw
9	cable to position sensors	10	ink bottle

Fig. 1. The arrangement of the printing station used for this work.

A 100 ml bottle served as an ink reservoir attached to the side of the print head mounting plate (Fig. 1). During printing, the ink level was adjusted between 10 and 110 mm below the level of the nozzle plate. The ink was pre-filtered through a syringe fitted with a 5 μm filter. An airtight cap to the nozzle plate and linked to a syringe was used for de-airing the ink supply. The ink was displaced from the bottle through the print head to the syringe several times until no bubbles were observed in the tubing. For ink viscosity greater than 10 mPa s, this filling process was difficult to effect so inks with viscosity greater than 10 mPa s were not prepared.

The viscosity of the inks was measured using a reverse-flow, suspended level viscometer suitable for opaque liquids and following the procedure described in BS188:1977. The density was measured using a pycnometer. The water bath was held at 25±0.5 °C. The surface tension was measured by the ring detachment method following the procedure described in ASTM D1331-89 at an ambient temperature of 23±0.5 °C.

3. Results and discussion

Studies of the fluid dynamics of drop-on-demand ink-jet printers suggest that a characteristic dimensionless number for the process is the ratio of the Reynolds number to the Weber number (Re/We) [12]. The former characterises flow in a pipe with viscous and inertial forces while the latter characterises flow influenced by surface tension. The ratio is related to fluid properties by:

$$\frac{\mathrm{Re}}{\mathrm{We}} = (\gamma \rho r_{\mathrm{o}})^{1/2} / \eta \qquad (1)$$

where γ is the surface tension, ρ the density, η the viscosity of the fluid, and r_{o} the radius of the orifice from which the fluid is ejected.

The variation of γ is typically 20–70 mNm^{-1} for organic liquids that can be considered as candidates. Density, for organic liquids and ceramic suspensions is likely to be in the region 800–1500 kgm^{-3}. The orifice radius for ink jet printer nozzles is typically a few tens of micrometers and in this case $r_{\mathrm{o}} = 25$ μm. Variation of the numerator should be considerably smaller than the variation in viscosity, η which can vary over an order of magnitude in such inks.

Physical properties of the magenta ink were measured and are shown in Table 1. The specialised construction of the piezoelectric ink chambers means that inks should effectively be non-conducting to prevent corrosion damage to the electrodes. The main properties to be matched are therefore viscosity and electrical con-

Table 1
Properties of the proprietary magenta ink and the ceramic ink

Ink	γ/mN/m, 23 °C	ρ/kg/m^3, 25 °C	η /mPa s, 25 °C	Measured drop volume/pl
Magenta ink	30	858	10.3	78
Ceramic ink	25 (20 °C)	1477	2.9	226

ductivity. Surface tension was also recorded because of the importance attached to it in the literature and because subsequent refinement of ink-jet print quality may be influenced by it.

In order to find the range of viscosity within which the printer operated, low electrical conductivity mixtures of solvents were prepared and small additions of the magenta ink were made to detect print and assess quality. Non-polar paraffin and mineral oil were mixed with ~4 vol.% of the magenta ink to vary the viscosity and test the effect of viscosity on printability. Table 2 shows the properties of hexane and mineral oil mixtures. By changing the hexane volume fraction from 0.77 to 0.24, the denominator of the right hand side of Eq. (1) changed by 637%, while the numerator changed only by 14%. Thus in this test, viscosity is effectively solely responsible for the fluid dynamics of the ink drop formation.

The hexane–mineral oil mixtures (inks 1–5) were printed keeping the ink level at 30 mm below the nozzle plate, (i.e. −30 mm: the minus sign is used to denote a position *below* the nozzle plate) as suggested by the manufacturer's specifications. The test pattern is shown in Fig. 2 and is designed to show nozzles that are out of action either as unprinted tracks in the block or large gaps in the slightly oblique lines. For all inks, the patterns of the first passes were almost complete. It is pertinent to note that the print-head was a used version in which some nozzles defined by Fig. 2 were out of action.

To test reliability, each ink was overprinted for 50 passes; the first and 51st pass were compared. The 51st pass of inks 1–5 all showed loss of transfer indicated by progressive loss of image. Fig. 3 shows deterioration between the 1st and 51st pass for ink 2. Yet ceramic printing may involve many thousands of passes. Much of the loss could be recovered by wiping the print-head nozzle plate with an absorbent paper but recovery by this means was not complete and none of these inks appears to be suitable for multilayer printing.

The exclusivity of viscosity as a defining criterion seems to be weakened by the fact that the reprographic magenta ink has a similar viscosity to ink 5. In the course of exploring the effects of printing process variables, the ink reservoir level was adjusted and levels of −70, −90 and −110 mm were tried. This had an immediate and pronounced effect. For these ink levels, the images of the first pass of ink 5 were almost complete and the image loss after 50 passes was negligible. The small amount of lost image could be recovered by wiping the nozzle plate. This is the practice with some proprietary printers, which clean the nozzle plate after several lines of printing. Ink 5 is therefore suitable for overprinting if the ink level is between −70 and −110 mm.

The experimental array indicated by Table 3 was then implemented by printing at ink levels of −50, −70, −90, and −110 mm for inks 1–4, and −130 mm for inks 1 and 2. The results are summarised in Table 3, which shows a relationship between repeat printability, ink surface tension and ink levels relative to the nozzle

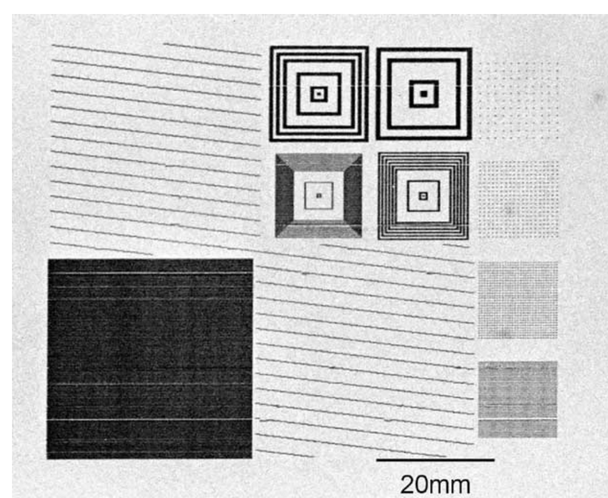


Fig. 2. The test pattern printed using the reprographic magenta ink.

Table 2
Properties and overprint test results of hexane and mineral oil inks

Ink (volume fraction of hexane in mineral oil)	0.77 (ink 1)	0.49 (ink 2)	0.43 (ink 3)	0.33 (ink 4)	0.24 (ink 5)
γ/mNm^{-1}, 20 °C	24	25	26	27	28
ρ/kgm^{-3}, 25 °C	750	777	783	804	822
η/mPa s, 25 °C	1.3	2.3	2.7	5.0	9.5
Printable ink level/mm	–	–	−90 to −110	−70 to −110	−70∼−110

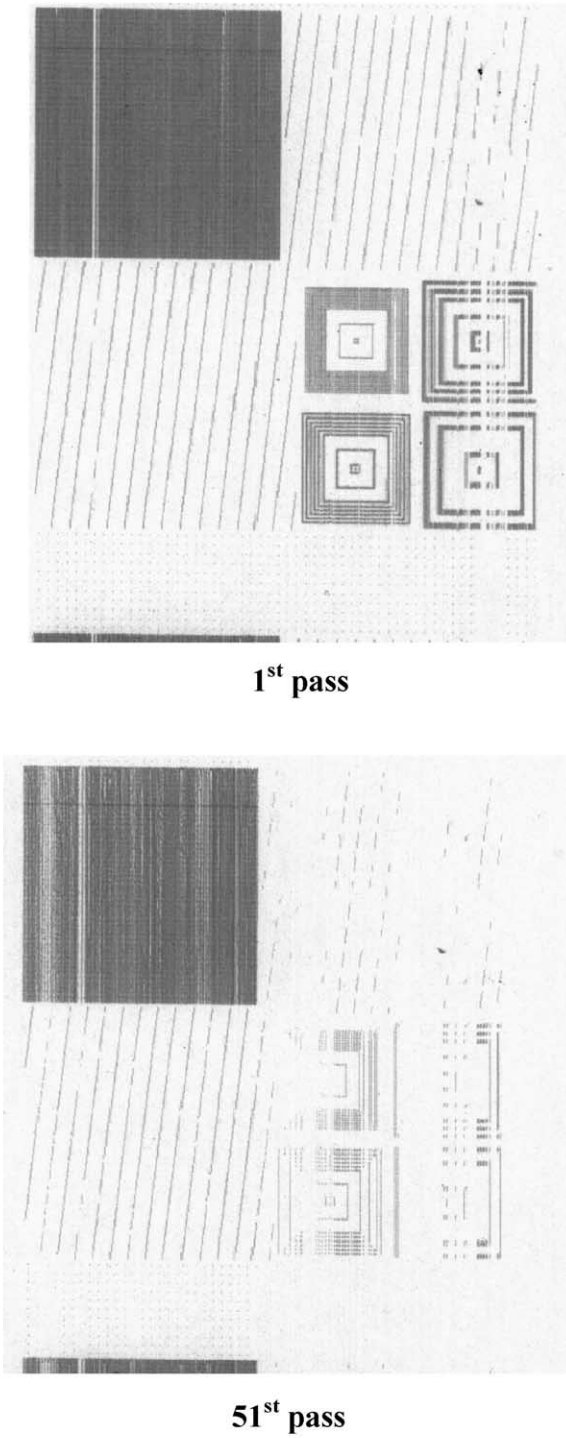


Fig. 3. Loss of print quality of ink 2 when the reservoir was at –30 mm.

plate. Table 3 shows clearly that none of the inks produced satisfactory overprinting images at –30 mm as used for the proprietary magenta. It was only when ink levels were lowered substantially that the image loss was prevented. A clear trend (Table 3) is that the lower the ink surface tension, the more the ink level needs to be lowered below that of the nozzle plate. The ranges of ink level that allow for over-printing of these inks are summarised in Table 2.

Table 3
Image loss after 50 passes of overprinting for different inks (ref. Table 3)

Ink Ink level	Ink 1	Ink 2	Ink 3	Ink 4	Ink 5
−30 mm	×	×	×	×	×
−50 mm	×	×	×	∪	∪
−70 mm	×	O	O	√	√
−90 mm	×	∪	√	√	√
−110 mm	×	∪	√	√	√
−130 mm	×	×	NT	NT	NT

(√: negligible; ∪: noticeable; O: significant; ×: severe, NT: not tested).

Tables 1 and 2, indicate that the properties of the magenta and ink 5 are almost identical. Nevertheless, the reservoir level of ink 5 must be lowered more than 40 mm below that for magenta to achieve acceptable overprinting quality. Ink level changes the nominal pressure at the nozzle orifice. For a drop to separate from a nozzle of radius r_o the pressure at the nozzle inlet must at least overcome the surface tension. This pressure is:

$$P = \frac{2\pi r_o \gamma}{\pi r_o^2} = \frac{2\gamma}{r_o} \tag{2}$$

To eject a droplet fully, the combined pressure arising from the hydraulic head of ink and from the actuator must exceed that in Eq. (2). Like other types of drop-on-demand inkjet printer, ink level in the printer is set lower than the nozzle plate to avoid bleeding of ink from the nozzles. From Eq. (2), for a nozzle radius of $r_o = 25$ μm, a surface tension difference, $\Delta\gamma$, of 1 mN/m, results in a pressure difference of $\Delta P = 80$ Pa. The pressure difference due to a 10 mm head of ink 5 is 80.5 Pa. The difference in surface tension between ink 5 and the magenta is ~2mN/m, therefore by lowering the ink level to −50 mm (20 mm lower than that for the magenta ink), ink 5 should perform the same way as the proprietary magenta ink and hence be suitable for overprinting. At −50 mm the image loss for ink 5 was improved as shown in Table 3. The experimental printing ink level range was −70 mm to −110 mm.

Ink 1, on the other hand, cannot be made suitable for multiple printing even by lowering the ink level. This is also true for ink 2 but does not apply to inks 3, 4 and 5. The lower reservoir level for ink 3 was between −90 and −110 mm, i.e. 60–80 mm lower than that of the magenta. The ink surface tension difference between the magenta ink and ink 3 is ~5 mN/m, which, from Eq. (2), represents a pressure difference of 400 Pa. For ink 3, the pressure difference due to a 10 mm column of ink is 74 Pa. Thus to compensate for the pressure difference due to 5 mNm^{-1} of surface tension difference, 54mm lower ink level is required. A further 3 mm is required to compensate for the ink density difference at −30 mm, the ink level suggested by the manufacturer's recommendation. Therefore a total of 57 mm ink level difference is required to compensate for the pressure change due to the different ink. This almost accounts for the operating ink level difference. The surface tension difference is therefore considered to be the main reason for the need to adjust the reservoir level between the proprietary ink and the inks tested here.

As well as the surface tension difference there is also a systematic variation in viscosity for inks 1–5 and observation of the size of droplet relics of this series showed that the relic diameter of ink 1 was about twice that of ink 5 suggesting inverse proportionality to viscosity. The manufacturer's data for droplet volume for the magenta (the reference ink) is 78 pl [13]. The droplet volume for the ceramic ink (Table 1), measured from the ink consumption while printing 31×10^6 drops was 226 pL. This method underestimates volume because during prolonged printing ceramic ink viscosity tends to increase near the nozzle plate because of settling of particles. So for these inks, with a ratio of viscosity of 3.55, the lower viscosity and higher density ceramic ink produces 2.9 times the droplet volume. The difference in these ratios (18%) could reflect additional energy used to accelerate the larger drop but may also be influenced by the underestimation of droplet volume of the ceramic ink. The result shows that drop volume is strongly influenced by ink viscosity.

Thus large volumes for inks 1 and 2 combined with low surface tension are considered to contribute to ink spreading over the print-head nozzle plate as observed. The deposited ink film around the nozzles, when dried, contributed to gradual blockage of nozzles with the low volatility component. This explains why the overprinting quality was poor at all ink levels for inks 1 and 2 and is supported by the observation that acceptable image quality could usually be obtained for the 1st pass for all inks, independent of the printing conditions. Also, the loss of image could be partially recovered by cleaning of the nozzle plate. Both ink 3 and the ceramic ink with viscosities of 2.7 and 2.9 mPa s respectively can be printed suggesting, as a guide that 2.7 mPa s is a lower limit for this print-head.

The ceramic ink having a viscosity and surface tension within the printing range was prepared. The ink-making process has been described elsewhere [14]. The ink composition is shown in Table 4, and the ink properties in Table 1. The viscosity of this ceramic ink is close to that of ink 3 and it is suitable for overprinting [15]. This 14.2 vol.% ZrO_2 ink was tested using the same printing station. The ink level was held at 30 mm below the nozzle plate which was its optimum level and corresponds to the magenta because of the density difference between the two inks, which, at −30 mm ink level, largely compensates for the surface tension difference. The test pattern was printed on release paper and Fig. 4 shows the accumulation of 50 passes. The images are identical; there is no sign of loss. This means that the ink developed to meet the viscosity criterion is capable of producing overprints without compromising image quality provided the pressure at the nozzle plate is adjusted. To confirm the reliability of the ink, fibre arrays were printed with 4900 passes. These are shown in Fig. 5 in their as-printed state. They demonstrate both the reliability of the ink and the possibilities for forming complex surface topographies.

Table 4
Ceramic ink compositions

Material	ZrO_2 powder	Solsperse 13940	I.P.A.[a]	Octane	Wax
Vol.%	14.21	11.85	14.21	56.89	2.84

[a] I.P.A.: isopropyl alcohol.

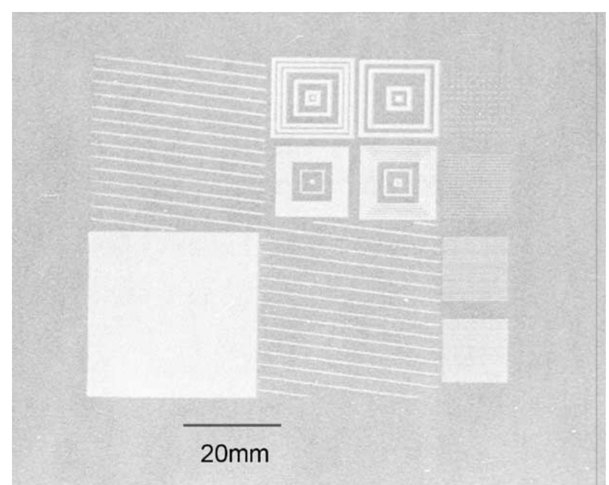


Fig. 4. The test pattern repeatedly printed with the zirconia ink (50 passes).

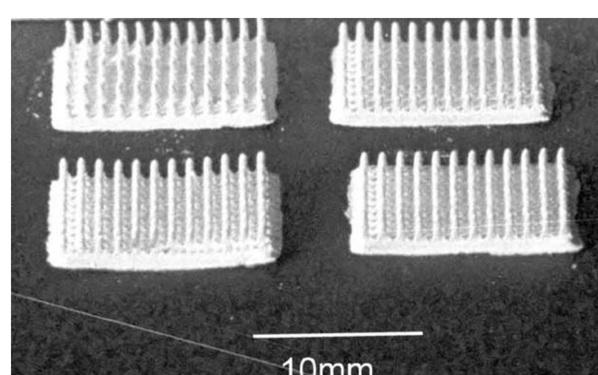


Fig. 5. Sintered zirconia fibre arrays prepared using the ceramic ink showing that this ink could be printed for 4900 passes.

4. Conclusions

Although viscosity provides the main criterion to be met when creating a ceramic ink, the surface tension can affect image loss during overprinting. The ink level should be adjusted to an appropriate level below the nozzle plate to avoid bleeding of ink and spreading on the nozzle plate, which is responsible for image loss. The lower the surface tension of an ink, the lower the ink level should be to provide a pressure defect at the nozzles. Viscosity had a pronounced effect on droplet volume as reflected in the size of printed relics. Low viscosity ink resulted in high droplet volume and ink spreading over the nozzle plate. The ability to adjust the printer to print with different viscosity inks allows wide area coverage on the one hand (low viscosity) and fine line width and line spacing in the printing of thin tracks on the other (high viscosity).

Acknowledgements

The authors are grateful to Angus Condie (Xaarjet,-Cambridge, UK) for providing an ink-jet printing assembly and to EPSRC for funding this work under Grant No. GR/M07755.

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