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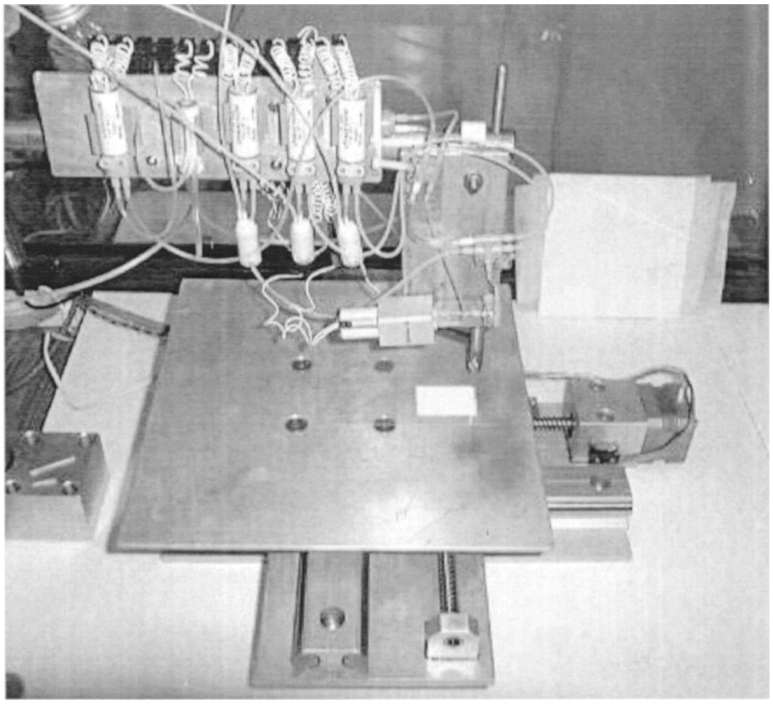

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A Drop-on-Demand Ink-Jet Printer for Combinatorial Libraries and Functionally Graded Ceramics

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A printer has been designed and built for the preparation of combinatorial libraries of ceramics and for solid freeforming of functionally graded ceramics with three-dimensionally programmable spatial variation in composition. Several ceramic suspensions (as inks) can be subjected to micromixing behind the nozzle and printed at precise positions. Both mixing and positioning are computer-controlled. The machine consists of an *XY* table to control the geometry, a set of electromagnetic valves that manage the mixing, a combined electromagnetic valve and sapphire nozzle that form the print head, and a computer that controls the whole system. The mixing valves can eject as little as 1 mg/s ink into the mixing chamber. The printer has been controlled, run, calibrated and tested; the composition and geometry of printed mixtures can be controlled precisely. This method for the controlled mixing of powders facilitates the advance of combinatorial methods within the materials sciences.

1. Introduction

Ink-jet printing is a noncontact reprographic technique that takes digital data from a computer representing an image or character and reproduces it on a substrate using ink drops.[1] Ink-jet printers can be classified as continuous or drop-on-demand. In the former, an ink stream is broken into equal-sized droplets by applying a piezoelectrically modulated pressure wave behind the nozzle.[2] These drops are charged and deflected during flight to the substrate. In a drop-on-demand printer, ink drops are ejected only where and when they are needed to create an image on the paper. This concept is attributed to Zoltan[3] and Kyser.[4] The methods to create drops on demand include thermal (incipient boiling), piezoelectric, and electromagnetic methods. Most of the ink-jet printers use the thermal or piezoelectric mechanisms and achieve operating frequencies of about 10 kHz.

In thermal ink-jet printing, creating a bubble by incipient boiling and then allowing it to collapse provides the pressure pulse for ejecting a drop and ink is replaced from an unpressurized reservoir. In piezoelectric ink-jet printers, an actuator of polycrystalline piezoelectric ceramic (usually lead zirconate titanate) on each ink nozzle provides the transient pressure for ejecting ink onto the paper.[5] Generally ink-jet printers use an ink with low viscosity that is typically in the range 4−20 mPa s. The ink normally consists of solvent, colorant (dye or less often a pigment), binder, and additives.[6]

Considerable progress has been made in recent years in the direct ink-jet printing of ceramics as a solid freeforming pathway.[7−19] This means that complex shapes and functionally graded materials can be built from a computer file with spatial control of composition. The value in this technology is that any ceramic can be used because all are available as a powder while only some are available as polymeric or oligomeric precursors.

Most types of printer have been used for ceramics including continuous,[7,11] piezoelectric drop-on-demand,[10,16−18] thermal,[9] and electromagnetic printers.[15] The last of them offers the benefit of robustness and control of droplet size by varying the reservoir pressure and the valve-opening time. The present instrument is based on this type of printer.

In previous work,[12] two different ceramic inks were mixed to provide a functionally graded material but there was no direct control of mixing. Color printers do not generally mix colored inks together, but rather each color is printed as a separate dot; color mixing effectively takes place in the human eye. In contrast, the device described here mixes inks behind the nozzle. Guidelines for the preparation of diverse ceramic suspensions have evolved in terms of powder dispersion, viscosity control, and stability against sedimentation so that many ceramic powders can be deposited by ink-jet printing processes.[13,14] The electromagnetic valve and pressurized reservoir device is a robust and forgiving arrangement, and ceramic drops have been printed using a high solids concentration and viscosity.[15] The present work extends this method to provide “behind the nozzle” mixing, thus enabling the printer for combinatorial searches as well as shape and compositional freeforming in ceramic materials.

The use of ink-jet printing in combinatorial chemistry is not new. They are used for bulk reagent dispensing, redistribution, and reformatting of high-resolution (9600) well plates, for direct preparation of compound array plates, and for dilution over 4−6 orders of magnitude for dose−response curves.[20] Piezoelectric drop-on-demand printers have been developed for fast automated unattended titrations at densities of 10^6 m^{-2} using laser-induced fluorescence detection for

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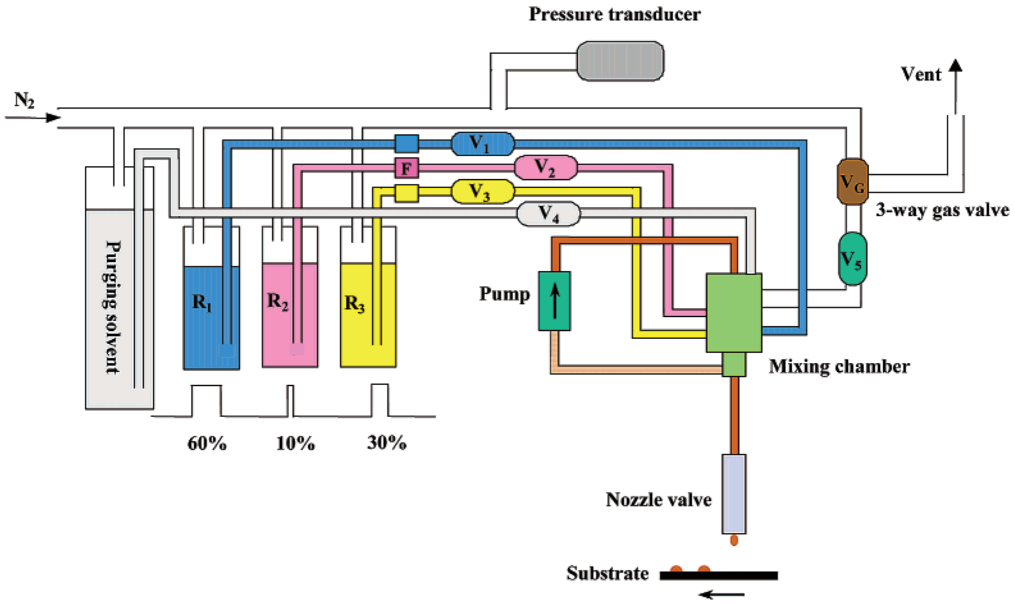


Figure 1. Schematic design of the pipe-work (inset shows signal pattern for mixing).

indicator end points.[21] Droplets in the 100 pL range are generated from a piezoelectric dispensing device with an 8 μm diameter nozzle for mass spectrometry.[22]

These methods are effective in the combinatorial management of liquid reagents, but our quest is to assemble ceramic powders prior to sintering. It therefore represents one of the most difficult challenges for combinatorial methods in the materials sciences. Combinatorial techniques have been debated in materials science since Hanak's original proposals,[23] which emerged from his search for low-temperature superconductors. Only recently, and with an emphasis on thin film masking methods, have they begun to be embraced by the materials science community. The opportunities for a combinatorial approach to ceramic research have recently been described.[24] The case for combinatorial methods is supported by the suggestion that less than 1% of ternary and fewer than 0.01% of quaternary systems have been explored.[25]

Direct ink-jet printing assembles powders and should be distinguished from thin film methods. It therefore corresponds to the main ceramic forming methods. Indeed, components can be made using the same technique so that complex-shaped combinatorial test pieces could be prepared, for example, in electrical property measurement. Furthermore, the need to disperse fine (~200 nm) ceramic powders to their ultimate particles by high-energy bead milling in the preparation of ceramic jet-printing inks means that mixing of fine powders is possible at a fine scale. Thus, uniformity of composition can be achieved during sintering because diffusion distances are low.

2. Experimental Details

2.1. Printer Construction. An electromagnetic printer was built using electromagnetic mixing and dispensing valves mounted over an *XY* table. The pipe-work diagram is shown in Figure 1. The three reservoirs holding ceramic inks were pressurized using a compressed nitrogen supply equipped with a pressure regulator and a 0−172 kPa pressure transducer (PT213-034 Kulite Sensors, Basingstoke, U.K.). The transducer was operated with a 12 V power supply, and the output was read on a digital millivoltmeter and calibrated with a Bourdon gauge. The reservoirs were 25 mL glass bottles fitted into nylon-reinforced tubing for safety. Inks were transferred via 0.5 mm (i.d.) stainless steel hypodermic needles (grade SY217/55, Taab, Berkshire, England) into PTFE 0.5 mm (i.d.) tubing (Cole-Parmer Instruments Co., IL) to three 24 V micro-inert-mixing-valves (LFVA2410320H, Lee Products, Gerrards Cross, Bucks, U.K.). These are labeled V_1-V_3 in Figure 1. Three in-line 35 μm nominal filters (model LFFA4202035A, Lee Products) were placed in the ink lines. Mixing occurred in a PEEK manifold (model TMMA3201950Z, Lee Products) to which all three ink lines were connected.

The mixing chamber was equipped with a 24 V fixed volume solenoid micropump (model LPLA2410050L, Lee Products) providing circulation and hence distributive mixing. This pump can be operated at a maximum frequency of 2 Hz. An additional pressurized reservoir and delivery line holding solvent (usually ethanol) were placed in parallel to lines 1−3, and the solvent entered the mixing chamber using valve V_4, a valve identical to valves V_1-V_3. A similar valve V_5 was placed between the mixing chamber and the three-way gas admittance valve (described below) in order to allow the mixing chamber to be sealed without an applied pressure.

A three-way neoprene 5 V gas valve (model LFAA-0500118H, Lee Products) was placed between the gas line and the mixing chamber either to admit gas or to vent the manifold. A (0−70 kPa) 24 V high-speed integrated nozzle valve (model INKA2437210H, Lee Products) was used to print the mixed composition. The nozzle diameter was 75 μm; an optical micrograph is shown in Figure 2.

This mixing and delivery assembly was placed over an *XY* table that included a keypad indexer (model MC20, Parker, Dorset, England) and two stepper drivers and stepper

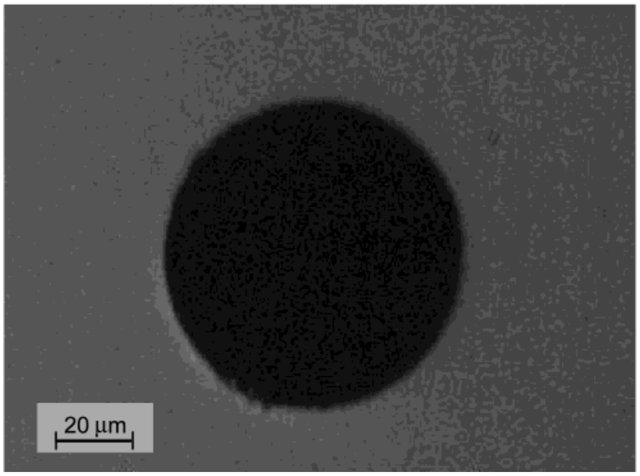


Figure 2. Optical micrograph of the nozzle.

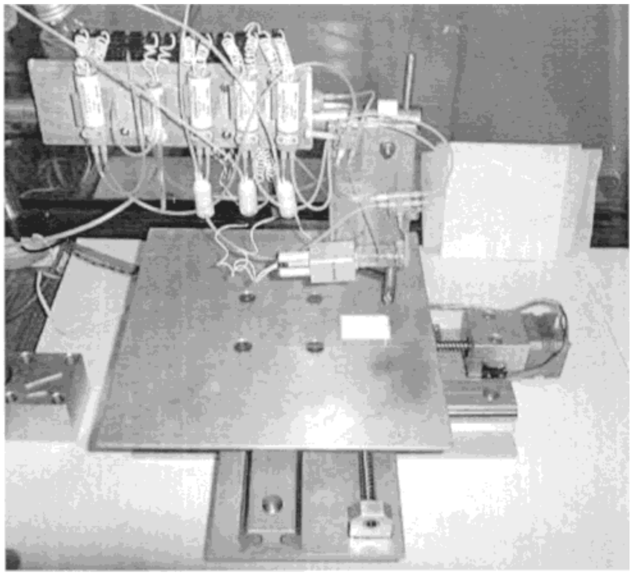


Figure 3. Arrangement of the *XY* table, mixing chamber, and printer nozzle.

motors (model PK3, Parker) for the *X* and *Y* axes. A 0.2 m × 0.2 m support formed the printing area as shown in Figure 3.

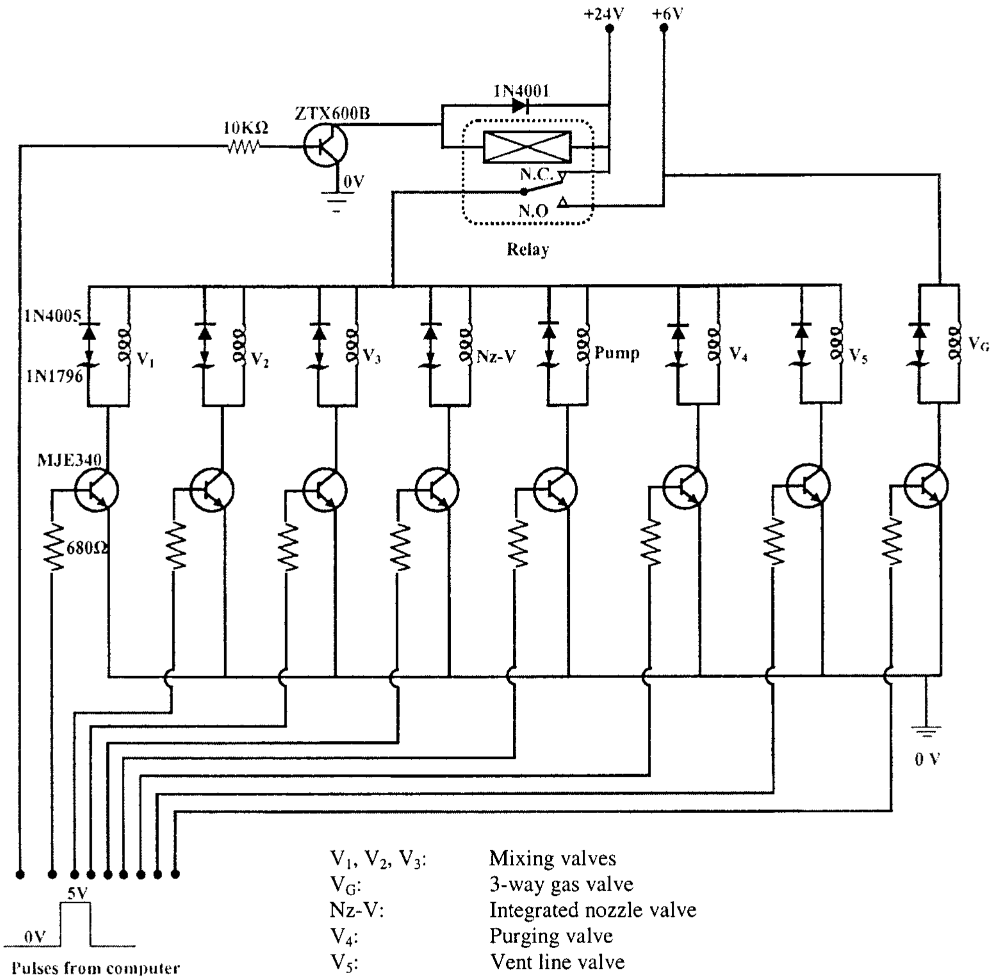
Both the *XY* table and printing assembly were run by a 486 computer (model Genie Professional, Viglen, Middlesex, UK) using a 24-line programmable input/output (I/O) card (model VT05 IBM expansion kit, Maplin, Essex, England). A fast response circuit was built to operate the printing system (Figure 4) equipped with two power supplies at 6 and 24 V dc. The mixing valves and nozzle valve were operated by either 24 V for pulse activation or 6 V for continuous opening during purging. This circuit was activated by 5 V signals from the computer.

2.2. Programming and Calibration. To operate the entire system with one controller, the *XY* table indexer was replaced by the computer and the output signals from the indexer were detected with an oscilloscope and reproduced at the computer output. The I/O card was compatible with BASIC language, so QBASIC version 4.5 was used for programming. Four lines of the I/O card were connected to each stepper driver, and nine lines were connected to the firing circuit (Figure 4). The movement and speed of the *XY* table and the opening time of the mixing and the nozzle valves were coordinated.

The mixing valves were calibrated using different mixtures of water−glycerol (Analar grade, BDH-Merck, Poole, U.K.) and applying different gas pressures at constant temperature (20 °C). The water−glycerol mixtures as standard liquids for calibration were prepared in the range of 40−75% glycerol in water and were always kept in sealed bottles to avoid moisture absorption by glycerol. The viscosities of these mixtures were measured on the basis of BS-188: 1977 using a certified U-tube viscometer (type BS-IP-RF, Rotogold, U.K.) for which the calibration was checked by measurement of the viscosity of distilled water using a temperature-controlled water bath (model FT10AE, Techne, Duxford Cambridge, U.K.). Room temperature was controlled by an 18−29 °C air conditioner (model RAV-260 KH(W)-P, Toshiba, U.K.). The printing system was placed in a glass box to keep the temperature more stable. For calibration purposes, the output masses of the mixing valves were measured using a four-place balance (model TR-104, Denver Instrument, CO). While being weighed, the valves were operated at different opening times and reservoir pressures at 20 °C. The temperature inside the glass box was recorded using a digital thermometer calibrated to 0.1 °C (model THV-220-010Q, Brannan Thermometers, Cumbria, England).

2.3. Registration Tests. When ordinary black ink (grade S020047/MJIC4, Epson, Japan) mixed with ethanol (BDH-Merck, Poole, U.K.) was used, different sizes of “chessboard” patterns were printed in one to five layers on transparent polyester sheets (Melinex, DuPont Teijin Films, Middlesborough, U.K.) as substrate. Different sizes of the “QM” symbol were printed containing 650 dots to evaluate the capabilities of the printer.

2.4. Mixing Tests. Calibration of mixing was carried out using three different organic materials, namely, 2-butanone (>99%, spectrophotometric grade, Aldrich, Dorset, UK), 1,4-dioxane (>99%, spectrophotometric grade, Aldrich), and silicone fluid (Dow Corning 200/5cS, BDH-Merck). These organic liquids were chosen from a short list of 20 candidates selected from the Nicolet/Aldrich condensed-phase infrared spectra library (Nicolet Analytical Instruments, December 1989) on the basis of having (a) at least one strong absorption band in a distinct region of the spectrum and (b) minimal toxicity and chemical reactivity. The first selection was based on a careful study of overlapping peaks in the spectra. Calibration curves of absorption intensity as a function of composition were prepared for the binary system and for the ternary system by gravimetric preparation of mixtures that were stored in sealed 25 mL bottles. The valves were then calibrated for the liquids whose viscosities fell outside the calibration range deduced from water−glycerol systems. Mixtures in the binaries and the ternary were then prepared by computer operation of the valves and stored in sealed 2 mL vials. They were characterized along with the standard mixtures using a FT-IR spectrophotometer (model 1720X, Perkin-Elmer Ltd., Beaconsfield, Bucks, U.K.). Samples were placed on a diamond surface and held by a sapphire crystal



V_1, V_2, V_3: Mixing valves
V_G: 3-way gas valve
Nz-V: Integrated nozzle valve
V_4: Purging valve
V_5: Vent line valve

Figure 4. Fast response firing circuit used to operate the mixing assembly and printing valve.

1 mm above to give a similar thickness of sample in all tests. Neither thickness nor extinction coefficient were used in the calibration; the peaks were referred to each other directly.

3. Results and Discussion

3.1. Design Aspects. The primary design issue in setting up a combinatorial ink-jet printer is where to conduct the mixing. The three main choices are (a) the mixing of inks behind the nozzle, (b) the mixing of inks in the nozzle or in well plates ,or (c) the mixing on the substrate. In the last case there are several options; a printer with a separate nozzle for each ink can be used to deposit successive drops of each component and subsequent sintering can be used in an attempt to achieve homogeneity. This is effectively a conventional color printer. The alternative is to use an aspirating printer such as that being developed at Queen Mary, University of London, for combinatorial materials science.[24] This uses electromagnetic valves similar to those used in the present work to draw from well plates, reformat, aspirate and then print samples on a series of ceramic substrates. This is a slower option and cannot be used for solid freeforming, but it has the advantage of being able to mix a large number (>50) of components.

The device described here has the capability of producing continuously variable samples in any geometry. The mixing is extremely efficient because suspensions of fully dispersed powder can be mixed in pumped circulation. The printer is not limited to the construction of small dots or pads, but quite substantial samples can be prepared. Indeed, it can be used to make devices.

The secondary design issues are associated with the mixed volume. This printer can be used in two distinct mixing modes. In the incremental mode, the composition of the mixing chamber is adjusted after printing a fixed volume of ink. This is the mode most suited to the manufacture of functionally graded materials. In this application, steady changes in composition throughout a component are sought. In the full chamber dump mode, distinct compositions are mixed and printed and the excess is ejected to waste before refilling the chamber with a fresh composition. This purging facility allows the chamber and nozzle to be flushed with solvent between compositions. This cleaning procedure is necessary for ceramic suspensions because of the tendency for fine (<1 μm) particles to adhere to polymeric tubing despite the use of steric dispersants.

The mixing chamber volume V_m, is the volume between the outlet of the mixing valves and the inlet of the printing valve, and in this case it is 2.5×10^{-7} m^3. This represents the maximum volume of a fixed composition that must be mixed, and if less is required, then the remainder is dispensed to a waste reservoir. However, if small increments of composition are sought, this can be achieved by deposition

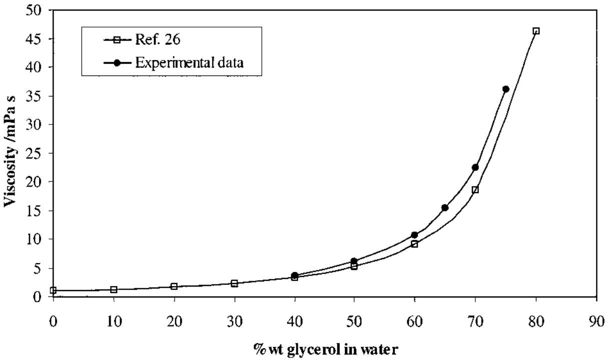


Figure 5. Viscosity of water−glycerol mixtures at 20 °C compared with data from ref 26.

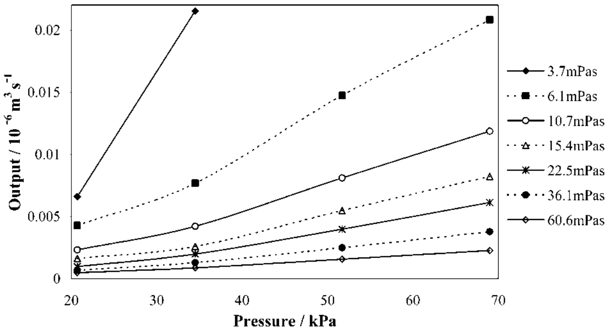


Figure 6. Volumetric flow rate as a function of reservoir pressure and fluid viscosity.

of the sample volume V_s and a discharge volume to waste V_w. The residue is

$$V_m - (V_s + V_w)$$

and in a binary system, if an addition is made of the second component equal to that discharged, then the volume fraction of the initial ink component C is given by

$$C = \left[1 - \frac{(V_s + V_w)}{V_m}\right]^n \tag{1}$$

where n is the number of samples printed. Thus, linearity of composition can be achieved by gradually increasing the volume V_w.

The smallest droplet that can be discharged from the nozzle has a volume of 2.5×10^{-11} m^3, and the smallest amount of ink that can be imported from one of the mixing valves has a volume of 5.7×10^{-10} m^3. This means that the smallest decrement of concentration that can be achieved is set by the mixing valves and is 0.23 vol %. If smaller changes in composition are required, this can be achieved by increasing the volume of the mixing chamber. This is most easily done by lengthening the pipe between pump and manifold. Alternatively, selective ink dilution can be used.

3.2. Calibration. The measured dynamic viscosities of the water−glycerol mixtures are shown in Figure 5 where they are compared with data from the literature[26] with good agreement. Calibration of mixing valves as a function of opening time and pressure was conducted by fitting the exit point of tubing above the precision balance and recording the mass of output liquid. A similar liquid was placed within the balance chamber to establish the same partial pressure and hence to compensate for evaporation during weighing. The length of tubing had an effect on the output mass; longer tubing caused less output under the same conditions. Therefore, the same length of tubing (0.2 m) was used for all delivery lines to eliminate this variable from the calibration process. The output masses were very sensitive to temperature because of the effect of small fluctuations in temperature on the viscosity, and for that reason, the enclosure was essential. Typically at about 20 °C, a 1 °C variation causes a 3.5% change in viscosity. Thus, calibration tests were only carried out when the room had achieved stable temperature and the door and enclosure were kept shut. Viscosity, pressure, and opening time of the mixing valves were the only variables for calibration. The mixing valve calibration curves are shown in Figure 6 in which the output volume per unit time increased as the applied pressure increased and the viscosity decreased.

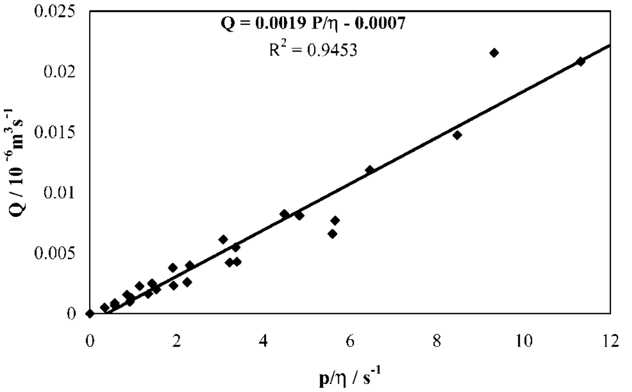


Figure 7. Generalized effects of pressure P and viscosity η on flow rate Q.

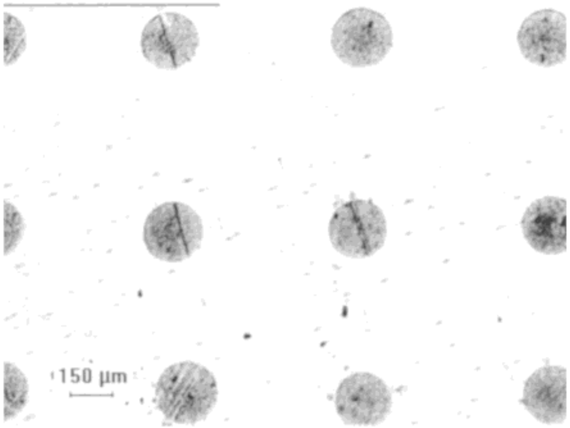


Figure 8. Printed "chessboard" array of one layer on polyester sheet (Melinex).

The data in Figure 6, when fitted by the linear regression equation, yield a general relationship between flow rate Q, pressure P, and viscosity:

$$Q = 0.0019\frac{P}{\eta} - 0.0007 \tag{2}$$

This general expression can be used by the software to program the delivery of components into the mixing chamber. The correlation coefficient deduced from Figure 7 is

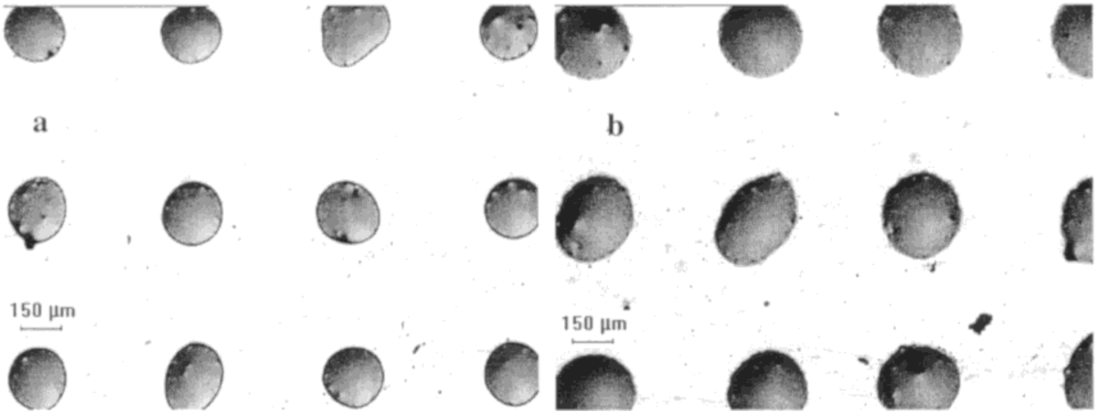


Figure 9. Three (a) and five (b) layer “chessboards” arrays showing the quality of registration.

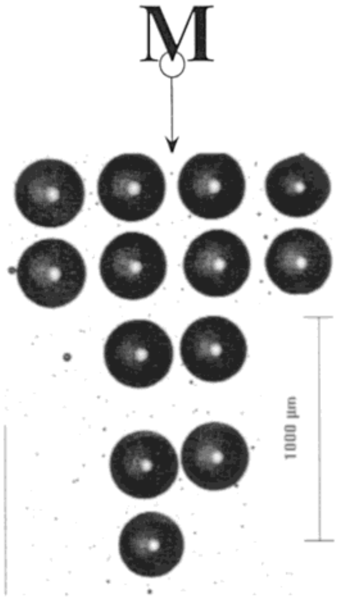


Figure 10. Printed symbol (QM) showing droplet array.

0.97. The volume discharged was proportional to the valve opening time, Δt, so that

$$U = Q\,\Delta t \tag{3}$$

where Q is known from eq 2 and, for calibration $\Delta t \geq 70$ ms.

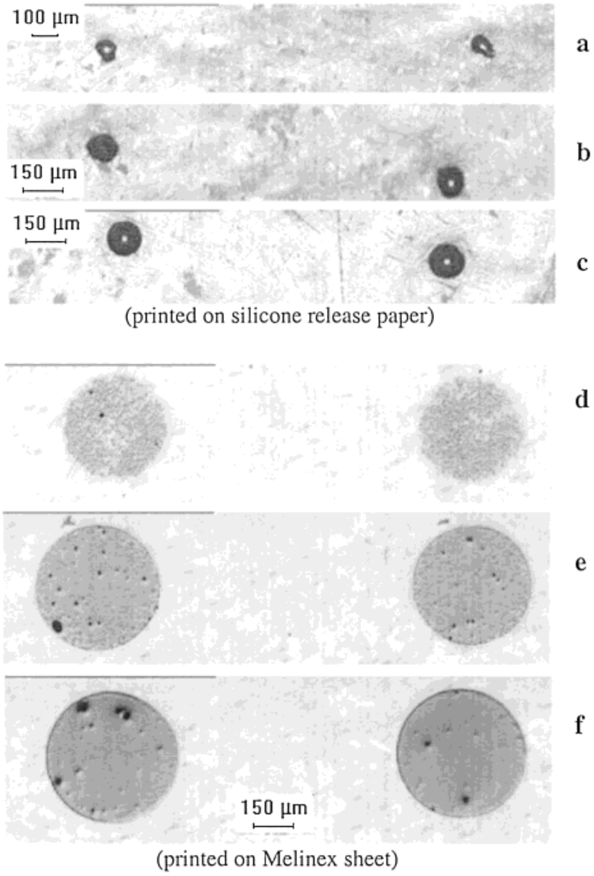


Figure 11. Arrays of dots printed on silicone release paper (a−c) compared with those on Melinex (d−f), which are printed in one (a, d), three (b, e), and five layers (c, f). The registration errors in parts a−c are larger than those in parts d−f.

3.3. Registration. Initial printing tests were carried out by applying different reservoir pressures and different opening times using black ink diluted with ethanol. There was a minimum opening time of 0.186 ms below which the valve does not discharge a drop. This minimum time was independent of reservoir pressure and viscosity of ink. It is associated with inertial effects in the valve. At lower reservoir pressures, there was a *maximum* opening time above which the nozzle did not eject a drop properly; the out-coming liquid spread around the nozzle exit hole and splashing started. Under this condition and after a short printing time, the ejected drops were absorbed by the existing ink on the flooded nozzle area. When dilute black ink was used, the maximum time was in the range 0.27−0.31 ms in the applied reservoir pressure range from 7 to 21 kPa. At higher pressures, this maximum does not exist or is very high. In the case of 69 kPa, by operation of the nozzle valve with an opening time up to 60 ms, dots up to 1 mm diameter were printed and no splashing was observed.

Figure 8 shows the printed chessboard pattern in which the dots are printed at a separation distance of 650 μm. Chessboards printed in three and five layers are shown together in parts a and b of Figure 9, respectively. The registration is good taking into account the low resolution of the table. The “QM” symbol was printed using a mixture of black ink with 65% glycerol in water in order to establish that an ink with a higher viscosity could be adequately deposited (Figure 10). Considering the results, the *XY* table provides good registration precision and is repeatable. It has a 65 μm step distance, and positioning errors attributable to

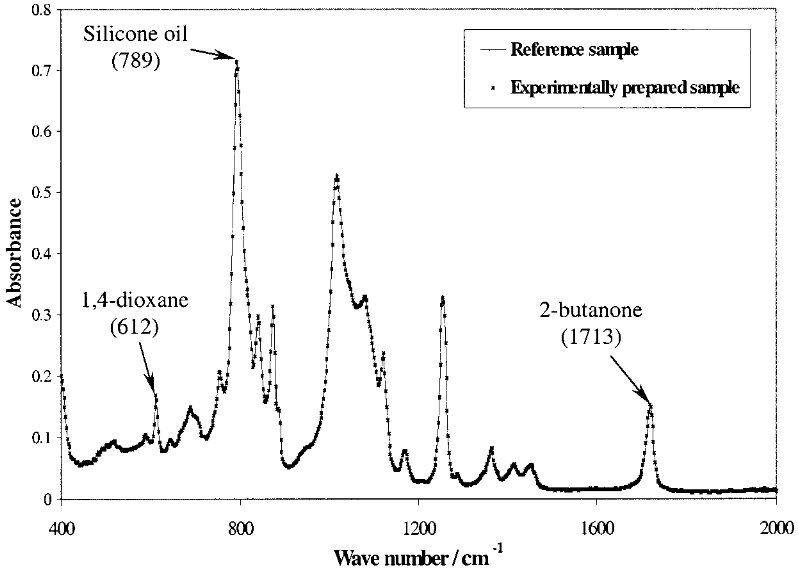


Figure 12. FT-IR spectrum of a ternary mixture of 25% (wt) 1,4-dioxane, 50% (wt) silicone oil, and 25% (wt) 2-butanone (points) indicating the three characteristic peaks compared with a spectrum of the reference sample (line). Each point is the average absorption from four spectra.

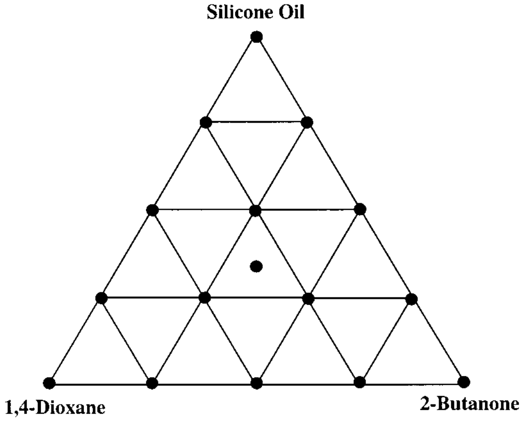


Figure 13. Ternary diagram showing the composition of mixtures used for testing mixing accuracy.

screw wear were generally less than 10% of the droplet diameter. The smallest printed dot using dilute ink and a minimum opening time of the nozzle valve was about 170 μm in diameter. However, dots down to 70 μm were printed on silicone release paper (grade Steralease SL31 ex Sterling coated Materials, Hyde Cheshire, U.K.). Accurate positioning of uniform arrays of dots was not achieved on this substrate because after initial impact and spreading, the drops receded to establish a near-equilibrium contact angle but did not retain their initial centers (Figure 11). These displacements were not due to the table errors discussed above, and they were not systematic.

3.4. Mixing. The liquids selected for confirmation of the mixing capability of the printer provided the following distinct nonoverlapping peaks. The $Si{-}CH_3$ (silicon methyl group) mode absorption of silicone oil at 789 cm^{-1}, the $CH_2{-}O$ mode of absorption of 1,4-dioxane at 612 cm^{-1}, and the $C{=}O$ (carbonyl group) absorption of 2-butanone at 1713 cm $^{-1}$ were used.[27,28] Gravimetrically prepared calibration mixtures were compared with mixtures prepared by the printer. Figure 12 shows a typical spectrum in the ternary. The three distinct absorption peaks are labeled and compared with the reference sample, the spectrum of which is given by the solid line.

Differences between peak heights due to different sample thickness do not affect the result, and the peak height ratios within a spectrum were measured using the method of Liu[29] for quantitative composition measurements:

$$H_r = \frac{H_n}{\sum_{1}^{m} H_n} \tag{4}$$

where H_n is the distinguishable peak height read, modified, and corrected by the FT-IR software "SpectrumV2" (version 2.00, Perkin-Elmer Ltd. 1998) after baseline correction. These corrected ratios were directly correlated with the mass percentage of each component in the mixture. Figure 13 shows the plan of the compositions made for mixture testing in the ternary diagram. Five compositions span each binary, and four are found within the ternary.

Figure 14 shows the intensity ratios of the average of four samples for each point for (a) the binary 1,4-dioxane and silicone oil system and (b) the ternary system containing 25% (wt) 2-butanone and a 75% (wt) mixture of silicone oil and 1,4-dioxane. The compositions of mixtures made by the combinatorial printing machine are very close to those made as reference samples by a gravimetric method for binary and ternary mixtures. The compositional errors are typically 0.3% at a concentration of 50% (wt) 1,4-dioxane, 25% (wt) silicone oil, and 25% (wt) 2-butanone.

4. Conclusions

After considering various design approaches for combinatorial printers, this paper describes the design, construction, and testing of an electromagnetic printer equipped with an anterior ink-mixing facility. The printer has been calibrated for the effects of viscosity, reservoir pressure, and valve opening time, and the mixing accuracy has been validated

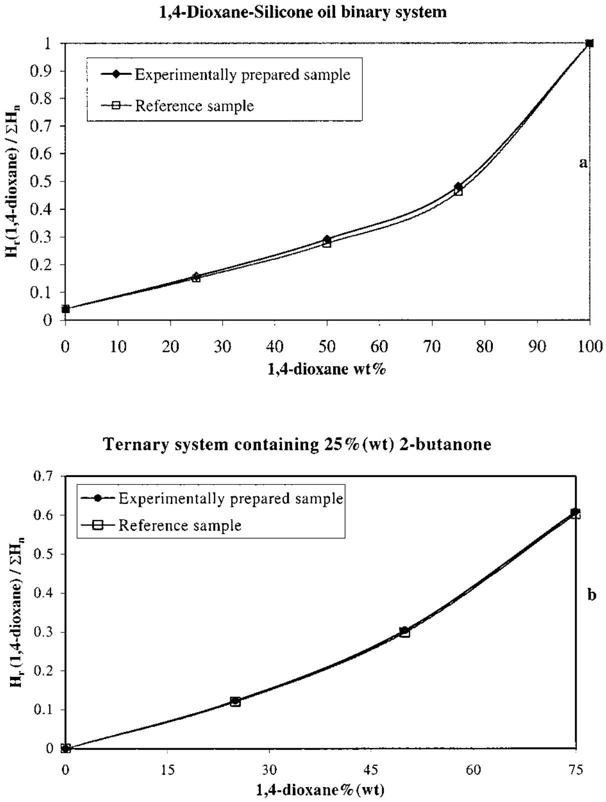


Figure 14. Peak height ratios of test and reference samples.

by infrared spectroscopy of selected test liquids. The design, the methods of construction, and sources of materials and components are explicitly stated. The sources and magnitudes of errors are given.

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