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ORIGINAL ARTICLE

Coloration Technology

Development of a novel three-dimensional printing technology for the application of "raised" surface features

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Abstract

A simple procedure to ink-jet print raised images using two water-soluble inorganic inks is reported and it has the potential to be utilised in domestic and commercial environments. The advantages of such a procedure lies in the ability to print moulded objects, Braille type and to engineer special gonio-specific effects that may have value in the security printing area. The study focuses on printing gypsum through the ready precipitation of calcium sulphate dihydrate by co-jetting calcium chloride and ammonium sulphate solutions. The results in this preliminary study are encouraging and offer a potential method for durable surface structuring of material surfaces with haptic and visual effects for both the blind and the sighted.

1 | INTRODUCTION

The widespread use of ink-jet printing equipment has enabled inexpensive and convenient access to hard copy documents for the domestic market. However, a significant exception to this statement are the important group of blind and partially sighted people. Traditionally, they can access information via their computers through voice recognition packages or by using Braille embossers to produce hard copies. However, the former solution does not address the problem of obtaining hard copies in Braille format and the latter approach is relatively expensive.

Globally, it is estimated that there are about 39 million people who are blind, with up to 1 billion people who have a vision impairment that could have been prevented or has yet to be addressed.[1-3] Therefore, with this ongoing situation there is a potential worldwide customer base of millions of blind or partially sighted people all requiring an ink-jet printer capable of delivering "hard copies" in Braille. In addition, this sector requirement does not recognise other alternative market needs such as customised Braille printing for transportation tickets, lottery tickets, theatre tickets and tickets for sports events. These latter markets will be further influenced by increasing widening access legislation, where sales items must eventually contain Braille-printed information.[4]

Typically, Braille is printed by an embossing machine giving an image height of 0.794 mm, but these machines are too expensive for general home use.[5-7] Although it is reasonable to use this height dimension as a minimum requirement for any ink-jet–printed Braille research development, there is some ambiguity concerning this target height. In the UK, the minimum standard for "touch" reading set by the Royal National Institute for the Blind is a print height of 0.46 mm but in practice it is more likely to be 0.25 mm.[3] Similarly, within Europe there are varying standards for geometric dimensions of the dot and the actual printed dimension.[8]

Recently, KW Special Projects Limited developed an on-demand digital Braille and tactile printing technology as part of a European consortium project.[9-11] Known as "b.my. jet", the new home- or office-based printer digitally prints, via a powder dispersion system, tactile matter in the forms of Braille, as well as figures, maps and graphics. This system enables access to a wide range of Braille material at a significantly reduced cost compared with current embossing technology. Nevertheless, its commercial impact has been limited.

Another approach to printing Braille text has been using a blue light radiation curable printer system, which has the advantage over ultraviolet (UV) curing lamps of deeper cure depth and being potentially less hazardous than the comparable UV lamps.[12] Epoxy-based inks were identified as the “best” in offering greater curing and less tackiness, although dot durability was dependent on the substrate material. More recently, Mimaki have also proposed the use of their flatbed LED UV printers, the UJF-3042FX and UJF-7151plus printers, as Braille printers.[13] However, while these systems offer accurate high quality registration, instant curing of the ink and accurate build-up of multiple layers of ink to create the requisite raised feature, the printers are relatively expensive. Nevertheless, it is reported that:

- The Braille is printable with clear or coloured inks;
- It is possible to print on any surface;
- It is ideal for bespoke signs and prints.

Therefore, in this project, in addressing the market needs, it was felt important to consider two ink-jet Braille printing systems, one a simple addition to existing home ink-jet technology and the other a larger machine capable of the high outputs required for the ticket market. For both markets, this study focused on delivering raised typographical images using simple water-soluble salts that can be contained in existing desktop printers.

Since the 1980s, ink-jet printing has become well established, with the low cost of simple, reliable desktop printers, particularly in the domestic and business markets, accelerating its acceptance and impact. The technology is essentially based on a printhead ejecting drops of ink, which are 20-100 μm in diameter with a volume of a few picolitres, onto the underlying substrate. The two main types of ink-jet technologies are continuous ink-jet (CIJ) and drop-on-demand (DOD) ink-jet printers; CIJ printers are mostly used for coding and marking applications while DOD printers are mainly used in graphics and text printing.[14-17]

Plaster of Paris is a material based on calcium sulphate hemihydrate (nominally $CaSO_4.0.5H_2O$) that can be produced by heating gypsum to at least 150°C.[18-21] For normal use, dry plaster powder is mixed with excess water; hardening commences after about 10 minutes, and the reaction to form the dihydrate should be complete after 45 minutes, although sometimes it may require longer to achieve maximum mechanical performance.[22-24] As a viscous liquid it can be cast in moulds, extruded, applied as a thick slurry to a surface or laminated between paper boards.

This exothermic chemical reaction to form the hard dihydrate (gypsum) typically requires 18.3 parts of water per 100 parts of plaster by weight (Scheme 1) and can reach 60°C. However, in practice, 60-80 parts of water are used so that the plaster can easily be poured into a mould before it sets.[22-24]

In this study, a commercial desktop ink-jet printer was used to print two aqueous chemical solutions from separate cartridges. On mixing, the two distinct solutions react to form a hard, strong, white solid material, nominally “Plaster of Paris” but better termed “gypsum”. The technological approach of this water-based system to deliver gypsum-based structures as multidimensional prints is innovative in terms of its novelty, durability, strength, cost and safety.

2 | EXPERIMENTAL

Calcium chloride (anhydrous, 93%), sodium carbonate (99.5%), ammonium sulphate (99%) and hydrochloric acid (technical grade) were supplied by Aldrich. Paper was supplied by Viking and was the “Everyday” A4 grade.

A HP DeskJet 5550 printer was used to produce the prints on paper and is based on thermal ejection technology. The HP cartridge 57 (colour cartridge with three chambers) and 58/56 (black cartridge with one chamber) were flushed with distilled water and refilled with the selected inorganic solution inks. The two inks were prepared by dissolving the inorganic salt in distilled water followed by filtration to remove any undissolved impurities. The printer mode was set to Inkjet Paper/Best/, which gave a print resolution of 1200 dpi and a print speed of two pages per minute for the black cartridge and one page per minute for the colour cartridge.

Early trials showed, as expected, that insoluble gypsum ($CaSO_4.2H_2O$) was instantly precipitated by the reaction of calcium chloride with ammonium sulphate solutions (typically prepared by dissolving 50 g of each chemical in 75 g of distilled water). During subsequent ink-jet printing trials, these chemical concentrations were adjusted to provide the optimum raised feature profile on the paper substrate.

Ink 1 was ammonium sulphate (41.7% w/w) and Ink 2 was calcium chloride (20% w/w) and both solutions were adjusted to pH 7.0-8.0 by adding dilute ammonia solution. Ink 1 was injected into cartridge 57, Ink 2 was injected into cartridge 56/58, and when mixed/combined on the

$$\underset{\text{Plaster of Paris}}{CaSO_4.1/2H_2O} + 1\tfrac{1}{2}\,H_2O \rightarrow \underset{\text{Gypsum}}{CaSO_4.2H_2O}$$

Scheme 1 Chemical reaction of Plaster of Paris with water to form gypsum

SCHEME 1 Chemical reaction of Plaster of Paris with water to form gypsum paper an insoluble gypsum salt was formed immediately (Scheme 2).

3 | RESULTS AND DISCUSSION

3.1 | Concurrent cartridge printing

The 58/56 black cartridge containing the 20% w/w calcium chloride solution and the 57 colour cartridge containing the 41.7% w/w ammonium sulphate solution were installed in a standard HP DeskJet 5550 printer that was set to print the two inks simultaneously. The image colour was set to “dark colour” on the computer screen and the printing features were set as:

- paper set-up—“plain paper”;
- printing quality set to “best”;
- printing colour feature set as grey-scale;
- “high quality”.

To control how much ink was printed from the two cartridges operating in this specific mode, multicoloured rectangular images were printed. The selected coloured printed images were printed on white paper in “normal mode” (Figure 1A), and comparable rectangular prints were produced on black paper with the calcium chloride and ammonium sulphate solutions using the same settings (Figure 1B).

$$CaCl_2 + (NH_4)_2SO_4 + 2H_2O \rightarrow \underbrace{CaSO_4.2H_2O}_{\text{Insoluble gypsum}} + 2NH_4Cl$$

Scheme 2 Chemical reaction to form gypsum

SCHEME 2 Chemical reaction to form insoluble gypsum

The colours originally showing on the PC screen, which are represented in Figure 1A, controlled how much ink was delivered from the black cartridge and from the colour cartridge onto the paper. Using the same “colour settings”, Figure 1B shows that white solid images of varying density were formed on the black paper. Delivering the optimum ratio of the two inks from the two selected cartridges essentially determines the quality and quantity of the final printed solid. When the image selected on the PC screen is 100% black, the calcium chloride ink from the black cartridge is relatively “overdosed” compared with the amount of the ammonium sulphate ink delivered from the colour cartridge. The resulting visual effect on the print produced on black paper is that an intense white solid was not produced. By contrast, when printing of the PC screen image was reduced to “80% grey”, the resultant gypsum chemical print appeared as a solid white.

To further demonstrate the image definition that could be achieved using the “80% grey” setting, an image of the front of Gloucester Cathedral formed from white gypsum was printed onto black paper (Figure 2). To produce the requisite positive image on the black card it was necessary to print using a negative photographic image on the PC screen.

3.2 | Sequential cartridge printing

The HP DeskJet 5550 printer with Ink 1 and Ink 2 installed was set to print the two inks sequentially under “plain paper” conditions and “best” print quality. In printing colour feature

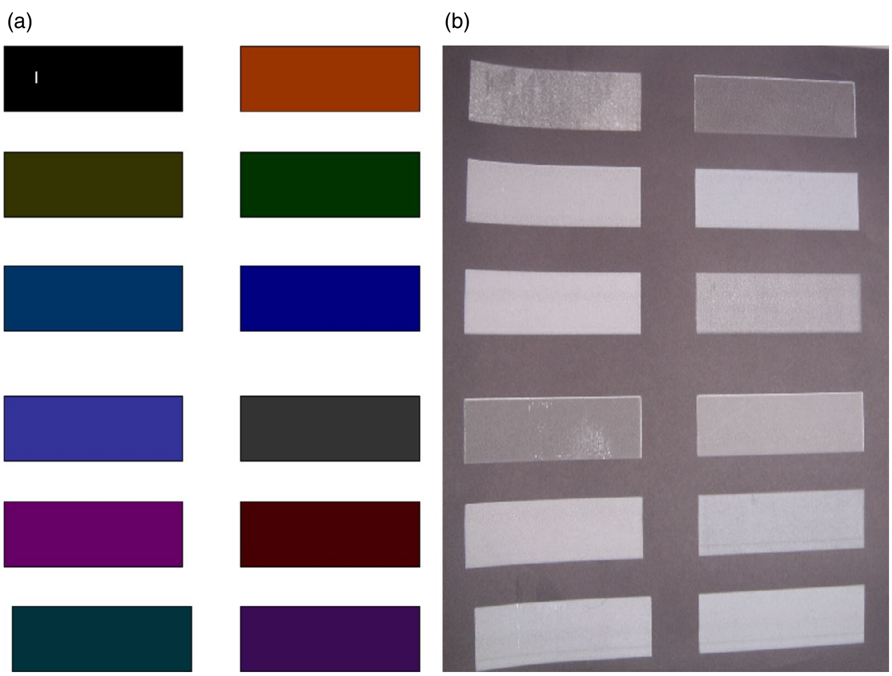

FIGURE 1 Digitally printed images of (A) coloured blocks on white paper and (B) “white” gypsum chemical blocks on black paper printed with comparable instrumental settings

FIGURE 2 Digitally printed image of Gloucester Cathedral formed from white gypsum on black paper using a negative image on the PC screen

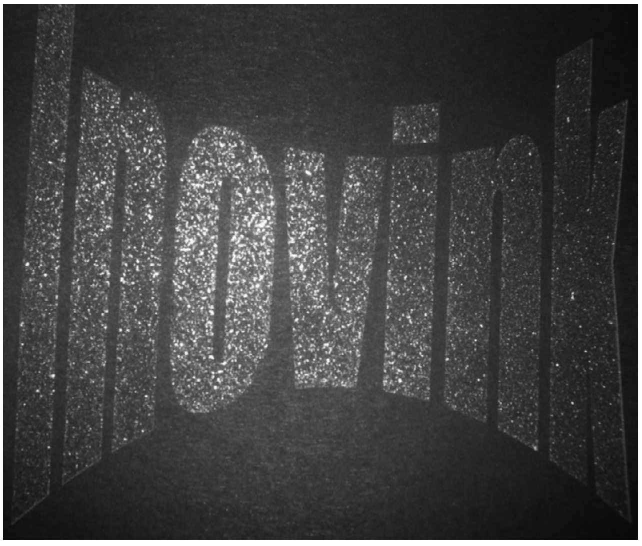

FIGURE 3 "Inovink" logo printed on black paper with ammonium sulphate solution only

mode, the printer was set to grey-scale and it printed from the black cartridge only. Figure 3 (one pass of colour cartridge containing Ink 1 [ammonium sulphate] to produce the printed "Inovink" logo) shows the presence of a shiny crystalline ammonium sulphate raised layer formed firmly on

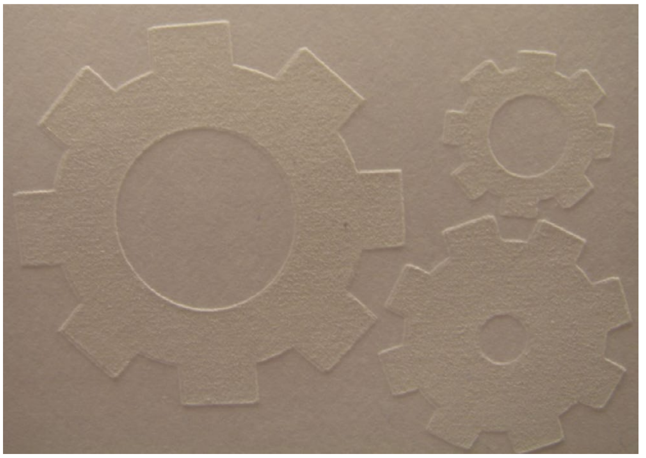

FIGURE 4 Photograph of "gear wheel shape" printed on paper with three initial passes with ammonium sulphate ink and a final last pass with calcium chloride ink

the paper surface. When touched by a moist finger there was stickiness but also the feel indicated that ammonium sulphate alone gave a perceptible topographical "raise" using just one pass of the ink-jet. However, the printed overlayer was not wet resistant due to its high water solubility.

When Ink 2 (calcium chloride ink) was sequentially printed on top of the above printed layers the raised print became stronger and more solid. The Ink 2 print conditions were set as:

- "HP premium photo, gloss";
- "best" printing quality;
- "brightness" in the printing colour feature set to "darkest".

A "gear-shaped" image (Figure 4) was produced using three initial passes of the ammonium sulphate cartridge, followed with a single application pass from the calcium chloride cartridge. It was evident from examination of the materials that the resultant raised gypsum image was durable to abrasion and scratching-off. A beneficial feature of this simple technological approach to three-dimensional (3D) printing is the ability to progressively increase the surface topographical height by increasing the number of ink printing cycles (3 × Ink 1, followed by 1 × Ink 2), as illustrated in Figure 5. This concept offers interesting opportunities for designers and rapid prototyping.

3.3 | Braille printing

Initial studies with sequential gypsum printing on paper revealed that the human finger detected Braille dots after 18 passes with the ammonium sulphate ink and six intermediate

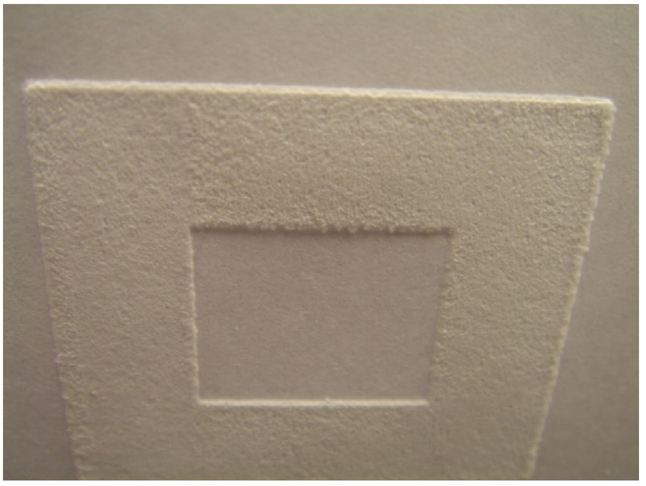

FIGURE 5 Photograph of a "square shape" printed on paper with nine passes with ammonium sulphate ink and a further three passes with calcium chloride ink. The calcium chloride ink was printed after every three print passes with ammonium sulphate ink

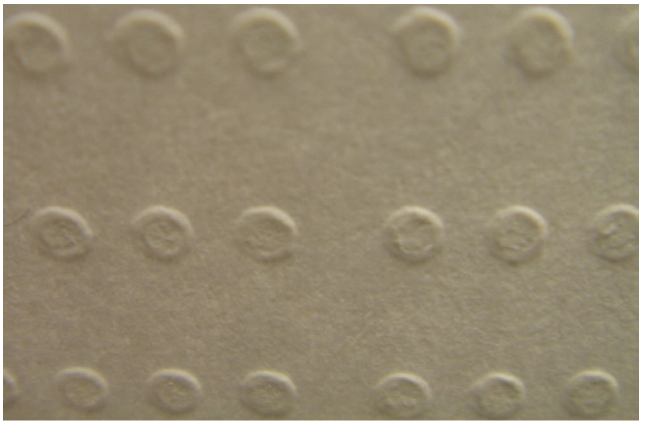

FIGURE 6 Photograph of size 12 Braille printed on paper with 18 passes with ammonium sulphate ink and a further six print passes with calcium chloride ink. The calcium chloride ink was printed after every three print passes with ammonium sulphate ink

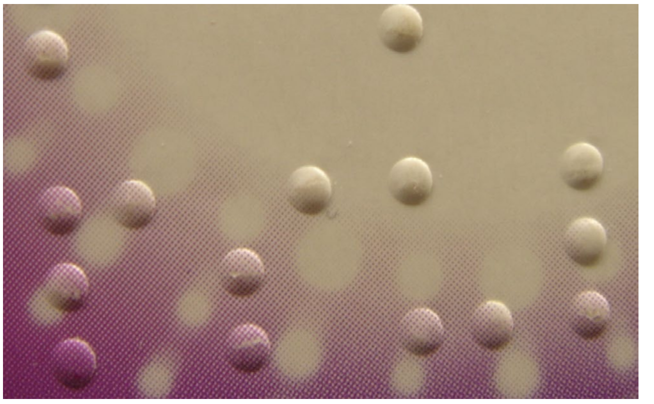

FIGURE 7 Photograph of Braille embossed printed on a commercial pharmaceutical package

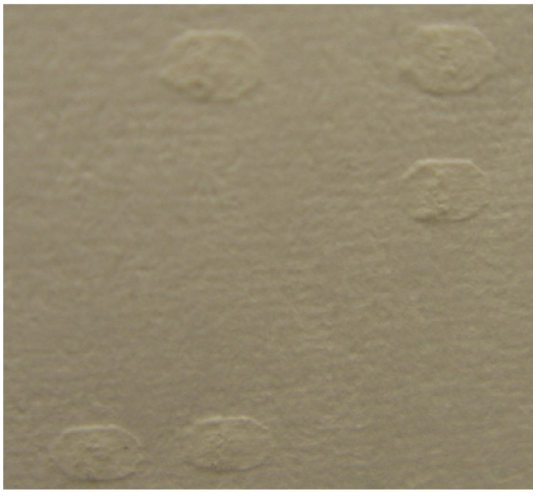

FIGURE 8 Higher magnification photograph of size 12 Braille printed on paper with three passes with ammonium sulphate ink and a further three print passes with calcium chloride ink

applications from the calcium chloride ink cartridge. Microscopic examination of the resultant gypsum dots (Figure 6) indicated that they were comparable in height with the commercially embossed Braille dots (Figure 7) but were not as uniform in structure. The visual analysis of the gypsum dots indicated that the build-up of calcium sulphate was uneven and there was typically a depression in the middle of the dots.

This printing defect was probably due to the chemical migration of Ink 1 on the paper and/or incomplete gypsum formation. The solution to this problem could be to print the two chemicals in alternative passes or to print the two chemicals simultaneously. Some improvement can be seen in Figure 8, when the Braille is alternately printed with three passes of ammonium sulphate and three subsequent passes of calcium chloride, and it is evident that the white solid is deposited more evenly (including the centre of the individual dots) on the paper substrate.

One of the key performance criteria for Braille printing is abrasion durability. In subjectively assessing the rub fastness of the applied dots it was evident that hand rubbing did not abrade the surface deposit significantly or cause "lifting off" of the dot. In our follow-up study to the current paper, in which will also address the issue of wash fastness durability, we will undertake further rub fastness studies using a Martindale Flat Abrasion system or the Taber abrasion tester.

The major focus of this paper was Braille printing and the site-specific application of gypsum as dots. In this application, the small amount of gypsum being printed had little effect on the paper's overall bending stiffness. However, when printing uniformly over a large substrate surface, we did observe some increase in rigidity and a reduction in paper

FIGURE 9 Photographs of white plaster prints of a negative screen image viewed at different angles: (A) vertically at 90° and (B) at 45°. The calcium chloride and ammonium sulphate inks were ink-jet–printed sequentially three times onto white paper

flexibility. This effect is not unexpected and in our subsequent fastness/flexibility/colour study we will undertake further objective characterisation of the printed material using the Kawabata Evaluation System to expand on the current subjective analysis.

3.4 | Smart printing

A further novel feature of 3D printing of gypsum using this sequential ink-jet method may also offer some promise in the security sector. Figure 9 shows the printed images produced from negative photograph images, respectively, with the photographs captured either vertically at 90° or with the camera tilted at an angle of 45°. The raised plaster images clearly give rise to a most unusual effect, whereby the viewing angle determines whether a positive or a negative image is seen. The effect is highly durable and it has high photostability.

4 | CONCLUSIONS

In this paper, we report a novel method, based on simple inorganic chemistry, for printing 3D images or Braille using a quality "home" printer. Printing, sequentially or simultaneously, aqueous solutions of calcium chloride and ammonium sulphate resulted in the formation of a hard, durable gypsum solid on a paper substrate. To manufacture the raised features that are perceptible to a blind person it was necessary, under the specified application conditions, to repeat the printing process by up to 10 cycles. The raised images produced by this safe and inexpensive manufacturing approach were of high quality and durable to abrasion.

"Photographs" produced using this 3D printing method are surprisingly gonio-specific, changing from positive to negative images depending on the viewing angle. This effect has not been reported before and could be valuable in the security printing sector.

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