

CHAPTER 1

Inkjet Printing Technologies

Alan Hudd

Xennia Technology Limited

INTRODUCTION

Inkjet has become a household word through its ubiquitous presence on the consumer desktop as a low cost, reliable, quick, and convenient method of printing digital files. Although inkjet technology has been utilized since the 1950s in products such as medical strip chart recorders by Siemens,¹ and has seen commercial success in high speed date coding equipment since the 1970s,² the potential impact of the technology in industrial applications is only now becoming widely recognized.

In theory, inkjet is simple. A print head ejects tiny drops of ink onto a substrate. In practice, implementation of the technology is complex and requires multidisciplinary skills. Reliable operation depends on careful design, implementation, and operation of a complete system where no element is trivial.

Given the underlying complexity, what drives the industrial adoption of inkjet? The characteristics of inkjet technology offer advantages to a wide range of applications. Inkjet is increasingly viewed as more than just a printing or marking technique. It can also be used to apply coatings, to accurately deposit precise amounts of materials, and even to build micro or macro structures. The list of industrial uses for inkjet technology seems endless and includes

the reduction of manufacturing costs, provision of higher quality output, conversion of processes from analogue to digital, reduction in inventory, the new ability to process larger, smaller, or more flexible, fragile, or non-flat substrates, reduction of waste, mass customization, faster prototyping, and implementation of just-in-time manufacturing.

The introduction of industrial inkjet technology into manufacturing environments can provide a modest improvement, or it can prove to be revolutionary; the commercial benefits are usually obvious.

CURRENT AND EMERGING MARKETS

Commercially successful implementations of industrial inkjet technology include high speed coding or marking of packages or products, mail addressing, the manufacture of simulated-wood doors and furniture, and wide format graphics for indoor and outdoor signs and posters, trade show displays, billboards, and banners.

Emerging applications range from utilitarian to glamorous. Up and coming industrial applications include the decoration of textiles, ceramics, and food; using inkjet to replace existing analogue manufacturing processes such as pad printing, screen printing, spraying, roll coating, and dipping; and the introduction of high speed digital narrow web presses to enhance (or in some cases replace) analogue high speed flexographic or offset lithographic printing equipment for applications like labels, magazines, or books on demand. Particularly hot topics that receive a great deal of press attention and research focus, but are for the most part still on the cusp of commercial success, include the use of industrial inkjet deposition in life sciences applications (such as proteomics, DNA sequencing, or even printed scaffolding for the growth of live tissues);³ 3D rapid prototyping;⁴ optical implementations such as lenses,⁵ light pipes, and films; and electronic applications such as flexible displays, manufacture of color filters, conductive backplanes, LCD functional layers, spacer beads, black matrix, and printed electronics⁶ including RFID, sensors, solar panels, fuel cells, batteries, and circuits.

Various technologies implement inkjet for varying reasons. Some examples:

Application	Benefit of Inkjet
Automotive coatings	Replaces spraying or dipping, thereby reducing waste and increasing coating uniformity.
Plastic part decoration	Non-contact accommodates curved surfaces. Improved print quality over pad or screen printing. Digital eliminates requirement for inventory of screens or pads, resulting in faster prototyping and a wider variety of designs. Process color capability reduces the number of ink colors that must be stocked.
Conductive patterns	Minimizes waste of costly materials; very suitable for short runs.
Rapid prototyping	Rapid formation of three-dimensional structures designed by using computer software.
Variable information	Allows fast changing of the printed information, unlike analogue printing methods which require formation of new hardware (e.g., screens in silk screen printing).
Ceramics	Minimizes setup time, eliminates requirement for inventory of screens.

Industrial Inkjet Explained

While all inkjet technologies can fundamentally be described as the digitally controlled ejection of drops of fluid from a print head onto a substrate, this is accomplished in a variety of ways. Industrial inkjet is broadly and most typically classified as either continuous (CIJ) or drop-on-demand (DOD), with variants within each classification.

As the name implies, continuous inkjet technology ejects drops continuously² (Fig. 1A). These drops are then either directed to the substrate or to a collector for recirculation and reuse. Drop-on-demand technology ejects drops only when required^{7–9} (Fig. 1B).

Continuous Inkjet (CIJ) is considered amateur technology. It is primarily used for marking and coding of products and packages. In this technology, a pump directs fluid from a reservoir to small nozzles that eject a continuous stream of drops at high frequency (in the range of roughly 50 kHz to 175 kHz) by way of a vibrating

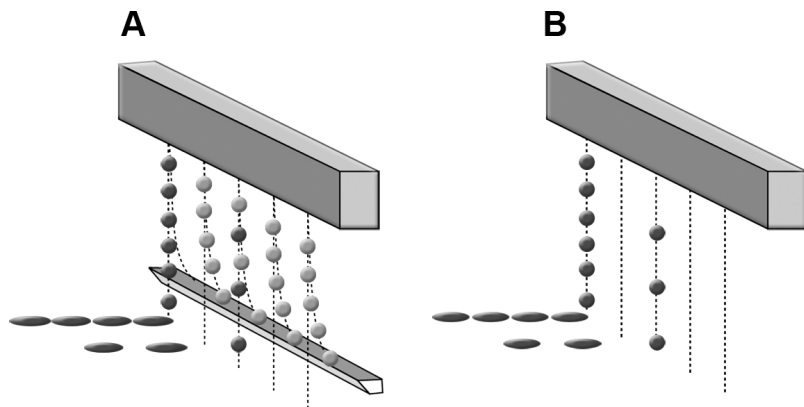


Fig. 1. Schematic representation of: (A) Continuous Inkjet (CIJ) and (B) Drop-on-Demand Inkjet (DOD).

piezo crystal. The drops are subjected to an electrostatic field to impart a charge, the charged drop then passes through a deflection field, which determines where the drop lands. Unprinted drops are collected and returned for reuse. The high drop frequency of CIJ directly translates to high speed printing capability as evidenced by such applications as the date coding of beverage cans. An additional benefit of CIJ is the high drop velocity (of the order of 25 m/s) that allows for relatively (compared to other inkjet technologies) large distances between the print head and the substrate, which is useful in industrial environments. Finally, historically, CIJ has enjoyed an advantage over other inkjet technologies in its ability to use inks based on volatile solvents, allowing for rapid drying and aiding in adhesion on many substrates. Disadvantages include relatively low print resolution, notoriously high maintenance, and a perception that CIJ is a dirty and environmentally unfriendly technology due to the use of volatile solvent-based fluids. Additionally, there are limitations associated with the requirement that the printed fluid has to be electrically chargeable.

Drop-on-Demand Inkjet (DOD) is a broad classification of inkjet technology where drops are ejected only when required. In general, the drops are formed by the creation of a pressure pulse.⁷⁻⁹ The

particular method used to generate this pressure pulse is what defines the primary subcategories within DOD. The primary subcategories are thermal,^{10,11} piezo,^{7–9} and electrostatic.¹² Sometimes, an additional category is discussed (MEMS), but MEMS drop-on-demand print heads are invariably still based on either piezo or thermal inkjet technology.

Thermal inkjet is the technology most used in consumer desktop printers and is making inroads in industry. In this technology, drops are formed by rapidly heating a resistive element in a small chamber containing the ink (Fig. 2). The temperature of the resistive element rises to 350–400°C, causing a thin film of ink above the heater to vaporize. This vaporization rapidly creates a bubble, causing a pressure pulse that forces a drop of ink through the nozzle. Ejection of the drop then leaves a void in the chamber that is subsequently filled by replacement fluid in preparation for creation of the next drop.

Advantages of thermal inkjet include the potential for very small drop sizes and high nozzle density, which leads to compact devices and lower print head and product costs. Disadvantages are primarily related to limitations of the fluids that can be used. Not only does the fluid have to be something that can be vaporized (implying most generally an aqueous solution), but it must withstand the effects of ultra high local temperatures. With a poorly designed fluid, these high temperatures can cause a hard coating to form on the resistive element, which then reduces its efficiency and, ultimately, the life of the print head. The high temperature can also cause problems if, for example, the functionality of the fluid is damaged due to the high temperature (as is the case with certain delicate fluids and polymers).

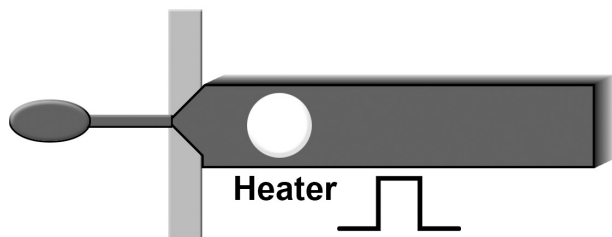


Fig. 2. Schematic representation of a thermal print head.

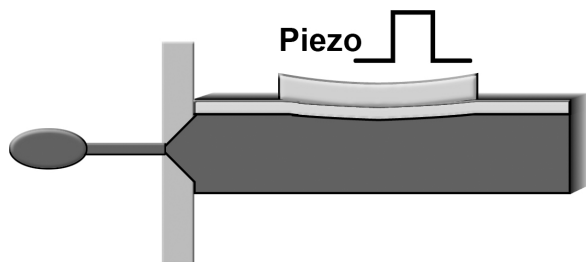


Fig. 3. Schematic representation of a Piezoelectric print head.

Piezoelectric inkjet is currently the technology of choice for most emerging industrial applications. In this technology, a piezo crystal (commonly lead zirconium titanate) undergoes distortion when an electric field is applied, and this distortion is used to mechanically create a pressure pulse that causes a drop to be ejected from the nozzle (Fig. 3). There are many variations of piezo inkjet architectures including tube, edge, face, moving wall, and piston.

Advantages of piezo inkjet technology include the highest level of ink development freedom of any inkjet technology, and long head life. Disadvantages include higher cost for print heads and associated hardware, limiting cost effective integration in low-end products.

There are very few commercial implementations of electrostatic inkjet, though these are increasing. Electrostatic inkjet (of which the most widely known is Tonejet by TTP) is characterized by drops being drawn from an orifice under the influence of an electrostatic field. This field, acting between an electrode and the orifice, attracts free charges within the ink (sometimes described as a liquid toner) to its surface in such a way that a drop is produced when the electrostatic pull exceeds the surface tension of the ink (Fig. 4). As this technique relies on the attraction of free charges, the ink is required to be conductive.

The advantages of an electrostatic inkjet are that it allows you to print a more concentrated fluid than the formulation that actually passes through the print head, and that the achievable resolution is not a function of the nozzle diameter so that potentially higher resolutions than piezo inkjet are possible. Additionally, very small drops can be formed while still using pigments, as the size of the drop

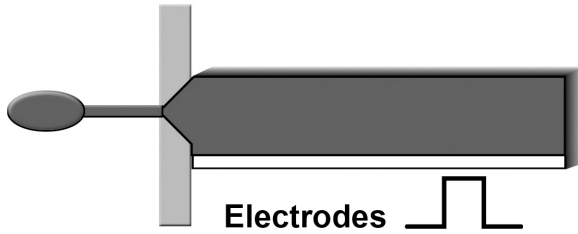
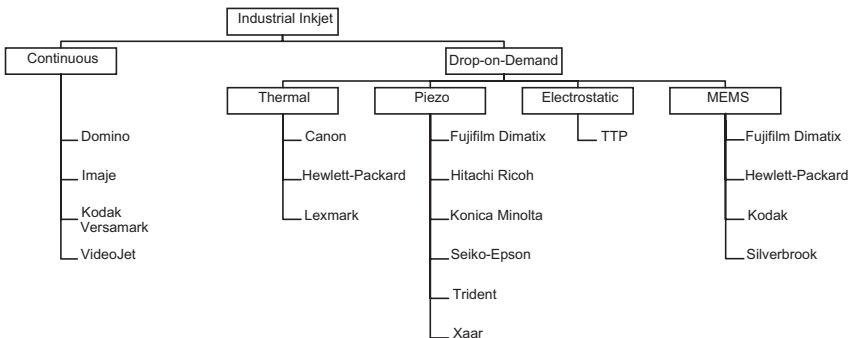


Fig. 4. Schematic presentation of an electrostatic print head.

is controlled by the voltage on an ejection point and the properties of the particles, rather than by the size of the nozzle. As the printed material is significantly concentrated in the ejected drops, there is also the potential for high optical density images. Disadvantages include the limitation of only being able to use conductive fluids and the high cost of implementing the technology. As implementation increases, the cost is expected to go down.

There are literally thousands of companies participating in the design and/or delivery of industrial inkjet systems. Some are extremely vertically integrated (e.g., Hewlett-Packard) and are able to provide most or all parts of the complete solution, from ink to hardware to system integration to distribution, while others are focused on a particular aspect of the value chain (e.g., Xaar). The chart below gives a non-exhaustive indication of some of the major players in the various industrial print head technology variants. It should be noted that while MEMS print heads typically adopt either a piezo or thermal inkjet configuration, here they are shown separately due to the significant implications for the future of inkjet progress.



Inks

In achieving specific printing applications, the whole printing system should be evaluated, namely the print head, the fluid that is jetted from the print head (inkjet ink), and the substrate onto which the ejected droplets are placed. For applications, the requirements are established, defining the type of fluid chemistry, which directs the selection of the hardware and drives the implementation.

There are currently four main types of inkjet inks: phase-change,¹³ solvent-based,¹⁴ water-based,¹⁵ and UV curable.¹⁶ Other types exist, but are less prevalent, such as oil-based and liquid toner (for electrostatic inkjet technology). Hybrid versions of the four main types also exist (e.g., water-based inks containing some amount of solvent). The various inkjet ink types will be discussed briefly in this chapter, and will be followed by detailed description in separate chapters (solvent-based, water-based, and UV curable inks).

Phase-change inks, also known as hot melt, are distributed in solid form and, when introduced into a compatible system, are melted before being inkjet printed. Advantages of phase-change inks include that they are very fast drying (solidifying), environmentally friendly, and exhibit good opacity. It is also relatively easy to control the quality of the print because they do not tend to spread, due to their rapid solidification. Their primary disadvantages are the lack of durability and poor abrasion resistance. Phase-change inks are currently used in applications such as printing of barcodes on non-porous substrates.

Solvent-based inkjet inks have been around for many years and have traditionally been the formulation of choice for grand format and wide format applications due to exceptional print quality, image durability, and range of compatible substrates. They are also generally perceived as low cost. Benefits include the ability to adhere to a variety of substrates and fast drying time (which is often accelerated by heating). Solvent inks can be formulated with either pigments or dyes (or less commonly, both). Disadvantages include environmental concerns and a requirement for high maintenance, due to the potential of the fast drying fluid blocking the print head nozzles.

Water-based or aqueous inks are prevalent on the desktop and enjoy the advantage of being relatively inexpensive and environmentally friendly, but penetration in industrial applications has been slow for a variety of reasons. Water-based inks tend to require porous or specially treated substrates or even lamination to impart durability and the ink tends not to adhere to non-porous substrates. Additionally, many piezoelectric industrial print heads are incompatible with water-based ink formulations, although this is changing in some part due to market demand for systems that can jet water-based biological or food contact fluids.

UV curing chemistry for inks and coatings has been used in printing markets for many years, and thanks to recent investment in the R&D of inkjet print head and fluid formulation, inkjet is now an established and robust deposition tool for UV curable fluids. This is not surprising considering the benefits brought about by the partnering of UV and inkjet technology. UV inks are designed to remain as a stable liquid until irradiated with a particular wavelength and intensity of light.

UV inks are now reliably and successfully employed for a variety of inkjet applications across many different sectors. The benefits afforded by UV, coupled with the flexibility of digital printing, have proved a compelling proposition for many industrial applications and have seen the breadth of UV ink implementations spread from the more traditional wide format/flatbed sectors into the niche application areas of product coatings, primary package decoration, and labelling. Current limitations are in edible and food contact applications. Disadvantages include cost and facility requirements (space, extraction, power) for the UV curing hardware.

As stated earlier, inkjet printing is a system, which should take into consideration the hardware, the ink properties, and the interaction with the substrate. Once the requirements are defined and the ink chemistry and inkjet printing technology have been chosen, there are additional considerations including image/information processing, speed, print quality, cost trade offs, fixed vs. scanning heads, and maintenance systems. In the case of graphics printing, the optical properties of the colorants play an essential role in the

final perception of the image. The image is actually a combination of process colors¹⁷ — cyan, magenta, yellow, and black — and, therefore, the placement of each ink drop and the order of placement, as well as bleeding issues, play significant roles in the print quality. In recent years new inkjet systems have been developed to include, beyond the CMYK set, light magenta, light cyan, and white to widen the color gamut.

For emerging materials deposition applications such as printed electronics, inkjet system requirements are diverse and can include ultra-high precision substrate handling, drop visualization, and fiducial recognition for printing of multiple layers, not to mention the requirement for inkjet fluids that may incorporate “difficult” ingredients such as nano or large particles that must remain in suspension, aggressive acids or alkalis, fragile biological materials, magnetic materials, and in some cases, even radioactive substances.

Technology Trends

Innovation in industrial inkjet is fast and furious. As an indication of the technological activities in this field, there were 3553 US and European patents and patent applications in 2006 alone (translating to roughly 300 per month), making inkjet one of the most actively patented technologies in the world. Hewlett-Packard, Canon, Seiko Epson, and Silverbrook lead the patenting pack, but their efforts cover less than half of all the current activity.

In the past, the primary focus of new inkjet technology development was in the increase of print resolution. By the use of smaller and more accurately placed drops, clever image processing/manipulation and greyscale techniques, inkjet has reached the limit of what the human eye can differentiate (evidenced by today’s low cost, ultra-high image quality consumer printers).

Today, emphasis is placed on throughput improvements by way of increases in raw jetting speed as well as inline, single pass implementations; reliability improvements through the development of self-recovering print heads, integration ease and scalability resulting in elegant and lower cost industrial implementations, development

and extension of pre- and post-processing techniques (such as e-beam curing and UV LED pinning) to extend the capabilities of inkjet, and last, but certainly not least, the enabling of new applications through smaller drop sizes, increasingly accurate drop placement (fueled by the adoption of MEMS technology) and new fluid developments.

Most existing inkjet implementations are multipass, where single or multiple print heads move backwards and forwards across a substrate, building up an image. This can offer high print quality since multiple passes can be engineered to mask the effects of blocked nozzles, but this comes at the cost of speed. In single pass configurations, one or more print heads cover the entire width to be printed. This has great potential for higher throughput, but has historically presented reliability, manufacturing, and cost challenges. These challenges are being addressed and a number of companies are introducing, or announcing, single pass solutions. In particular, the Xaar 1001 print head has been specifically designed for single pass printing; Fujifilm Dimatix announced its SAMBA technology — a single pass prototype head — in May 2008; and Kodak's Stream technology, targeted for shipment in 2010, is a single pass solution that claims to have the print quality and speed of offset lithography. Single pass solutions are ideal for web-based applications such as label printing or any application requiring high throughput. Hewlett-Packard has announced a web press targeted at newspaper and digital book printing that has a speed of 122 m/min at 600 dpi (shipping toward the end of 2009) and Kyocera recently announced availability of what is reportedly the world's fastest high resolution piezo print head with a top speed of 150 m/min at 600 dpi.

Another vector of development in industrial inkjet printing is reliability. It is not unusual for piezo drop-on-demand industrial print head nozzles to achieve successful lifetimes in excess of 10^{13} drops, but this masks the real world requirement of 24/7 operation since print heads can sometimes require a significant amount of ongoing maintenance including purging and cleaning. For example, Xaar is addressing this with the implementation of "self recovery" techniques in the 1001 print head, in which a continuous ink flow through

the channels at 10× the flow rate through the nozzles provides a quick recovery from air ingestion and increased operational time between maintenance of hours rather than minutes.

Other attempts to improve system reliability include implementation of vision systems to detect misfiring nozzles, increasingly being incorporated in manufacturing tools for functional printing (such as electronics or bio) because these applications typically require perfect deposition to ensure functionality.

Partly due to the large amount of attention being put on replacing existing manufacturing technologies with inkjet deposition, there is increasing focus on providing scalable print head technologies that can be reliably and economically integrated. While pursuing their quest for the ideal print head, Silverbrook has developed a technology that is highly scalable from the standpoint of width.

Even mature applications, such as grand format printers, continue to pursue ever increasing print widths in a scalable fashion though not necessarily economically. As an example, Inca Digital is offering the Inca Onset which includes an array of 576 Dimatix print heads (translating to 73 728 nozzles) situated in plug-in print bars with an innovative alignment system.

With the push for smaller feature sizes to enable the benefits of inkjet printing in functional applications, such as printed electronics,¹⁸ a great deal of effort is going into developing technologies that can produce ever smaller drop sizes. As drops get smaller, the energy needed to eject them from the print head must increase so that the effects of fluid surface tension can be overcome. Additionally, as drops become smaller, their surface area to mass ratio changes and, as a result, they tend to decelerate more quickly, which reduces the allowable throw distance. These challenges impact both print head design and fluid formulation. The smallest current drop size for production is technology from FujiFilm Dimatix at 1 picolitre. Today, a print head with the smallest drop size coupled with an optimized fluid formulation, coupled with the perfect ink/substrate combination, coupled with ultra-precise substrate handling, is likely to lead to consistent spot sizes of roughly 30 microns, with sizes as low as 10 microns in laboratory settings.

To further reduce feature sizes, there are a number of non-inkjet techniques presently under investigation, such as self-aligned printing and surface energy patterning. Some predictions suggest that feature size will get down to as low as 10 microns in high volume manufacturing in as few as 5 years.

Many of these technological advances are enabled by the use of IC manufacturing techniques to produce ever finer print head features. DRIE (Deep Reactive Ion Etching) also allows for near vertical walls. Other benefits of MEMS fabrication methods include sub-micron accuracy, robust materials, and the ability for high volume, low cost manufacturing. MEMS techniques are ideal for the creation of nozzles, manifolds, and channel structures in inkjet print heads. Hewlett-Packard is a pioneer in using MEMS for the manufacture of print heads, and Silverbrook has only ever offered MEMS print heads. Fujifilm Dimatix offers an M-class of print heads that take advantage of MEMS technology. The silicon nozzle plate of these heads is much more resistant to scratching than other piezo print heads, and it also offers ultra-precise directionality of ink drops.

Inkjet developments are not limited to inkjet technology. Great success has been made with the combination of UV curing and inkjet, and this is being expanded to related technologies such as e-beam curing and low cost LED (Light Emitting Diode) UV for pinning. In one example, UV curing has limited use in food or food contact related applications due to the requirement of photoinitiators in the formulation. These photoinitiators can be toxic. E-beam curing, which does not require photoinitiators in the ink, is being considered as an alternative, having the advantages of UV curable inkjet (adhesion, abrasion resistance, print reliability, high speed) without the disadvantages. However, the price of the e-beam equipment is currently a limiting factor. In the case of LED UV, these devices are low power, low cost, and do not generate much heat. They can be used to "freeze" rather than fully cure printed drops immediately upon impact with the substrate. This allows precise control of substrate wetting and print quality and can significantly aid throughput and/or print quality when multiple fluid types are required.

Of all these trends, arguably the most important for adoption of inkjet technology is increasing the range of jettable fluids. As an example, in textile printing applications, the use of sublimation dyes that volatilize at high temperature to migrate and bond strongly to the textile fabric to produce a water washable robust image are less than desirable due to the ancillary heating and washing processes required. Utilization of pigmented textile inks can remove some of these process requirements as well as be more suitable for a wider range of textiles (natural and man made). Other examples, such as printing of ceramic inks, direct printing of conductive patterns by using metallic nanoparticles, and printing of 3D plastic structures, will be discussed in separate chapters. Obviously, a main area of activity in formulation of inkjet fluids is the conversion of existing non-inkjet fluids to inkjet, by adjusting the physicochemical properties of the liquids to the overall inkjet system requirements.

Challenges

Inkjet must be understood as a complete system. Many disciplines (materials science, chemistry, device physics, system integration, production engineering, software, mechanical engineering, electronics) must be brought together. Customers still face application challenges and available production tools, still in their infancy, often do not meet all requirements. It is not uncommon for systems to exist that work in the laboratory but are not yet ready for a 24/7 industrial environment.

The main challenges in improving the performance and utilization of inkjet printing are:

Materials: Increasing, but still slow, is the development of jettable materials. There is no such thing as a universal ink. In each case, many issues have to be considered, among them: application performance (functional), print quality (bleed, surface wetting), compatibility, drying/curing time (relating to speed), adhesion (sometimes inter-layer interactions), image robustness (water fastness, gas fastness, light fastness, abrasion resistance) jetting characteristics (viscosity, dynamic surface tension, particle size, compatibility), reliability

(volatility, wetting of capillary channels, priming, purging, shelf life), ease of manufacturing (milling, cost and availability of materials), regulatory (FDA, etc.), post- or pre-processing requirements (UV, e-beam, heating, inert atmospheres).

An abundant approach to achieving jettable materials is based on adjusting the composition of an existing ink to match the printing system requirements. Usually this approach is not trivial, since non-inkjet formulations usually have very different properties to inkjet inks. For example, converting a silk screen printing ink would require, among other changes, a significant decrease in the viscosity, and a significant decrease in particle size in pigment-containing inks. Decreasing the viscosity, in the case of large pigment particles, would lead to sedimentation and aggregation of the particles. To prevent this would require a submicron pigment size (also important for not clogging the print head). Such pigments (metallic, ceramic, etc.) are not always available commercially, and in that case they should be manufactured specifically for the new inkjet ink.

Feature size: Another challenge is associated with feature size reduction, especially for sophisticated printing of functional materials,¹⁹ such as in printed electronics. This can be achieved by combined effects of the whole printing system, such as surface treatment of the substrates (see separate chapter) and achieving unique rheological behavior of the ink.

Resolution and productivity: Higher resolution and substrate handling at higher speed is a very demanding task. While approaching the fundamental limits of increased jetting frequency, the productivity needs to be improved in other creative ways. To date, this has been accomplished through increasing the number of nozzles, although this is directly related to increased cost.

Drop placement accuracy: Exact drop landing position is uncertain, due to various parameters such as jet-to-jet variations, single jet-over-time, sensitivity to nozzle straightness, nozzle and surface wetting, nozzle plate contamination, ink formulation and condition, and drop velocity. This issue is worse for longer flight paths or “throw distance”.

In summary, inkjet success is based on treating the “inkjet detail” with respect. Although it is elegant in concept, it is very difficult to implement in practice, especially in very demanding applications such as very high throughput systems, and printing of functional and unique materials.

REFERENCES

1. Elmqvist R. (1951) US Patent No. 2,566,443.
2. Sweet R. (1971) US Patent No. 3,596,275.
3. Sachlos E, Wahl DA, Triffitt JT, Czernuszka JT. (2008) The impact of critical point drying with liquid carbon dioxide on collagen-hydroxyapatite composite scaffolds. *Acta Biomater* 4(5): 1322–1331.
4. Napadensky E. (2003) U.S. Patent No. 6,569,373.
5. Momma T. (2006) European Patent No. EP 1683645 A1.
6. Siringhaus H, Tatsuya S. (2003) Inkjet printing of functional materials. *Materials Research Society Bulletin* Nov: 802–806.
7. Zoltan S. (1972) US Patent No. 3,683,212.
8. Stemme N. (1973) US Patent No. 3,747,120.
9. Kyser E, Sears S. (1976) US Patent No. 3,946,398.
10. Kobayashi H, Koumura N, Ohno S. (1981) Liquid recording medium. US Patent No. 4,243,994.
11. Buck RT, Cloutier FL, Erni RE, Low RN, Terry FD. (1985) US Patent No. 4,500,895.
12. Silverbrook K. (1998) US Patent No. 5,781,202.
13. Berry JM, Corpron GP. (1972) US Patent No. 3,653,932.
14. Bhatia YR, Stallworth H. (1986) US Patent No. 4,567,213.
15. Chandrasekaran CK, Ahmed A, Henzler TE. (2003) European Patent WO 2003076532 A1.
16. Noguchi H, Shimomura M. (2001) Aqueous UV-curable ink for inkjet printing. *RadTech Report* 15(2): 22–25.
17. Pond SF, Wnek WJ, Doll PF, Andreottola MA. (2000) Ink design. In Pond SF (ed), *Inkjet Technology and Product Development Strategies*, pp. 153–210. Torrey Pines Research, Carlsbad.
18. Isobe M, Takiguchi H, Kiguchi H, Shibatani M. (2008) Japan Patent No. 2008233572 A.