Surface Modification Technology for Inkjet Industry

Toshimitsu Hirai, Hiroshi Kiguchi

IJ Industrial Applications R&D Department, Seiko Epson Corporation; Fujimi-machi, Nagano/Japan

Abstract

Ink-jet printing is based on the concept of a micro-liquid process and is expected to be an innovation process in FPD manufacturing. In precision Ink-jet printing, basic technique of controlling dot-landing, location, process of film formation, surface design and surface treatment of substrate are each very important elements of the process. The technique that is mainly used is a combination of both bank structure with photolithography and Ink-jet, which enables high definition printing. The bank has a property designed to repel ink solvents via surface treatment. In addition to discussing this technique, various surface treatments utilized in inkjet printing to produce a variety of devices are reported. The current situation of surface treatment technique for several applications will be introduced.

Introduction

There are two types of ink-jet printing methods: a continuous type and an on-demand type. In the former, ink droplets are continuously discharged and, in the latter, ink droplets are selectively discharged. The latter is now widely used in terminal printers for personal computers. The drop-on-demand type using piezoelectric elements has a feature that a uniform and fairly spherical droplet of ink can be discharged to a targeted position and it also offers great flexibility to ink choices. For this reason, application of the piezoelectric drop-on-demand type ink-jet printing method to other manufacturing and industrial use has been expected. Our company has been focusing on piezoelectric inkjet technology to produce high resolution and high quality printings on papers. The minimum volume of 1.5 picoliter droplet has enabled extremely high dot density marking with reduced dot to dot spacing. In addition, Variable Sized Droplet Technology (VSDT) [1], in which three different sized droplets, small, medium and large droplets can be discharged from the same nozzle by changing a driving waveform, has been further evolved to the extent that the different sized droplets are selectively discharged according to an output image, achieving a high speed printing. Optimized sizes of the three different sized droplets as the multi-dots are, for example, 4, 7, 11 picoliters in the case of 1,440 dpi, and 6, 10, 20 picoliters in the case of 720 dpi. 6 color ink pallet is normally adopted and this realizes printing in realistic color tone. Unevenness in printed color caused by variation in the volume of droplets discharged from different nozzles or by linefeed of a head in a printer can be resolved by introducing the VSDT processing and an error diffusion method.

An ink absorbing layer called an ink receiving layer is usually formed on the surfaces of a print medium in order to make ink-jet droplets permeate and color the medium immediately after the droplets land on the medium. Such technique is important in providing a high-quality image printing as well as a technique concerning a printer head. In the light of the application of the ink-jet technology to other manufacturing and industrial use, an accurate ink patterning directly on unabsorbent substrates made of glass, plastic, metal and so forth will be required. However, in many cases, a thin film other than the receiving layer is previously formed on a substrate and the receiving layer cannot be used. In such case, it is necessary to develop a different technique from the ones used in the ordinary printing, for example, a technique to precisely control the spreading behavior of a droplet after it landed on a substrate.

Elemental technologies for industrial application of the inkjet technology

The following six elemental technologies are important for the industrial application of the inkjet technology.

(1) Inkjet Head

For the industrial application of the inkjet technology, a highly reliable inkjet head which can precisely and quickly split ink into minute droplets is required. We actually use Multi-layer Actuator Head (MACH) which is driven with a piezoelectric element. The ink flight accuracy of this head is within ±11.2 μm in 300 μm distance from the nozzle surface. Moreover, variation in the droplet volume discharged from the nozzles in this head is so small that normal measurement approaches cannot detect the variation.

(2) Ink

The ink used in the industrial application is a functional liquid that includes metal, semiconductor, ceramic, organic polymer material, pigment or the like and can be formed into a functional thin film through a drying process. For instance, a metal ink has functional properties such as conductivity and its ink properties should include stability in the ink discharge operation. Selection of the solvent in the functional liquid should be carefully considered in terms of viscosity and dryness on the nozzle surface.

(3) Inkjet Apparatus

The inkjet apparatus should be equipped with its own head supporting system in order to achieve a high throughput and a stable mass production operation. The head supporting system includes a wet maintenance mechanism maintaining a nozzle plate clean, an independent sequence that prevents the viscosity of the ink from increasing in the nozzle, a measurement function of droplets in flight and after landing for monitoring the nozzle clogging and straightness in the flight trajectory of a droplet, a discharge amount measuring device for keeping the volume of the discharged droplet constant, and a feedback control system.

(4) Surface Design and Surface Treatment

Commonly used substrates in the fields of the inkjet industrial applications usually don't show ink acceptability. The shape of an ink dot after landed on the substrate changes and gradually gets poised. The shape of the ink dot is eventually settled into a form decided by the contact angle which is the angle between the tangent line of the ink liquid contour and the solid surface of the substrate. Therefore, the surface property of the substrate and the surface tension of the ink need to be optimized according to a desired print pattern.

(5) Dot Arrangement and Liquid Adhesion

The print pattern by the inkjet method consists of overlaid dots and a dot arrangement. The dot arrangement and the arranging order should be designed in consideration of the interaction between the droplet that has just been discharged onto a substrate and the droplet that has already settled on the substrate.

(6) Drying and Film Forming Techniques

It has been reported that a drying behavior affects the film formation. The solute in the droplet is generally separated out after the droplet adhered to the substrate and it shows a film thickness profile like a 'coffee stain' [2]. This happens because the droplet turns into a film from its peripheral part where the solvent firstly starts to evaporate ahead of the other part of the droplet. The solvent and the solute are transported to the peripheral by convection during the drying process and the solute is concentrated in the peripheral, forming a ring-shaped film. Therefore, it is important to figure out parameters and the drying behavior in the drying process so as to obtain the film profile with even thickness.

The six essential technologies in the fields of the inkjet industrial applications have been given as described above. One of the most important elemental technologies among them is the surface design and the surface treatment. This is because the surface design and the surface treatment most affect the behavior of the droplet that landed on the substrate after discharged. In this paper, focusing on a wettability control method which is most important in the droplet pattern formation, an overview of the wettability control method is hereinafter described.

Common Surface Treatment

In the method of controlling the wettability on the surface, it is required to form the functional surface effectively. Here, 'effectively' means that a desired function is given to only a targeted surface. In order to realize this, various surface modification methods have been studied. The surface modification methods include a modification by energy ray radiation represented by plasma processing, a modification by surface modification agents, a modification by chemical adsorption (chemical treatment) and so forth [3].

In the modification by the energy ray radiation such as plasma processing, a surface is fluorinated through a fluorine gas treatment using CF_4, SF_6 and the like. This modification method is generally used as a versatile method to give water/oil repellency only to a surface made of polymer such as plastic without using expensive fluorine contained compounds. If an active group such as a carbonyl group (-C=O) and a carboxyl group (-COOH) is formed on the surface by using O_2 gas, the surface can be made hydrophilic or lipophilic. Dry process methods such as UV treatment, corona treatment, CVD treatment and so forth can be performed instead.

The modification by surface modification agents can be exemplified by a surface modification with fluorine surface modification agents mainly targeting on a plastic surface. In this modification, the surface modification agent is added to a plastic resin and the surface modification agent is segregated in the interface between the resin and the air. Though it is different from the surface modification agents in form, fluorine series polymer material which is soluble in organic solvents and easy to be mold is under development. The surface can be modified by coating the substrate with this material [4].

As the modification by chemical adsorption, there is a film forming technique in which a combination of a substrate material and a reactive organic molecule is selected so as to form a film in a self-assembling manner. This kind of organic thin film is called Self-Assembled Monolayer (SAM) and its thickness is only some nanometer. The chemical reaction between the organic molecules and the substrate surface starts when the substrate is immersed into the solution of the organic molecules or the substrate is placed in the vapor of the organic molecules, the molecules are then chemically adsorbed or bonded to the substrate surface. After the SAM adsorbed or bonded, the substrate surface is covered with end-functional groups that are positioned opposite to the functional groups bonded to the substrate. The adsorption or bonding will stop when there are no more reaction sites in the substrate surface. Accordingly, the reaction stops when the monolayer covers the whole substrate. The physical and chemical properties of the surface can be controlled by selecting the end functional group. For example, the surface energy of the substrate can be made small if the surface is covered with an alkyl group or a fluorinated alkyl group. Organic silane type SAM is fixed to the substrate through siloxane bonds (covalent bonds) and it has excellent mechanical strength and chemical stability. Accordingly, it has attracted much attention as the SAM having a high possibility to be put into a practical use in the fields of the surface modification and a surface functionalization.

In addition, a high resolution patterning on the SAM through various lithography techniques is possible because the SAM is a dense, uniform and highly-oriented thin film. For example, when the SAM is irradiated with vacuum ultraviolet rays through a mask in an exposure equipment of the vacuum ultraviolet radiation (172 nm), the organic molecules composing the irradiated part of the SAM turn into gas molecules such as CO, CO_2, and H_2O and they are removed. The substrate is exposed in the area where the SAM is dissolved and removed, forming a micropattern that has different surface properties. Alternatively, a lithography using a photocatalyst such as titanium oxide has also attracted attention these days as the lithography technique for the SAM. The Photocatalyst is the material that absorbs photon energy and induces an oxidation/reduction reaction. It has a strong oxidizing power and is capable of decomposing organic contaminants. In such oxidative decomposition, its decomposing power can propagate to a target positioned in the area where the photocatalyst doesn't reach directly, and the oxidative decomposition can work there. Therefore, it is possible to form the hydrophilic/lipophilic pattern by decomposing the SAM through the mask made of the titanium oxide film [5].

Inkjet Technology and Surface Treatment

The most significant advantage of the inkjet technology as a pattern formation technique is that it is capable of dropping a desired amount of dots precisely at a targeted position. Many application cases of the inkjet technology have been developed and reported. The inkjet technology is used to manufacture various devices whose manufacturing process includes an application step. For example, there are color filters (CF) for a liquid crystal displays (LCD), organic electroluminescence (EL) devices, plasma display panels (PDP) [6], printed circuit boards, transistors made of liquid silicon material [7], low-temperature-polycrystalline silicon (LTPS) [8] and so forth. Especially, as for the application process in the formation of an alignment film of a liquid crystal panel, it is demonstrated that the inkjet method is a low-energy and highly efficient innovative production technology [9]. Moreover, it is possible to further advance the pattern formation technology by combining the inkjet technology and the substrate surface treatment technology.

The above mentioned common surface treatment methods can be combined with the inkjet method as the surface treatment and design method. From the aspect of the surface design, the formation of the lyophobic/lyophilic pattern that is made by a so-called bank structure, has some micrometer thickness and formed by photolithography techniques or Laser Induced Thermal Imaging [10] techniques is also included in addition to the formation of the high definition hydrophilic/lipophilic pattern formed by the SAM lithography technique. These surface treatment and surface design methods are categorized in Figure 1.

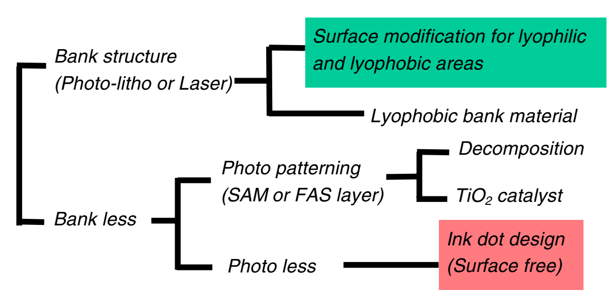

Figure 1. *Classification of surface treatments in industrial application*

For example, the surface design of the lyophobic/lyophilic pattern often used in the inkjet color filter production has the following steps. First, a bank is formed on a glass substrate by photolithography. A plasma treatment in an oxygen gas atmosphere is performed as the first step in the surface treatment. Subsequently, another plasma treatment is performed in a fluorine gas atmosphere is performed as the second step in the surface treatment. By conducting the plasma treatments in this order, the oxygen groups, the hydroxyl groups or the like which have a large surface energy are adhered on the glass surface and the surface is made lyophilic. On the other hand, the bank surface made of an organic material is processed so as to bond with fluorine and then the bank surface is made lyophobic [11]. The same type of the bank can also be obtained by adding a fluorine surface modification agent to the organic material that forms the bank. Practical examples of the surface treatment application are hereinafter described.

First Example of the Surface Treatment Application

The surface treatment and surface design method that is used to form color filters and the like by the inkjet method shown in Figure 2 is now introduced. Adopting the above-described surface treatment method, droplets including coloring materials of red, green and blue (RGB) are discharged into the areas surrounded by the banks by the inkjet technique. Even if the ink once flows onto the bank, the bank repels the ink, the ink then flows into the opening area surrounded by the bank where is going to be a picture element, and the ink is eventually settled there. This prevents the ink droplet from contacting the other droplets discharged onto the adjacent picture element or from flowing into the adjacent picture element area. Here, the ink that shows a small contact angle on the glass is used so that the ink can sufficiently spread out within the picture element and settle there [11].

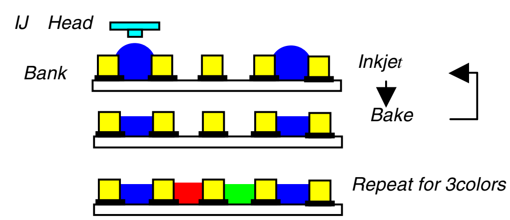

Figure 2. *Color filter production process*

Second Example of the Surface Treatment Application

A representative example of the pattern formation on the lyophobic substrate by the inkjet method is the application to a bus electrode wiring of the plasma display [6]. In order to form minute and fine wirings, the substrate surface needs to show a certain lyophobic quality preventing dots from spreading out too much on the surface. In this forming method, the wiring consists of a plurality of dots. When dots are sequentially aligned, discharged droplets congregate at a certain point by the interaction between the droplets already landed and the droplets just landed, forming bulges as shown in Figure 3. A theoretical model of the bulge formation has been reported [12]. In the report, focusing on inner pressures of a line part and the bulge part, each inner pressure is derived from the corresponding contact angle and the curvature. A variation in the dynamic contact angle caused by the motion of the ink droplet moving forward and backward and a time variation in the curvature of the ink droplet, in other words, a time variation in the inner pressures is estimated. In this way, the report modeled the mechanism of the bulge generation.

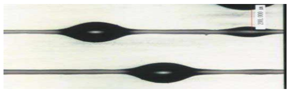

Figure 3. *Example Buldge* [6]

We optimized two parameters so as to prevent the budge generation and to pattern fine lines at the same time. One parameter is the contact angle between the ink and the substrate surface. The other parameter is an overlap width of two adjacent droplets (a distance between the two adjacent droplets). By adjusting and optimizing these two parameters, we were able to form the wiring with 30 µm width, 0.5 µm film thickness and 2 µm Ω cm specific resistance (see Figure 4)

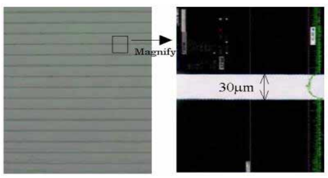

Figure 4. *Metal wiring with 30 µm width*

By applying this technique to the wiring of PDP, we formed the bus electrode with 50 µm width, 2 µm film thickness and 2 µm Ω cm specific resistance on indium tin oxide (ITO) (see Figure 5). The SAM was used for the surface treatment, and the contact angle was optimized in such a way that the landing diameter of the droplet becomes 50 µm. Furthermore, multi-layered drawing that has the drawing process shown in Fig6 was performed in order to avoid the bulge generation and to secure a sufficient film thickness. In the first droplet arrangement step, the two adjacent droplets, which are discharged and land onto the substrate virtually at the same time, are placed with a sufficient distance therebetween so as to prevent them from merging each other. In the next droplet arrangement step, a droplet is placed between the precedent droplets so as to fill the gap and the continuous wiring pattern is formed.

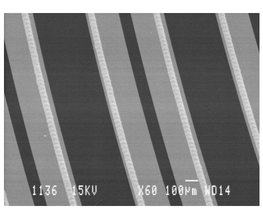

Figure 5. *Inkjet bus electrode (SEM image)*

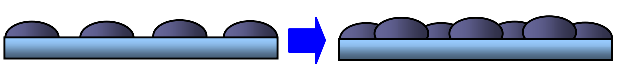

Figure 6. *The dot pattern for preventing the bulge.*

Third Example of Surface Treatment

In the lyophilic substrate, the droplet spreads wetting the substrate after landing thereon. It is an important surface property for forming a film with an even thickness together with the drying technique. As a specific application example, we have developed a proprietary device integrally including a preprocessing mechanism for controlling the surface property, an inkjet coating mechanism, and a drying mechanism. The alignment layer coating technique using the inkjet method has been introduced to a manufacturing line of high-temperature polysilicon TFT panels for LCD projectors, and mass-production thereof has been achieved. An improvement of the thickness evenness can be achieved in comparison with the conventional flexographic printing process (see Table 1). Further, by implementing a mechanism for preventing the head from clogging with the solvent ink and for detecting malfunctions, high stability and reliability of the process have been achieved.

In the substrate surface treatment here, the contact angle is controlled so that an even coating film can be formed by arranging about 50,000 through 100,000 dots of inkjet fine droplets each weighing about 10ng precisely on the substrate and then drying them. In addition, optimizations of the ink and the drying process have been also conducted, and it has become possible to achieve improvement of display quality of the LCD projector panels [9].

Table 1: Comparison of the film thickness variation in the alignment layer

	Flexographic printing Process	Inkjet Process
Uniformity of layer thickness	σ 13Å	σ 5Å

Efforts for Fine Wiring Formation

In general, 'Young's equation' is applied to the droplet landed on the surface of the substrate in its resting state.

$$\gamma_S = \gamma_L \cos\theta + \gamma_{SL} \quad \textit{Young's equation} \qquad (1)$$

In this case, the angle θ made by the tangent line of the contour of the liquid with the surface of the solid substance is the 'contact angle' and optimizing the contact angle in accordance with a printing pattern is a basic idea to precisely control the behavior of the droplet (see Figure 7).

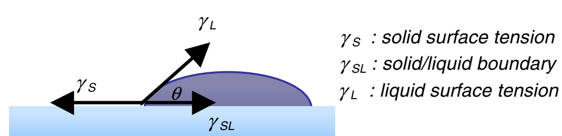

Figure 7. *Wetting state of the droplet on the solid surface*

In the case when the contact angle θ = 0, in other words, the surface tension of the liquid is equal to or less than the critical surface tension (γ_C) of the surface of the solid substance, the droplet completely wets the surface of the substrate. In the case when 0 < θ < 90 degree, the droplet spreads the surface in accordance with the contact angle. In the case when θ > 90 degree, the liquid wets the surface, but never spreads wetting the surface extending beyond the diameter of the droplet when it lands thereon. Since in the pattern formation using the inkjet method, the pattern is formed by overlapping a plurality of droplets, it is generally preferable for forming a fine pattern that the contact angle is set to be large.

Change of Droplet Behavior due to Substrate Surface Wettability Difference

We have developed an instrument that visualizes the droplet landing behavior, and have observed droplets landing on a lyophobic substrate and a lyophilic substrate using the instrument. The droplets ejected on the substrate using the inkjet method have substantially the same landing diameters in several tens of microseconds right after the landing irrespective of whether the substrate is lyophobic or lyophilic (see Figures 8(a) and 8(b)). In the case when the resting state lasted for a period of millisecond -order or longer, it was confirmed that the difference in the wettability of the substrates appeared as the difference in the width of the droplets according to Young's equation.

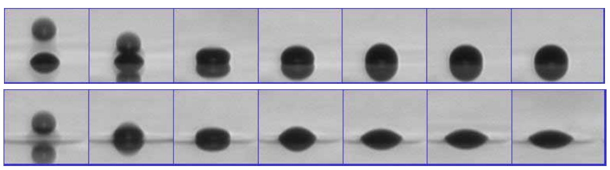

Figure 8. *(a)Droplet behavior on the lyophobic substrate*
(b) Droplet behavior on the lyophilic substrate

If the plurality of droplets ejected from the inkjet head can be fixed to the substrate within a few milliseconds, the droplet control by the surface treatment of the substrate can be eliminated. Meanwhile, it is thought that very high precision thin film formation becomes possible by actively utilizing the phenomenon that, in the condition when the contrast between lyophobicity and lyophilicity is sufficiently provided, the droplet voluntary moves from the lyophobic section to the lyophilic section so as to select the position until the balanced state is created, as a simplified measure for controlling the behavior of the droplet.

Future View of Industrial Inkjet Technology

Currently, the market of large-sized liquid crystal displays is rapidly growing, and it is conceivable that the only the inkjet technology can immediately handle with the multiobjective production with expansion of the mother glass in size or changes in the specifications of the thin film patterns [13]. The new manufacturing process is capable of eliminating the drawbacks in a lump such as heavy consumption of the materials or maintenance of huge and expensive manufacturing equipment in the existing manufacturing technology such as the lithography for color filters, the flexographic printing for alignment layer, the vacuum deposition technology for metal wiring or silicon material of TFT arrays. Further, as a result of a strict life cycle assessment in the mass production field, the new process can reduce 25%, 24%, and 25% with respect to manufacturing energy, consumption of the material, and the emission matter respectively [14]. This mass production field is like manufacturing alignment layer for the TFT panel used in the liquid crystal projector, which was the first practical use of the inkjet film formation process. We believe that, after the Kyoto protocol has been ratified, installation of this kind of energy saving manufacturing process is of increasing significance, and is the most effective measure for global environment conservation with respect to the cost reduction and CO2 dealing.

Conclusion

The surface design and the surface treatment techniques of the substrate, which are thought to be key points for expanding the inkjet technology to industry applications, are categorized and ordered, and further application examples are summarized for every surface treatment. The surface treatment and the surface design are newly optimized for higher resolution.

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Author Biography

Toshimitsu Hirai is the development leader of IJ Industrial Applications R&D Division in Seiko Epson Corporation. He received his B.S degree in Material engineering from Yamagata University, Japan, in 1997. He joined Riken Technos in 1997 as an engineer of color matching technique. He joined Seiko Epson Corporation in 2001, and has been working on metal wiring process development by using inkjet technology since 2001.

Hiroshi Kiguchi is the group leader of IJ Industrial Applications R&D Division in Seiko Epson Corporation. He received his B.S degree in Chemistry from Shizuoka University, Japan, in 1989. He joined Seiko Epson Corporation in 1989, and has been working on applied development by using inkjet technology for industry since 2000. He is a member of the Chemical Society of Japan. He was received the 21st Century Innovation Prize of National Commendation for Invention from Japan institute of invention and innovation in 2005.

