Journal of Imaging Science and Technology® 52(6): 060502–060502-6, 2008.

Novel Aqueous Ink Jet Technology Realizing High Image Quality and High Print Speed[1]

Takatsugu Doi and Ken Hashimoto
New Marking Systems Laboratory, Corporate Research Group, Fuji Xerox Co., Ltd., Ebina-shi, Kanagawa, Japan
E-mail: takatsugu.doi@fujixerox.co.jp

Abstract. *To obtain high quality color images on plain papers using ink jet printing, the authors studied a new marking technology, named "double-component liquid system (DCLS)." The DCLS technology, which uses an ink set comprising pigment inks and treatment liquid, is a design concept that achieves high speed and high image quality by utilizing pigment agglomeration and vehicle penetration. The authors found that optical density and drying time can be described by the increase in viscosity of the ink-treatment liquid combination on admixture, which simulates sequential application of these components to the substrate. They compared various agglomerating agents (organic amine, multivalent metal salt, and organic acid) in treatment liquid by this measuring method and found that both high speed and high image quality could be achieved at the same time regardless of the types of agglomerating agents. Organic acids were found to demonstrate relatively high performance. The functional mechanism of organic acids can generally be explained by* pH*, and it was possible to control DCLS behavior by acid dissociation constant (pKa), neutralization of organic acid, and molar concentration in treatment liquid. DCLS ink set showed high-speed drying performance of 0.6 s or less (equivalent of 100 ppm or higher) and high image quality (optical density of 1.3 or more) at the same time on a variety of plain papers without using a heater.* © *2008 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.(2008)52:6(060502)]

INTRODUCTION

The ink jet printer, which is characterized by its inexpensiveness, small size, and the capabilitly of providing photoquality images, is commonly used in the personal market. On the other hand, it is less prevalent in the office market. In the office market, the requirement is to output documents combining text and graphics on plain paper, at high speed, and with high image quality. Demand for water resistance of printed images is also high. Although the water resistance of printed images can be obtained by use of pigment inks, other demands are not fully satisfied by conventional ink jet technologies, which seems to be a major reason why ink jet printers are not accepted in the office market.

First, we will consider why high speed and high image quality are conflicting requirements in ink jet printing. In conventional ink jet technologies inks are classified as fast dry (FD) ink and slow dry (SD), depending on their penetration performance. FD ink, having high-speed drying, penetrates into paper at a high speed. On the other hand, SD inks, which provide high optical density, leave the colorant at high density near the surface of the paper. The colorant, however, also penetrates into papers with the ink vehicle. Thus, high speed and high image are of conflicting factor. In other words, FD ink is excellent in high-speed drying performance, but image qualities such as optical density, color gamut, and feathering are poor (see Figure 1(a)). SD ink is excellent for image qualities such as optical density, but is inferior in drying time on plain papers (see Fig. 1(b)).

We, therefore, studied the double-component liquid system (DCLS) method with the objective of achieving coexistence of both high speed and high image quality. The DCLS method uses a treatment liquid (TL) that includes an agglomerating agent in addition to the inks. Its basic concept is to independently control vehicle penetration and pigment penetration.[1]

There are some known technologies that use multiple liquids and control ink images by utilizing the reactions between the liquids. One of them is an ink technology that uses dye ink and special liquid.[2] This technology aims to improve image quality and water resistance by agglomeration of the dye ink by action of the special liquid. Another ink technology uses black SD pigment ink and color FD dye ink containing agglomerating agent, aiming at improving optical density and intercolor bleeding.[3] Neither of these technologies, however, is sufficient to achieve our goal of providing both high speed and high image quality at the same time.

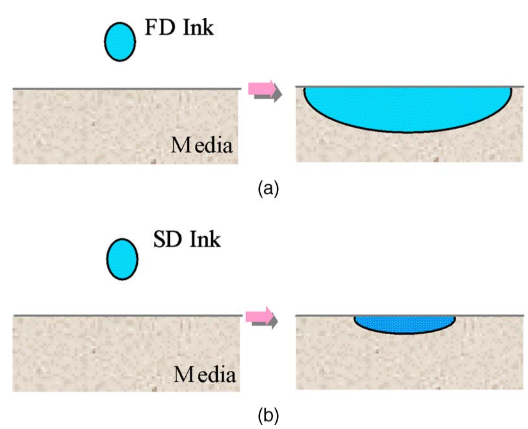

Figure 1. Image structure conceptualization: (a) FD ink; (b) SD ink.

[1]Presented in part at IS&Ts NIP23, September, 2007, Anchorage, AK.

Received Jan. 22, 2008; accepted for publication Sep. 30, 2008; published online Dec. 10, 2008.
1062-3701/2008/52(6)/060502/6/$20.00.

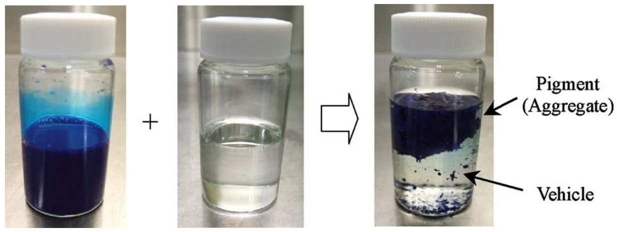

Figure 2. Pigment agglomeration behavior on admixture of ink and treatment liquid.

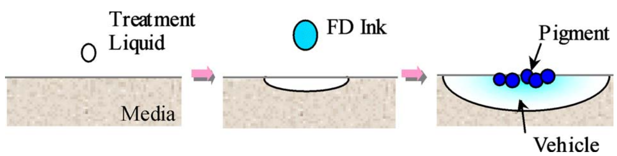

Figure 3. Concept of DCLS recording method and image structure.

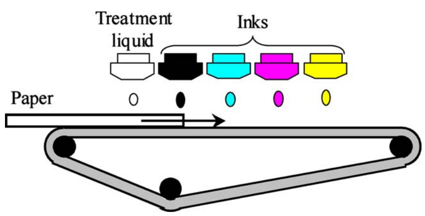

Figure 4. DCLS system concept.

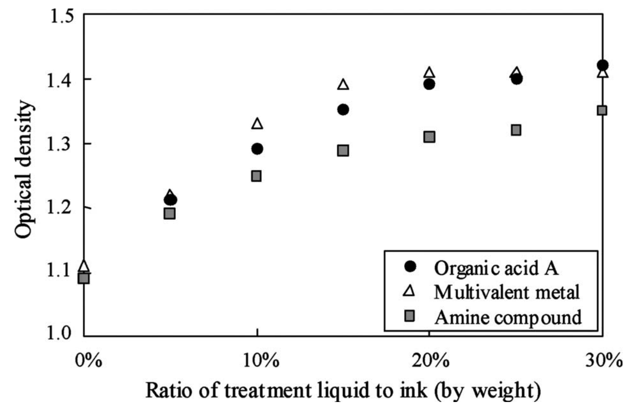

Figure 5. Effect of TL/ink ratio on optical density.

DCLS TECHNOLOGY OVERVIEW

The ink set of the DCLS technology consists of pigment inks and treatment liquid, which includes agglomerating agent. By mixing ink and treatment liquid on the paper, the pigment of the ink agglomerates (see Figures 2 and 3). In our experiments to demonstrate this concept, we used a printing method that first prints treatment liquid and then the inks on the recording media. The pigment of the ink agglomerates by contact of treatment liquid and ink on the recording media, so the pigment agglomerates cannot penetrate into paper. As a result, they remain on the surface (near the surface) of paper at high density, in order to obtain high image quality with high optical density and with no bleeding.

Meanwhile, the pigment and vehicle are separated. In the DCLS technology, both the inks and treatment liquid are of FD composition, and high-speed print performance is also obtained insofar as only the vehicle component penetrates into the paper at high speed.

Thus, the DCLS technology is an ink technology that aims at outputting high-quality images at high speed onto various types of plain papers without using an additional drying technology, such as a heater. Figure 4 shows a typical system configuration for application of a DCLS ink set.

EXPERIMENTAL

The main components of the experimental ink composition are pigment, polymer, water-soluble organic solvent, surface-active agent, and water. The treatment liquid mainly contains agglomerating agent, water-soluble organic solvent, surface-active agent, and water.

As for the agglomerating agent in the treatment liquid, multivalent metal salts (magnesium salt), organic amines (polyallylamine salt), and organic acids (proprietary organic acid A and organic acid B) were used. The concentration of agglomerating agent in treatment liquid was 0.1 M for a monovalent agent. For a divalent agent, it was 0.05 M.

For printing, single-pass printing was performed using a Fuji Xerox prototype printer. For the recording media, various types of plain papers (P Paper, C^2 Paper, Green100 Paper, Fuji Xerox 4200 Paper, etc.) were used. The following data show the results with C^2 Paper, unless otherwise specified. The ratio of treatment liquid to ink was adjusted by print coverage and drop amount of the treatment liquid so that it was in the range from 0% to 30% to ink by mass.

Optical density was measured using X-rite 404 (product of X-Rite, Inc.). Viscosity was measured using a B-type viscometer with a SS-1 type rotor. For high-speed print performance drying time was measured: the printed area was observed with a charge coupled device camera, and the time of ink penetration into paper was evaluated. For depth of ink penetration into paper, a cross section of the printed part was observed under a digital microscope.

RESULTS AND DISCUSSION

DCLS Effect by Treatment Liquid

We varied the ratio of treatment liquid to ink and evaluated the optical density behavior against the ink/TL ratio. Organic acid A was used as the agglomerating agent. As shown in Figure 5, the optical density tends to increase in proportion to treatment liquid ratio when the treatment liquid ratio is in the range of 0%–15% and it reaches the maximum value when the ratio is near 20% or higher.

Next, we examined the relationship between the ratio of treatment liquid to ink and drying time using the same method. As shown in Figure 6, drying time tends to be slower as the treatment liquid ratio increases. When the ratio is 20% or below, however, drying time of less than 0.6 s was achieved, which indicates that high-speed printing of 100 ppm or higher can be realized. From the above data, we

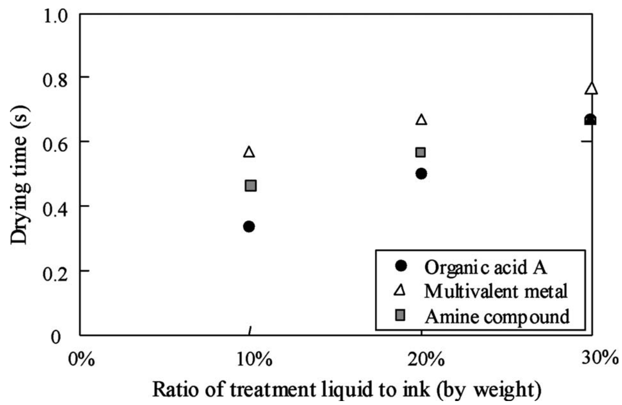

Figure 6. Effect of TL/ink ratio on drying time.

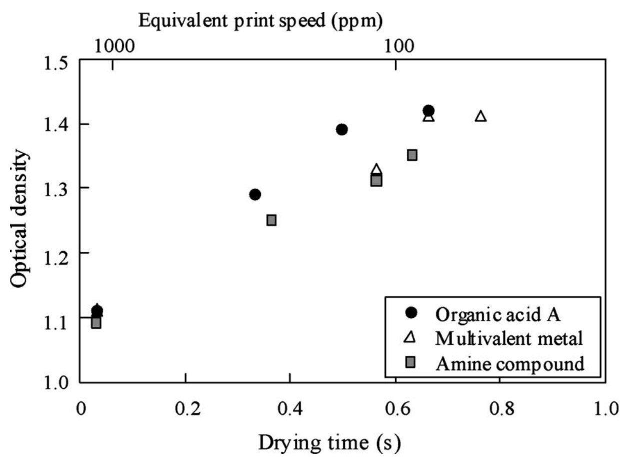

Figure 7. Relationship between drying time and optical density.

replotted the relationship between optical density and drying time (see Figure 7).

We confirmed that by using treatment liquid, both high speed and high image quality can coexist regardless of the types of agglomerating agent, and drying time of 0.6 s or less and optical density of 1.3 or more can be achieved. As for agglomerating agent, organic acid A proved to be the most effective in this experiment, followed by magnesium salt and organic amine.

Substitute Index of Agglomeration

In order to compare agglomeration performance, we measured the viscosity of the mixture of treatment liquid and ink (see Figure 8). Behavior of the mixture viscosity against the treatment liquid ratio showed an upward convex behavior. This behavior is considered to reflect the state of pigment agglomeration. In other words, it is estimated that an interaction between pigment and polymer occurs over a wide range in region A, while pigment also exists as aggregates in region B where there is no interaction among pigment aggregates. So, we evaluated the particle size of pigment agglomerates using a particle counting device, which counts the number of particles of 5 μm or larger within a 1 μL sample. The result showed that the number of particles larger than 5 μm in the mixture of treatment liquid and ink

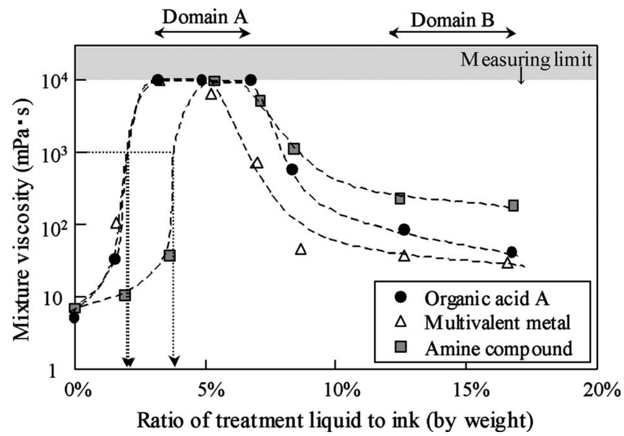

Figure 8. Viscosity of ink and TL mixture as function of TL/ink ratio.

Table I. (a) Isoviscous TL ratio, optical density, and drying time for each agglomerating agent. (b) Isoviscous TL ratio, optical density, and drying time for each agglomerating agent with different degree of neutralization.

(a)	Isoviscous TL ratio (%)	Optical density	Drying time (s)
Organic acid A	1.81	1.42	0.66
Multivalent metal	1.86	1.41	0.76
Amine compound	3.84	1.35	0.66
(b)	**Isoviscous TL ratio (%)**	**Optical density**	**Drying time (s)**
Organic acid A (high neutralization degree)	6.08	1.18	0.60
Amine compound (low neutralization degree)	2.05	1.38	0.63

was in the order of 10^5, while it was in the order of 10^0 in pigment ink.

In the experiments shown in Fig. 8, we used an amount of treatment liquid where the mixture viscosity became constant (1000 mPa s), as an index to show agglomeration performance (noted as "isoviscous TL ratio" below). The isoviscous TL ratio of multivalent metal salt (1.81%), organic acid A (1.86%), and amine compound (3.84%) is estimated using a linear function. We found that multivalent metal salt agglomerates with the least amount of treatment liquid, followed by organic acid A and organic amine, respectively. Table I(a) shows the isoviscous TL ratio, optical density, and drying time for each agglomerating agent. We examined the relationship of this treatment liquid ratio to optical density and drying time. To confirm the relationship over a wider range, we added two more data points for organic acid A and amine compound by changing their degree of neutralization (see Table I(b)).

As shown in Figure 9, the isoviscous TL ratio, which reflects the increase of viscosity, has demonstrated a favorable relationship with both optical density and drying time.

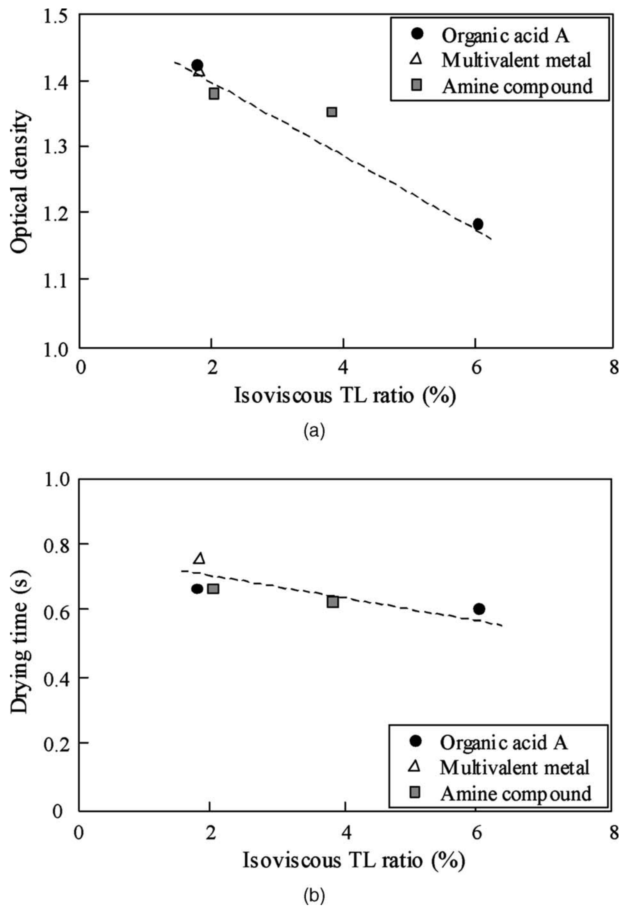

Figure 9. (a) Effect of isoviscous TL ratio on optical density. (b) Effect of isoviscous TL ratio on drying time.

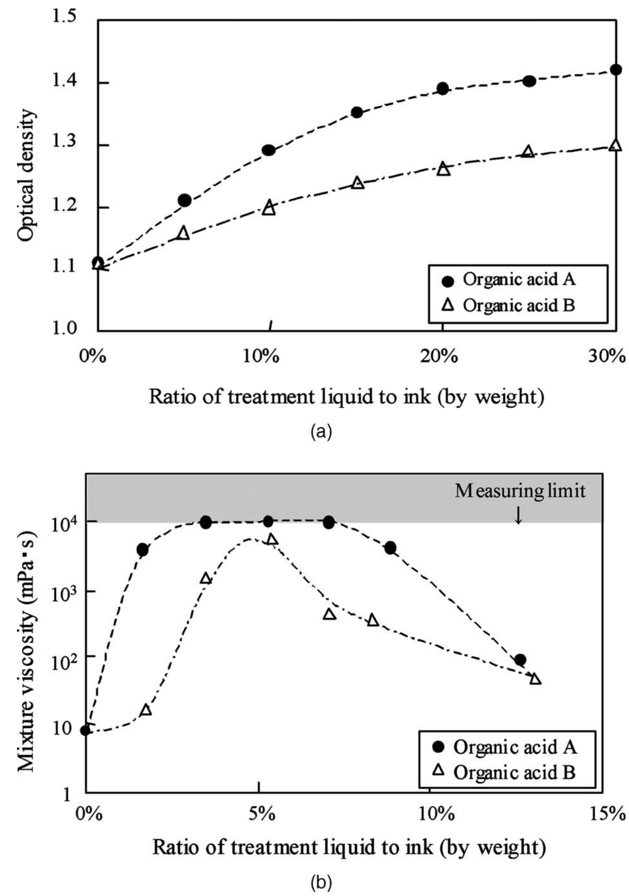

Figure 10. (a) Effect of TL/ink ratio on optical density. (b) Effect of TL/ink ratio on drying time.

The fact that the gradient of optical density to isoviscous TL ratio is steep while that of drying time is gentle indicates that it is possible to increase optical density while maintaining high-speed drying performance.

Controlling Factors in Organic Acid Treatment

We used organic acid as an agglomerating agent to study controlling factors. Some of the reasons for using organic acid here were because organic acid A showed the most effective result as an agglomerating agent in Fig. 7, and this class of materials offers wide latitude in material design.

Two kinds of organic acids were compared by the same method described above. By using organic acid A as agglomerating agent, higher optical density was obtained (see Figure 10(a)). In addition, the mixture of pigment ink and treatment liquid comprising organic acid A showed higher viscosity than that of organic acid B (see Fig. 10(b)). Thus, organic acid A appeared to be superior to organic acid B.

In response, we examined the relation between *p*H and viscosity of the mixture liquid of ink and treatment liquid (see Figure 11). The result suggests that the viscosity of the mixture is basically controlled by *p*H.

We also measured the titration curve of each agglomerating agent (see Figure 12). This result indicates that acid dissociation constant (pKa) and neutralization degree are determining factors for *p*H of the treatment liquid, and con-

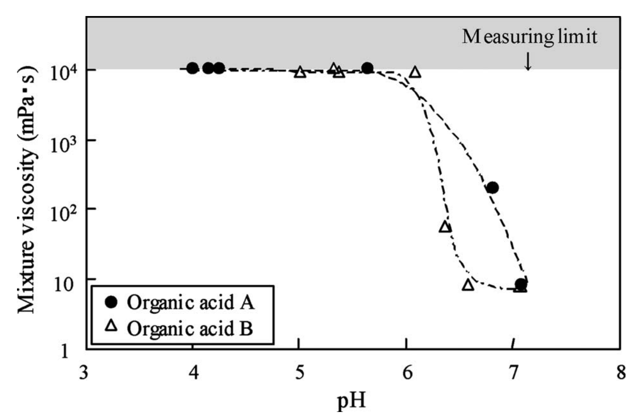

Figure 11. Relationship between viscosity of ink-TL mixture and *p*H.

firmed why agglomeration performance of organic acid A tends to be better than that of organic acid B. Furthermore, when taking the mixing ratio of ink and treatment liquid into consideration, concentration of agglomerating agent can also be considered as an effective controlling factor.

Image Quality

Figure 13 shows an example of a printed image using the DCLS ink set as designed above. By using the DCLS ink set, high image quality with high optical density and excellent feathering was achieved. The drying times and optical den-

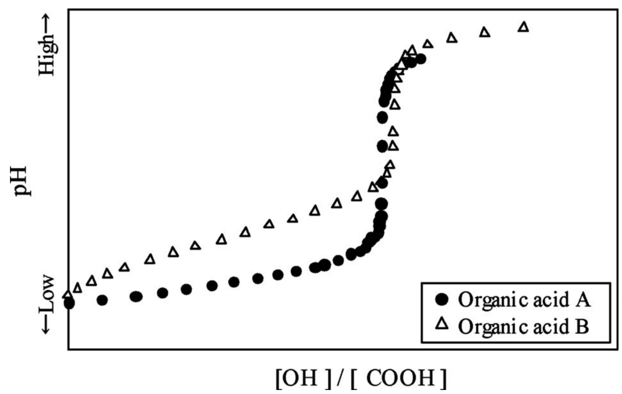

Figure 12. Titration curves of organic acids.

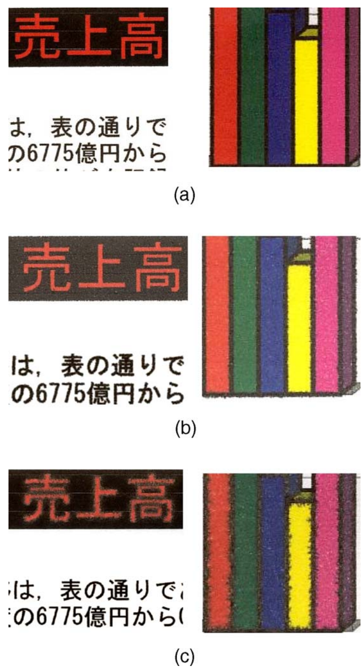

Figure 13. Print image: (a) DCLS ink set; (b) FD inks (without TL); and (c) SD black ink and FD color inks (without TL).

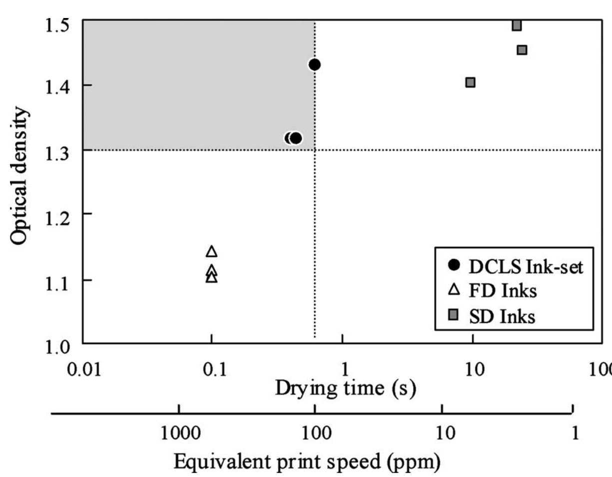

Figure 14. Comparative characteristics of ink sets.

Table II. Dependency of optical density and drying time on plain paper types.

	Optical density	Drying time (s)
Plain paper (C2)	1.31	0.36
100% recycled paper (Green100)	1.33	0.32

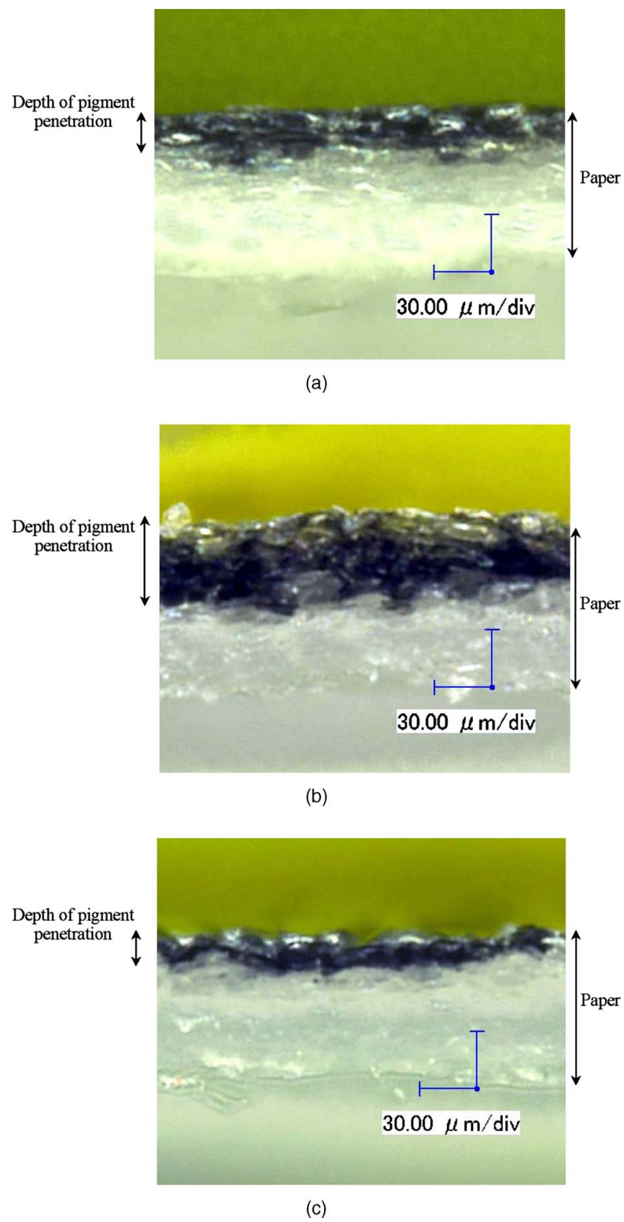

Figure 15. Cross-sectional views of printed paper: (a) DCLS ink set; (b) FD ink (without TL); and (c) SD ink (without TL).

sities achieved for these examples are shown in Figure 14. It is known that image quality obtained by ink jet printing generally varies according to types of recording media used. With the DCLS ink set, however, high-speed drying and high image quality can both be achieved regardless of paper type, e.g., plain paper or recycled paper, as shown in Table II.

Pigment Distribution in Recording Media

As mentioned above, ink jet ink drying is considered to involve ink penetration into the recording medium. The penetration rate can be described using the Lucas–Washburn equation.[4,5] We observed a cross section on which an image was printed using a DCLS ink set and with conventional inks, and compared the depth of pigment penetration (see Figure 15). The depth of penetration of the DCLS ink set was about 25 μm, which is equivalent to about 28% of the paper thickness (90 μm); the depths of FD ink and SD ink penetration were 50% and 20%, respectively. Thus, it was confirmed that the depth of pigment penetration can be inhibited with the DCLS ink set, while it has the same level of vehicle penetration as FD ink.

CONCLUSIONS

As a new marking method, we studied DCLS, which consists of FD pigment inks and a treatment liquid. The conclusions are summarized as follows:

(1) High-speed drying of 0.6 s or less (equivalent of 100 ppm or higher) and high image quality with optical density of 1.3 or more (matching that of SD ink) were achieved without using an additional drying step such as heating.

(2) It was also found that the basic behaviors (optical density and drying time) of the DCLS technology can be described by the increase in viscosity of the ink-treatment liquid combination on admixture.

(3) Organic amine salt, multivalent metal salt, and organic acid were studied as agglomerating agents in the treatment liquid. While all of them proved to be effective as agglomerating agents, organic acids tended to show especially high performance compared to the others.

(4) The functional mechanism of an organic acid can generally be explained by the *p*H of the ink/TL mixture, and it was possible to control DCLS behavior by the acid dissociation constant (pKa) and degree of neutralization of the organic acid, as well as its molar concentration in treatment liquid.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to Yoshihiko Ono, Kunichi Yamashita, and Manabu Numata for their cooperation in the printing and drying time measurements for this study.

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