https://doi.org/10.2352/ISSN.2169-4451.2017.32.75

Development of New Aqueous Resin Ink for Sign Graphics

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Abstract

An aqueous resin ink was developed which can offer excellent image qualities on non-permeating media such as plastic media with an inkjet printer. The print speed with this aqueous resin ink reaches the level of solvent-inks diffused as inks for non-permeating media for sign graphic, i.e., at least 30m2/h. In order to increase the print speed, it is important that the ink has good compatibility to the coating layer of non-permeating media. It was found that kinds of solvents added to the ink were highly related to the compatibility. Furthermore, such solvents have a particular feature in common. Solvents with specific range of fractional parameter have high coating layer-solving ability. To show validity of this mechanism, a new method for evaluation of ink fixation was developed. With this new method, it was proved that higher concentration of coating-layer-solving solvent gave ink faster fixation onto the non-permeating media. Furthermore, we also discovered that the characteristics of the pigment dispersion element in an ink formula greatly affected the discharging reliability.

Introduction

Digital printing employing inkjet system using solvent ink has been rapidly spreading to print images on non-permeating media such as plastic films for sign graphics. However, since most solvent-inks contain volatile organic compounds (VOC) and involve concerns about human health, installation of local ventilation equipment is required. Therefore, aqueous inks with which images can be formed on non-permeating media are demanded. To meet such demands, many companies are eagerly researching and developing aqueous resin-inks with dispersible resin particulates (emulsion) to water forming films on non-permeating media. [1][2][3]

However, the print speed of printers using such aqueous resin-inks currently ranges from around 5 m2/h to 10 m2/h, which falls far behind the print speed (30 m2/h) of printers using solvent-inks. Furthermore, aqueous resin-inks have problems with discharging reliability. Therefore, we newly developed an aqueous resin ink that solves these problems and make it substitutable for the solvent-inks..

Aqueous Resin-ink Technologies

Problems to be Solved for High Speed Printing

Aqueous resin inks contain solvent components, such as water, and water-soluble organic solvents to retain moisture and impart features of wetting the aqueous inks to non-permeating media. Such aqueous resin inks containing relatively lots of water never or little permeates into a plastic medium. Therefore, in printing images, ink droplets that have already landed on a medium are not fixed yet, then next ink droplets land thereon, which brings about a phenomenon called beading (adjacent dots are combined). Beading is not preferable because it degrades the image quality, for example, shortage of embedding of image or horizontal streaks. Since the degree of beading is worsened as the print speed increases, beading is a problem to be solved for higher speed printing (Figure 1).

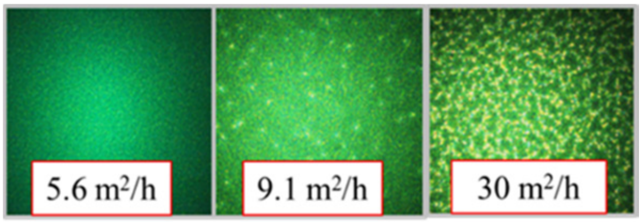

Figure 1. Images formed at various print speeds using aqueous resin ink (Product A) (1200 dpi. x 900 dpi. / PVC film / media heated to 55 °C)

Reduction of Beading by Increasing Ink Fixing Speed

To reduce beading, it is necessary that ink droplets are fixed on a medium by the time next ink droplets land thereon. Since the interval between landings of ink droplets becomes shorter in a higher speed printing, it is necessary to obtain a fast fixing ink.

Generally, solvent-inks are known as fast fixing inks. Inferentially, this has something to do with fast permeation of the solvent inks into media. Figure 2 illustrates the cross sections of the images formed on PVC media using Ink A (aqueous resin-ink) and Ink B (solvent-ink). As seen in the pictures, the colorants of the aqueous resin ink stay on the surface of the medium, whereas the solvent-ink compatibility to the medium. If compatibility of the aqueous resin ink occurs when it lands on the media, the ink will be quickly fixed like the solvent ink, which must be effective to reduce beading.

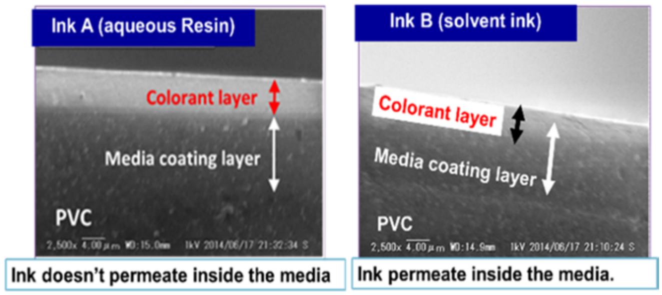

Figure 2. Comparison of Cross Sections of Printed Images, Ink A (aqueous resin-ink) on the left and Ink B (solvent-ink) on the right.

Improvement on Ink Permeation for Fast Fixing

This high level of compatibility of the solvent-ink to the medium inferentially related to the solvents contained therein. Indeed, the product B (solvent-ink) contains an ether-based solvent, which solves a plastic medium (Figure 3). Compatibility between ink and the medium occurs owing to the solvent which can solve the surface of the medium, the coating layer. Therefore, by adding solvents having high level of coating-layer-solving property to the ink, compatibility of the ink to the medium is improved so that fixing speed is inferred to be faster.

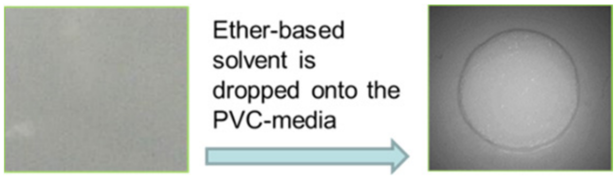

Figure 3. Solubility of PVC Medium by Ether-based Solvent Contained In Ink B (Solvent-Ink)

Mechanism Analysis / Solvents with Solvency for Coating Layer

Next, investigation for solvents which can solve coating layer on media was conducted. Solvency test shown above was done about a few dozen solvents. Then relations between the solvency and the properties of solvents were investigated.

As a result, it turned out that several solvents had such solvency. Furthermore, the solvents have a particular feature in common. The Solvents with specific range of [δH / (total of δH, δP and δD)] in Hansen solivility parameter have high conting-layer-solving ability.

Fig.4 shows the Teas's Fractional parameter (FP) plots of Fd(%), Fp(%) and Fh(%) regarding the solvents. The red marks mean the solvents solved the coating layer. The blue marks mean not solved. Fd(%), Fp(%) and Fh(%) are calculated shown below.

$$Fd(\%) = \delta D/(\delta D+\delta P+\delta H)*100 \quad (1)$$

$$Fp(\%) = \delta P/(\delta D+\delta P+\delta H)*100 \quad (2)$$

$$Fh(\%) = \delta H/(\delta D+\delta P+\delta H)*100 \quad (3)$$

Parameters δD for Dispersion (van der Waals), δP for Polarity (related to dipole moment) and δH for hydrogen bonding in Hansen's solubility parameters (HSP). HSP value of each solvent is available through the list on the software called Hasen solubility parameter in Practice (HSPiP / ver.3.038). Unless solvents are registered on the database, HSP of each solvent can be easily calculated with its chemical structure by using the software.

The region of the plots which solved the coating layer and other is sharply divided. The Fractional parameter of the coating layer, acrylic polymer (PMMA) is respectively Fd(%) = 54%, Fp(%) = 31% and Fh(%) = 15%, which plotted at around the center the red plots. It said that materials having close FP show high affinity. [4] Therefore, it seems that solvents plotted as red mark solved the coating layer. Based on the results, solvents having Fh(%) of not more than 30% showed the solvency of the coating layer.

Deployment of the Mechanism to other Medium

As described in Fig.4, when Fh(%) of solvents have close value to the Fh(%) of the coating layer, the solvents tend to solve the coating layer well. To ascertain this mechanism, additional experiments with other films having various resin layers. Experimental method is the same describe above. This time, the level of solvency to the resin layer from 1 to 3. Level 1 means "the trace of the solvency is slightly observed." Level 2 means "the trace of the solvency is easily observed." Level 3 means "the surface of the medium is highly solved."

The results of the experiments are shown in Table 1. In all cases of this experiment, as the Fh(%) of solvent and the resin are close, the resins are highly solved. Particularly, when the difference of F(%) between solvents and resins is below 5%, the level of solvency of medium is high.

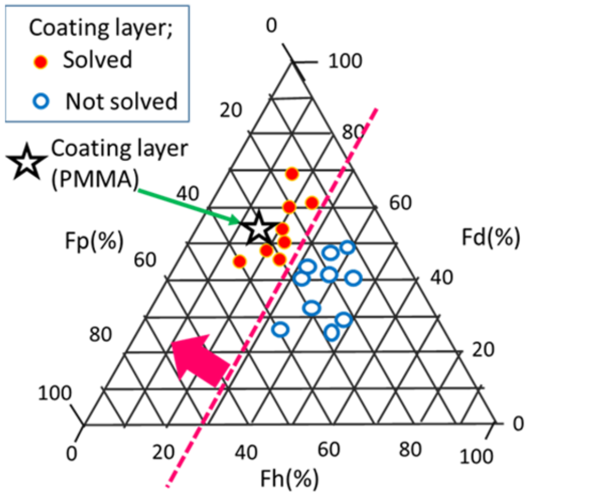

Figure 4. Teas graph of solvents' Fractional parameter ;Fd(%), Fp(%), Fh(%).

Table 1. Test of solubility level with a variety of solvent' Fh(%)

Polymer	Fh(%)	Solvent	Fh(%)	⊿Fh(%) [Solvent Fh(%) - Polymer Fh(%)]	Results / Polymer Solubility Level
Poly ethyl methacrylate	13%	A	16%	3%	2
		B	23%	10%	1
Poly methyl methacrylate	20%	A	20%	0%	1
		B	23%	3%	2
		C	25%	5%	2
		D	28%	8%	3
Poly vinyl acetate	23%	A	16%	7%	1
		B	23%	0%	3
		D	25%	2%	2
		F	32%	9%	1

Verification experiments / Effect of solvency of coating layer on fast fixation of ink

To verify the effect of the solvency of the coating layer on fast fixation of ink, a new evaluation method was developed. With this new method, it was proved that higher concentration of coating-layer-solving solvent gave ink faster fixation onto the non-permeating media.

The impact of the solvency of the coating layer on the fixing speed of the ink is verified by measuring the fluidity of the ink loaded on medium. To measure fluidity, a surface drying process measuring equipment (HORUS, manufactured by Formulacion) is used (Figure 5). HORUS is an equipment in which a sample is irradiated with a laser and interference fringes of scattering rays are taken by a CMOS camera (Figure 6). While particles in ink on a medium are moving fast, the changing speed of the interference fringes is high. As the particles move slowly, the changing speed of the interference fringes decreases. The fluidity of the ink is measured with this changing speed. The point where the fluidity starts decreasing is regarded as the starting point of fixing and the point where the change of the fluidity stops is regarded as the completion of fixation, which can be an indicator of the comparison of the fixing speed of the ink.

Figure 5. Illustration of HORUS®; An instrument for the analysis of ink fluidity)

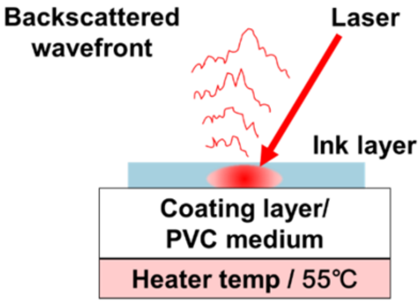

Figure 6.Measurement mechanism of HORUS®

As the experiment that verifies the effect of the solvency of the coating layer on fast fixation, the relations between the amount of solvents having the solvency of the coating layer in ink and fluidity on the medium were investigated by following steps. First, each ink was applied on the medium with a bar coater. After putting the sample on the hotplate and heated at 55 ℃, measurement of fluidity was started. Initial fluidity was defined as 100% and fluidity change was monitored.

As shown in Fig. 5, the higher concentration of coating-layer-solving solvent the inks contained, the earlier fixation speed started decreasing and reached the minimum value. The amount of water in ink is decreasing soon after the heating started. Then Fh(%) of ink vehicle and coating layer become closer, which seems to accelerate the compatibility of the ink and the coating layer. Thus, higher concentration of coating-layer-solving solvent gave ink faster fixation onto the non-permeating media.

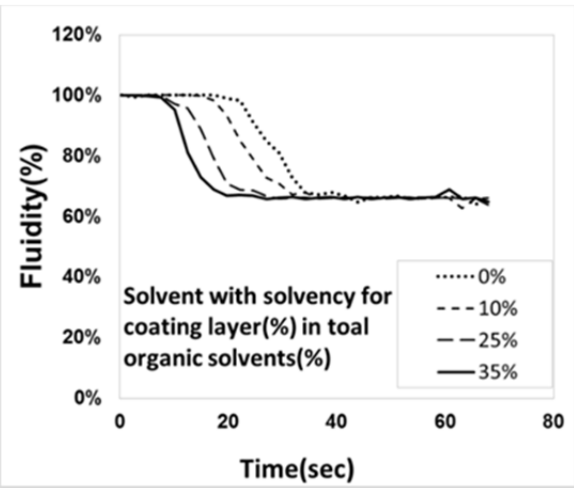

Figure 7. Evaluation of Fixing Speed of Ink (HORUS).

Investigation on Improvement of Discharging Reliability of Aqueous Resin-ink

Since the aqueous resin ink contains not only pigments but also relatively lots of resin particles to form a film on non-permeating media, the solid contents in the meniscus increases as the moisture of the ink evaporates, which makes it easy to form a skin layer. After the aqueous resin ink is charged into a capillary and stored under the certain temperature to accelerate ink drying, it is observed by using a manipulator that skin layers are formed on the ink surface and the formed skin layer can be peeled off (Figure 6).

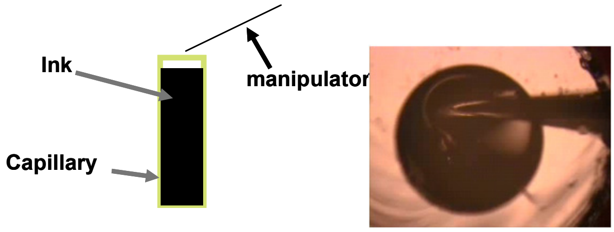

Figure 8. Observational method of the air-ink interface

Since this skin layer causes misfiring of ink, it has to be removed with the maintenance system every time it occurs. However, frequent maintenance during printing lowers the print speed and increases the consumption of ink.

In general, such skin layers are not easily formed if inks are not dried quickly. However, if a solvent having a high boiling point like humectant is used to keep discharging reliability, image blur and blocking tend to be worsened in a high speed printing. Therefore, improvement on discharging reliability is needed to be solved by optimizing the key components in ink other than solvents.

Improvement on Discharging Reliability

Figure 7 is the graphs illustrating impacts on discharging reliability when changing the formulation of inks such as the content of a surfactant, the content of a humectant, the kind of resin emulsions, and the kind of pigment dispersion element. LV1 to LV3 in Figure 7 represent the contents of the materials added to the inks. LV 3 is the largest of the three.

These graphs show that the kind of the pigment dispersion greatly affects discharging reliability and its impact is on a par with the effect of the humectant contents. In short, discharging reliability is improved by optimizing the prescription of pigment dispersions.

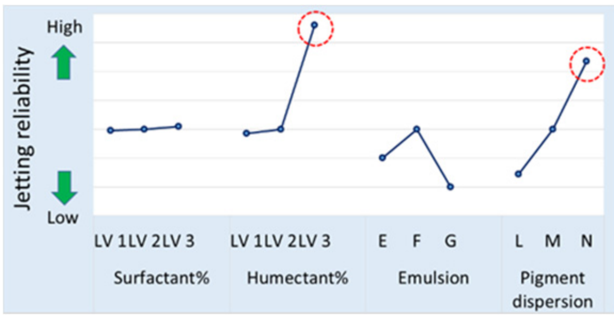

Figure 9 Ink Compositions' Impact on Discharging Reliability.

Furthermore, the relation between the prescription of the pigment dispersion and the discharging reliability of ink is shown by analyzing the prescription of the pigment dispersion elements. According to the latest findings, dispersion reliability is inferred to be better when stability of the pigment dispersion is good. Since the skin layer is formed in the process of evaporation of water in the meniscus at the end of nozzles, keeping dispersion stability seems to be important even after the moisture decreases.

Summary of Ricoh Resin Ink's Ability

Based on the newly obtained knowledge, new "Ricoh Resin Ink" was developed. Then images formed with the ink at high printing speed was evaluated.

Image formed at a printing speed of 30 m^2/h (Figure 8). The new Ricoh resin ink shows that the beading was suppressed even in a high speed printing.

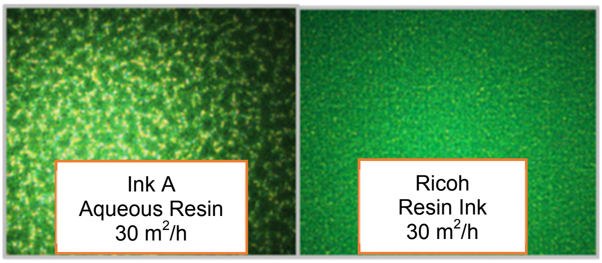

Figure 10. Images formed with ink A(aqueous resin-ink) and Ricoh aqueous resin-ink with high solvency for coating layer.

Next, the discharging reliability of Ink A (aqueous resin ink) and Ricoh resin ink was evaluated by the rate of misfiring nozzles after installed heads were left on a heater for 30 minutes (Figure 9). It was found that improvement on the rate of misfiring nozzles of Ricoh resin ink is significant in comparison with Ink A.

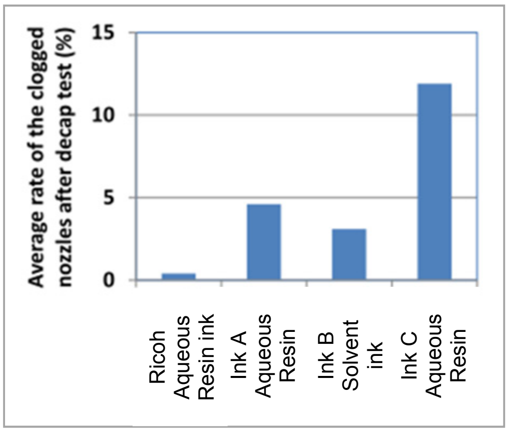

Figure 11. Average rate of clogged nozzles after decap test. Ricoh resin inks: 30 minutes decap time, the print-heads are located near 70 ºC heater.
Ink A: 20 minutes decap time, at room temperature.
Ink B: 30 minutes decap time, the print heads are located near 50 ºC heater.
Ink C: 30 minutes decap time, the print heads are located near 70 ºC heater

Conclusion

The newly developed aqueous resin ink is safe and it can offer excellent image qualities on non-permeating media in a printing speed as fast as a solvent ink. .

First, by observing illustrates the cross sections of the images formed on PVC media using the aqueous resin-ink and a solvent-ink, we found it is important that the ink has good compatibility to the coating layer of non-permeating media. And addition of the solvents with specific range of Fractional parameter can enhance the compatibility of ink to the media coating layer. The effect of such solvent was verified with the evaluation method applying the equipment detecting the change of ink fluidity.

Furthermore, we discovered that the prescription of a pigment dispersion has a great impact on improvement of discharging reliability of aqueous resin inks

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Author Biography

Masahiro Kido obtained his master degree in chemistry at the Tokyo University of Science in Japan in 2007. After working at a colorants manufacturing company, he entered Ricoh Co. Ltd. in 2014, and he specialized in inkjet ink formulation design.