Inkjet Printability of Phthalocyanine Dye Ink

Yumeizhi Jia, Alexandra Pekarovicova and Paul D. Fleming III
Western Michigan University, Department of Chemical and Paper Engineering,
Center for Ink and Printability,
4601 Campus Dr., A -231 Parkview, Kalamazoo,
MI 49008-5462

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Abstract

In this research, different water based dye ink formulations made of phthalocyanine blue were examined for suitability for inkjet printing. In this process, the Z number, a dimensionless combination measure of specific gravity, surface tension and viscosity was used to assess jettability. The specific gravity, surface tension and viscosity of nine different water based ink formulations were measured and used to calculate the Z number. The ink is considered to be suitable for ink jetting, if Z number is in the range $2 \leqq Z \leqq 14$.

Introduction

Inkjet printing techniques have been gaining attention recently because of their unique features, such as simplicity of fabrication, compatibility with different substrates, feasibility of non-contact and additive patterning, low temperature processing and low cost [Bao, 1999], [Rozenberg, 2002]. It can be used for pattern solution processable polymers or nanoparticle inks on various substrates including paper, glass, and semiconductor materials [Sankir, 2005].

Normally, there are two methods used in drop-on-demand inkjet printers, they are thermal drop-on-demand and piezoelectric drop-on-demand. In the piezoelectric inkjet printer, it uses a piezoelectric material in an ink-filled chamber behind each nozzle instead of a heating element [Kipphan, 2001].

In order to generate a droplet, two conditions need to be fulfilled. First, the kinetic energy must be higher than the surface energy of the drop. This is correlated with the Weber number ($We = v2\rho a / \gamma$). The second condition is that the kinetic energy should be higher than the viscous dissipation. This is described by the Reynolds number ($Re = v\rho a / \eta$). The Oh number combines these two conditions. Oh number characterizes the propagation of the pressure wave and its attenuation by viscous dissipation. $Oh = \sqrt{We} / Re = \eta / (\gamma\rho\ a)\ 1/2$ [Derby, 2011].

The Z number, a combination measure of specific gravity, surface tension and viscosity was used to assess ink jet printability [Reis, 2005]. Fromm identified the Ohnesorge number Oh, as the appropriate grouping of physical constants to characterize drop generation in an inkjet printer. The reciprocal value of this number, the parameter defined as $Z=1/Oh$ was used by Fromm [Fromm, 1984]. Fromm demonstrated a model of fluid flow in a drop generator of simplified geometry, and proposed that $Z > 2$ is needed for stable drop generation. Later, Reis and Derby refined this prediction. For Reis, he believes that when the Z number is in the range from 1 to 10, they could get a stable drop generation. Meanwhile Derby finds, when Z number is in the range from 4 to 14, they could get the stable drop generation. Empirically it was shown that fluids are ink jet printable within the range $2 \leqq Z \leqq 14$.

In our project, the ink formulations were printed by the Dimatix Inkjet Printer. This printer uses a disposable piezo inkjet cartridge. When a voltage is applied, the piezo-actuator changes and creates a pressure wave. In the nozzle region, the pressure wave accelerates the liquid and ejects a column of it that will break up into a droplet if the kinetic energy is high enough to overcome the surface energies [Vahid, 2009]. In this process, there are two phenomena. One is propagation of the pressure wave along the capillary tube, the other one is the conversion of the kinetic energy of the liquid jet into surface energy. Both of the phenomena can be characterized by dimensionless numbers, such as the Z number, which will be used in this work to estimate proper parameters for ink jettability.

Experimental

In the research, PET (Polyethylene Terephthalate) was used as the substrate. A UV oven (UVO Cleaner Model 144 AX) was used in order to increase the surface energy of the PET. In the process, the π bonding of phenyl groups in the PET is broken by absorbing UV energy, which leads to an increase in the number of ester groups at the surface. The greater the exposure time, the greater the number of ester groups through which the oxidization readily takes place, resulting in larger grains at the surface of the treated PET than that of untreated PET [Lim, 2012]. After UV treatment, the surface energy changed from 43 mN/m to above 60mN/m.

The surface energy was estimated by FTA200 (First Ten Angstroms, Inc., VA). The FTA 200, is an instrument for which the action appears live on the computer screen and the salient images are captured to the computer's memory for later image analysis [Annon A, 2013]. We use this FTA200 to catch the behavior of different dye ink formulations' drop and then analyse the surface tension of these drops.

The viscosity was measured by RA 2000 dynamic stress Rheometer (TA Instruments, DE). The Rheometer is an instrument which used to measure the way in which a liquid, suspension or slurry flows in response to applied forces [Annon B, 2013]. In this work, nine different dye ink formulations were measured by the Cone-Plate coquette cylinder. Viscosity measurements were performed at a fixed temperature 25˚C with the shear rate range from 0 s-1 to 1000 s-1. The results came out as the viscosity curve (viscosity vs. shear rate).

The ink formulations were printed on the PET substrate of 100 μm gage by the Dimatix Materials Printer DMP-2800. The DMP-2800, utilizing a disposable piezo inkjet cartridge, can create and define patterns over an area of about 200 × 300 mm and handle substrates up to 25 mm thick with an adjusted Z height [Annon C, 2013]. When printing with the Dimatix Materials Printer, both the drop spacing and percent of each drop can be controlled. The Temperature during the work is about 25 ˚C.

Results and Discussion

In this work, the Z number was used to examine the jettability of nine different water based dye ink formulations made of phthalocyanine blue. The fluid is considered to be suitable for ink jetting, if the Z number is in the range 2≦Z≦14. The equation Z=1/Oh [Oh = √We / Re= η / (γρ a) 1/2] [Derby, 2012] was used to calculate the Z number, where ρ, η and γ are the density, dynamic viscosity and surface tension of the fluid respectively, and a is a characteristic length (geometry of needle).

The specific gravity, surface tension and viscosity of the phthalocyanine blue dye solution was measured and used to calculate the Z number. The specific gravity of phthalocyanine dye was 1.0536 g/ml. The properties of original phthalocyanine blue are listed in the Table 1.

Specific Gravity (g/ml)	1.0536
Surface Tension (mN/m)	66.88
Viscosity (cp)	1.32
Z number	29.55

Table 1: *Physical properties of original phthalocyanine blue*

The surface tension of original phthalocyanine blue is rather high, and the viscosity is too low, which leads to a higher Z number than recommended for proper jetting performance. In order to make the Z number in the range 2 to 14, isopropyl alcohol (IPA) and ethylene glycol (EG) were added to the dye with the aim to decrease the surface tension and increase the viscosity. Nine different dye ink formulations were made and measured. The dynamic surface tension changes with time and addition of isopropyl alcohol and ethylene glycol is illustrated in the Fig.1 and Fig.2.

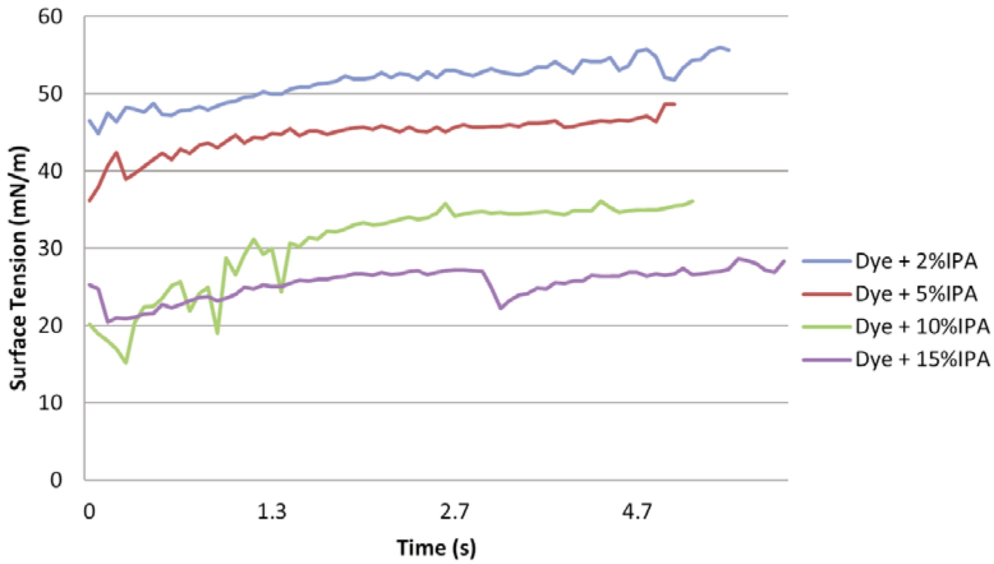

Figure 1: *Dynamic surface tension of phthalocyanine dye ink modified with isopropyl alcohol*

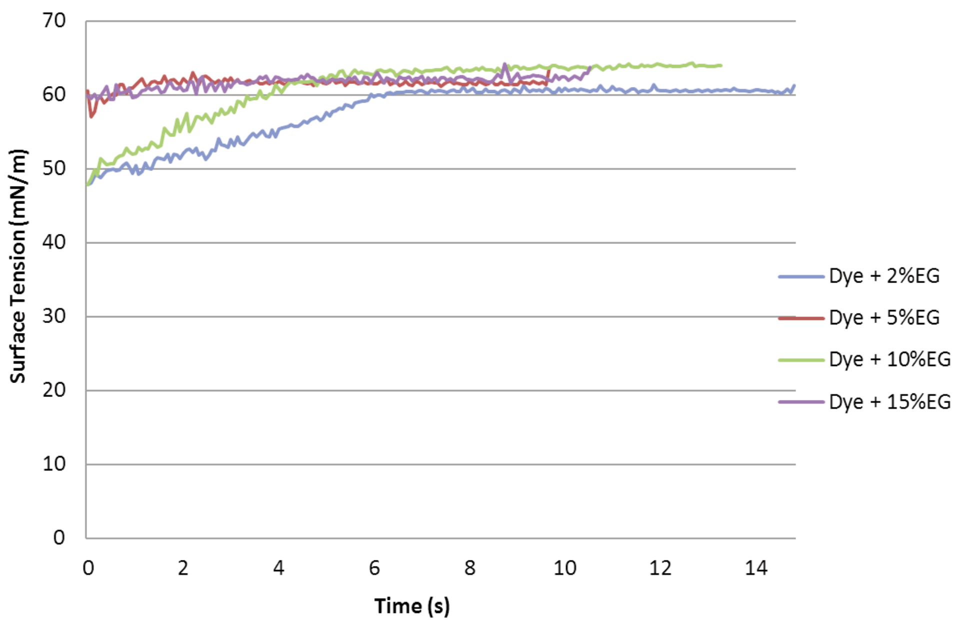

Figure 2: *Dynamic surface tension of phthalocyanine dye ink with ethylene glycol*

The FTA200 was used to measure surface tensions of the inks. The Table 2 summarizes the results of surface tension analysis.

Dye	Dye + 2%wt IPA	Dye + 5%wt IPA	Dye + 10%wt IPA	Dye + 15%wt IPA	Dye+ 2%wt EG	Dye + 5%wt EG	Dye + 10%wt EG	Dye + 15%wt EG
66.88	54.13	46.54	34.93	27.23	60.56	61.63	62.21	63.61

Table 2: *Surface tension [mN/m] of phthalocyanine solutions*

From Table 2 it is clear that the surface tension of virgin dye is rather high. The IPA and EG were added separately in order to decrease its surface tension (Fig.1 and Fig.2). When the IPA was added into the ink formulation (Fig.1), the surface tension deceased continuously from 66.88 mN/m to 27.23 mN/m. The EG was not very efficient in surface tension modification (Fig.2 and Fig.3), but could be helpful in changing drying speed and protecting nozzles from drying. Comparison of surface tension modification with EG and IPA is illustrated in the Fig.3, clearly showing that the IPA is more efficient in surface tension modification.

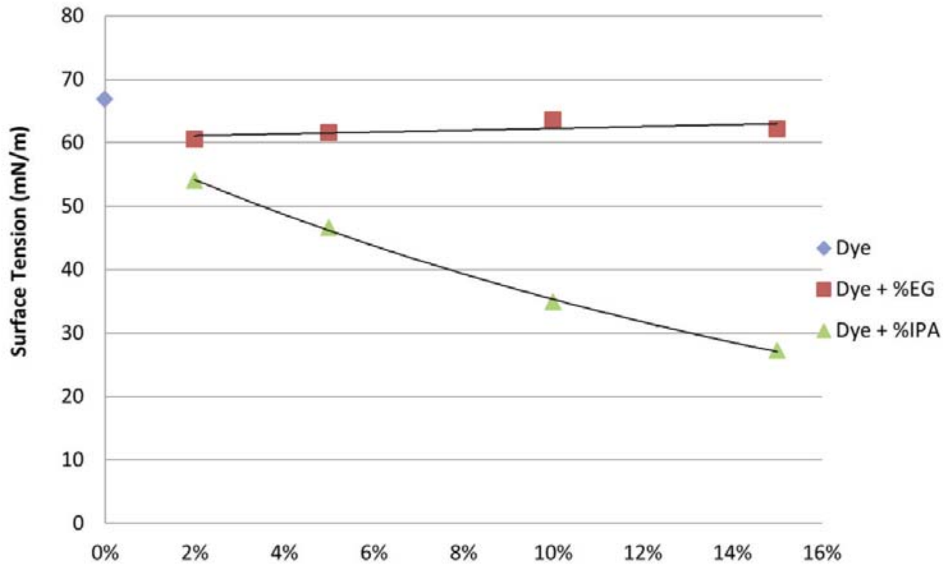

Figure 3: *The comparison of the change of surface tension of phthalocyanine dye with ethylene glycol and isopropyl alcohol*

Rheology of all nine different dye ink formulations was measured using the Cone-Plate geometry at a stable temperature of 25˚C. The results were illustrated as the viscosity curve (viscosity vs. shear rate). Figure 4 shows the change of viscosity with addition of isopropyl alcohol and Figure 5 the change of viscosity with addition of ethylene glycol. The viscosity of sole phthalocyanine dye is rather low and it slightly increased with the addition of the IPA or EG (Fig.4 and Fig.5). With the same addition of alcohol, IPA increased viscosity slightly more than EG (Table 3).

Dye	Dye + 2%wt IPA	Dye + 5%wt IPA	Dye + 10%wt IPA	Dye + 15%wt IPA	Dye+ 2%wt EG	Dye + 5%wt EG	Dye + 10%wt EG	Dye + 15%wt EG
1.32	1.44	1.59	2.02	2.36	1.48	1.53	1.64	1.83

Table 3: *Viscosity [cP] of phthalocyanine dye inks*

The data of specific gravity, surface tension and viscosity were combined and used to calculate Z number to check which dye ink formulation is suitable for inkjet printing. Normally, Z number within the range 2≦Z≦14 was proven jettable. Table 4 shows the results of Z number.

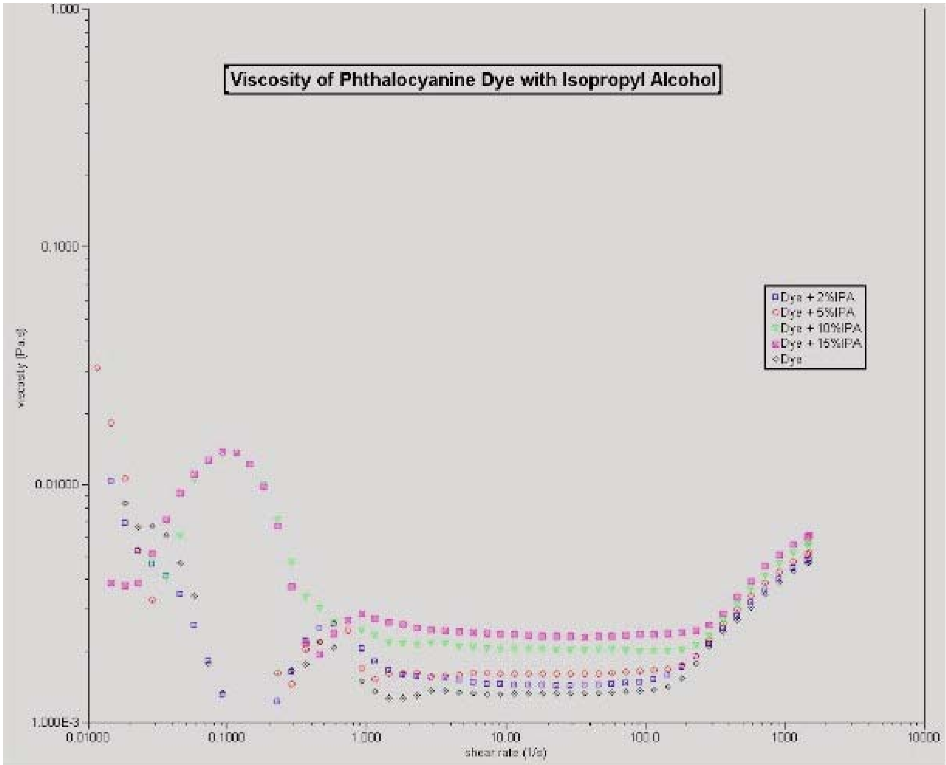

Figure 4: *The change of viscosity of phthalocyanine dye with addition of isopropyl alcohol*

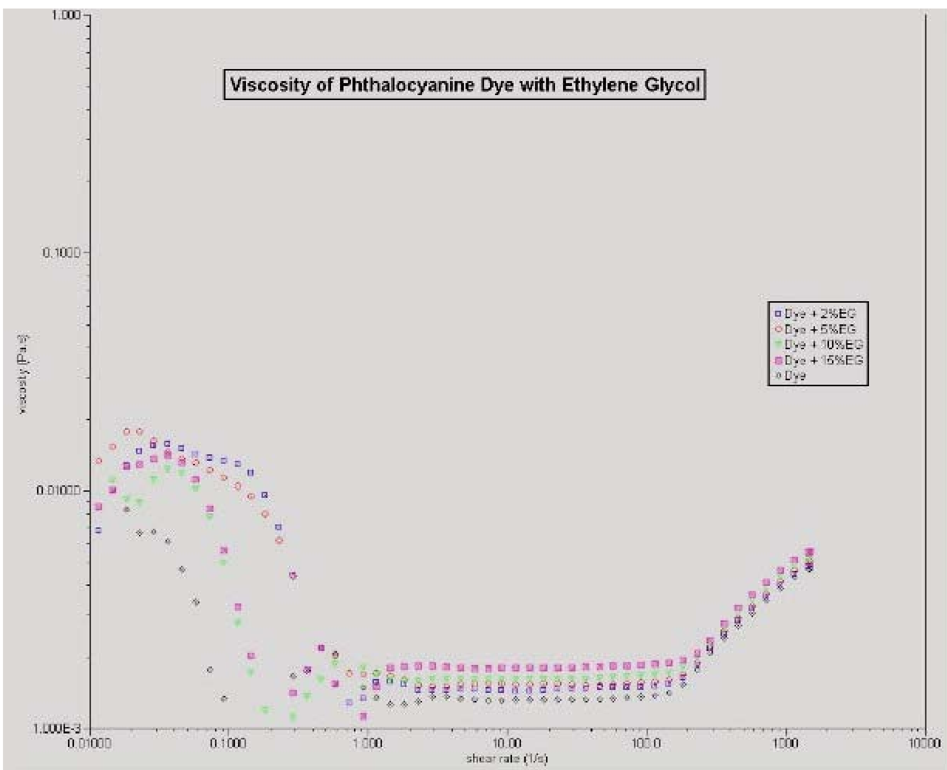

Figure 5: *The change of viscosity of phthalocyanine dye with addition of ethylene glycol*

Dye	Dye + 2%wt IPA	Dye + 5%wt IPA	Dye + 10%wt IPA	Dye + 15%wt IPA	Dye+ 2%wt EG	Dye + 5%wt EG	Dye + 10%wt EG	Dye + 15%wt EG
29.55	24.37	20.46	13.96	10.55	25.08	24.47	23.20	20.56

Table 4: *Z number of phthalocyanine dye inks*

EG was not very efficient in Z number adjustment. Z number decreased to 10.55 with 15%wt IPA addition (Table 4). Thus, the Z number of ink with 10%wt IPA and 15%wt IPA are in the range that is suitable for inkjet printing.

Phthalocyanine ink with 15%wt IPA was used to test the jettability by Dimatix Materials Printer. The Figure 6 shows the screenshot of the jetting movie.

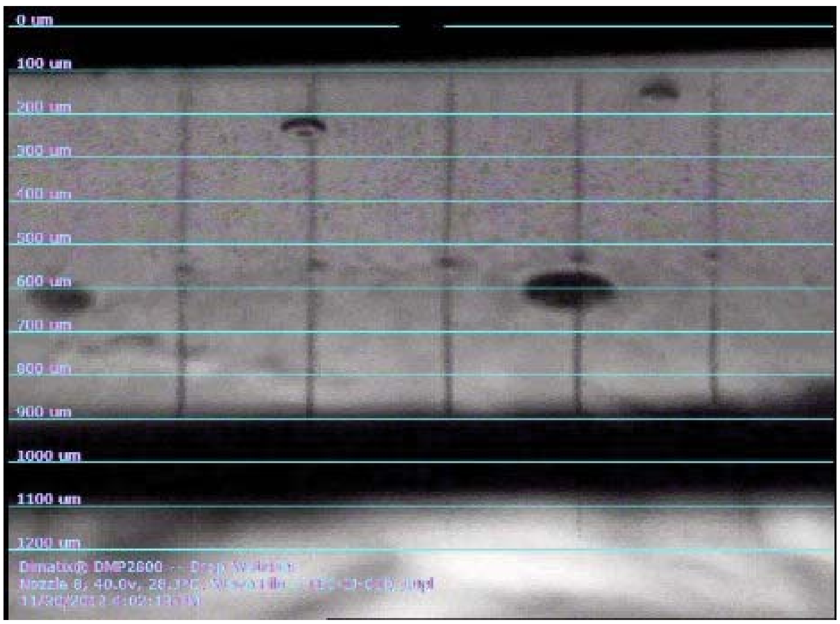

Figure 5: *The change of viscosity of phthalocyanine dye with addition of ethylene glycol*

From the Figure 6, it shows that the ink formulation could get a really good jettability. The ink was printed on the PET substrate of 100 μm gage by the Dimatix Materials Printer DMP-2800. Figure 7 shows rather non uniform print results, most likely due to mismatch of ink surface tension and substrate surface energy.

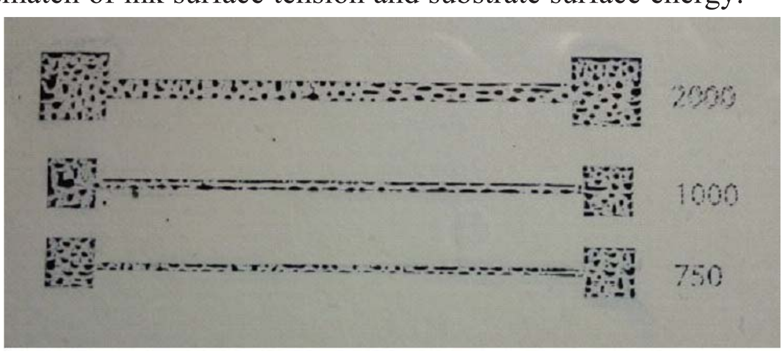

Figure 7: *Dimatix printing on non-treated PET*

Figure 7 shows that the ink cannot spread well on the PET and created a mottled image. The PET was treated by UV (UVO Cleaner Model 144 AX) for 15min UV time and 6min cooling down time to increase its surface energy. The UV oven creates a stream of ozone to oxidize the surface of PET, and thus increase its surface energy. The drop spacing and percent of each drop also has to be considered when printing with the Dimatix Materials Printer DMP-2800. For the drop spacing, 15 µm and 20 µm were used and 16V and 40V were chosen for controlling percent of each drop. Figure 8 shows the print results.

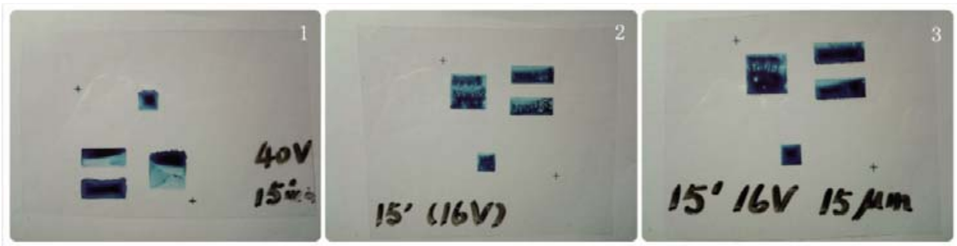

Figure 8: *Printing on treated PET (No. 1: 20 µm and 40V; No. 2: 20 µm and 16V; No. 3: 15 µm and 16V)*

As shown in Figure 8, No.1 used 20 µm and 40V; No.2 used 20 µm and 16V and No.3 used 15 µm and 16V. The ink still crawled and did not produce smooth print on the PET. The print results of No.2 and No.3 are better than No.1. Decrease of the drop spacing form 20 µm to 15 µm did not improve print quality.

Conclusion

Different water based dye ink formulations made of phthalocyanine blue were examined for inkjet jettability and printability. Based on the results, IPA is more efficient in surface tension, viscosity and Z number modification compared to the EG. Two of the ink formulations (phthalocyanine blue with 10% isopropyl alcohol and phthalocyanine blue with 15% isopropyl alcohol) were found to result in best Z number, thus the best jettability. However, this ink formulation caused the ink crawling due to ink and PET surface energy mismatch. PET treated with ozone improved the print quality.

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