Functional Properties of Phthalocyanine Dye Based Inks

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Abstract

Different phthalocyanine dye ink formulations were prepared. They were inkjet printed and tested for suitability as insulating or dielectric layers for printed electronics. In the process of ink making, Z number, a combination measure of specific gravity, surface tension and viscosity was used to predict jettability. Ink formulations are considered to be suitable for ink jetting when the Z number is in the range $2 \leq Z \leq 14$. In order to make the Z number in this range, isopropyl alcohol (IPA), ethylene glycol (EG), acrylic ink jet resins (Joncryl 678, Joncryl 682) and surfactant (Carbowet 300, Air Products) were used in the ink formulations with the aim to adjust the surface tension, viscosity and abrasion resistance [Yumeizhi, 2013].

Introduction

Rotogravure, screen printing, flexography and inkjet printing techniques have been used for printed electronics. The benefits of inkjet printing include the fact that material is only printed where it is required and that it is very easy to modify the patterns to be printed, and no image carrier needs to be produced [Andersson, 2012;Yumeizhi, 2013].

Compared to continuous inkjet printers, drop-on-demand printers can form smaller drops with higher placement accuracy. The drop-on-demand technology can be categorized into thermal drop-on-demand and piezoelectric drop-on-demand methods [Kipphan, 2001]. In this work, the piezoelectric drop-on-demand process was used.

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The Z number, a dimensionless combination measure of density, surface tension and viscosity was used to assess inkjet printability [Reis, 2005]. Fromm [Fromm, 1984] identified Z=1/Oh (Oh = $\sqrt{We}$ / Re = η / (γρ a) 1/2 [Derby, 2011]). Empirically, it was shown that inks are inkjet printable within the range 2≦Z≦14.

The surface energy is defined as the sum of the excess energies at the surface of the liquid compared to the bulk [Annon A, 2013]. In inkjet printing, it is very important to obtain an accurate drop placement and a uniform dried film, which can be controlled by adjusting the surface energy of the substrate [Annon B, 2013].

An insulator does not allow internal electric charges to flow freely or conduct an electric current [Annon C, 2013]. A capacitor is an electrical device, which consists of two parallel conductive plates separated by a dielectric, used to store electrostatic energy [Annon D, 2013]. This work was focused on making phthalocyanine dye inkjet inks with the aim to produce an insulating layer for printed electronic devices.

Experimental

Phthalocyanine dye Duasynjet Cyan FRL-SF(Clariant) was used to make ink jet inks. Isopropyl alcohol (IPA), ethylene glycol (EG) and two types of water-based inkjet resins (Joncryl 678 and Joncryl 682) were added to the dye to make different ink formulations. IPA was used in two levels: 12%wt and 15%. EG was used in two levels: 0%wt and 1%wt. Acrylic resins were used at three different levels: 1%wt, 2.5%wt and 5%wt. A Design of Experiments (DOE) was employed to formulate twenty-four ink formulations for a printed electronics insulating layer.

Both the Joncryl 678 and Joncryl 682 were in powdered form, and liquid resins needed to be made. The process to make Joncryl 678 resin solution was as follows (total weight 100g): add 59 mL 50 ˚C water into a beaker; add 9g ammonia (27%), then add Joncryl 678 solid resin in small increments (total 32g) into solution while dispersing. The process to make Joncryl 682 resin solution was similar with Joncryl 678, but with different percentages. The amounts used for the Joncryl 682 resin are 43mL water, 13g ammonia and 44g Joncryl 682; total weight 100g.

The inks were formulated and the jettability was calculated using the Z number. Specific gravity, surface tension and viscosity were measured in order to calculate the Z number. These were analyzed by pycnometer, FTA200 (First Ten Angstroms, Inc., VA), RA 2000 dynamic stress Rheometer (TA Instruments, DE) respectively [Yumeizhi, 2013].

Suitable formulated inks were printed to check the insulating or dielectric property. A design with four layers was made to measure the property. In this design, the base substrate was PET (Melinex ST 505, DuPont) of 125 µm gage. The first and third layers, which were printed on the PET were conductive silver ink (Electrodag, 479SS, Henkel). This silver ink was printed by screen printer (MSP-PC control, Affiliated Manufacturers Inc., NJ). The formulated inks were printed as a second layer with inkjet printing.

Results and Discussion

Twenty-four different phthalocyanine dye ink formulations were made as shown in the Table 1.

Number	Formulation	Number	Formulation
1	1%J678+12%IPA	13	1%J682+12%IPA
2	1%J678+12%IPA+1%EG	14	1%J682+12%IPA+1%EG
3	1%J678+15%IPA	15	1%J682+15%IPA
4	1%J678+15%IPA+1%EG	16	1%J682+15%IPA+1%EG
5	2.5%J678+12%IPA	17	2.5%J682+12%IPA
6	2.5%J678+12%IPA+1%EG	18	2.5%J682+12%IPA+1%EG
7	2.5%J678+15%IPA	19	2.5%J682+15%IPA
8	2.5%J678+15%IPA+1%EG	20	2.5%J682+15%IPA+1%EG
9	5%J678+12%IPA	21	5%J682+12%IPA
10	5%J678+12%IPA+1%EG	22	5%J682+12%IPA+1%EG
11	5%J678+15%IPA	23	5%J682+15%IPA
12	5%J678+15%IPA+1%EG	24	5%J682+15%IPA+1%EG

Table 1: *Phthalocyanine dye ink jet formulations*

The Table 2 shows the results of density for all twenty-four formulated water-based inkjet inks.

Formulation	Density (g/cm^3)	Formulation	Density (g/cm^3)
1%J678+12%IPA	1.022	1%J682+12%IPA	0.998
1%J678+12%IPA+1%EG	1.021	1%J682+12%IPA+1%EG	1.026
1%J678+15%IPA	1.004	1%J682+15%IPA	0.976
1%J678+15%IPA+1%EG	1.021	1%J682+15%IPA+1%EG	1.021
2.5%J678+12%IPA	1.018	2.5%J682+12%IPA	1.027
2.5%J678+12%IPA+1%EG	0.996	2.5%J682+12%IPA+1%EG	1.027
2.5%J678+15%IPA	1.001	2.5%J682+15%IPA	0.989
2.5%J678+15%IPA+1%EG	1.003	2.5%J682+15%IPA+1%EG	1.017
5%J678+12%IPA	1.028	5%J682+12%IPA	1.027
5%J678+12%IPA+1%EG	1.025	5%J682+12%IPA+1%EG	1.029
5%J678+15%IPA	1.015	5%J682+15%IPA	1.004
5%J678+15%IPA+1%EG	1.019	5%J682+15%IPA+1%EG	0.993

Table 2: *Density of phthalocyanine dye ink jet inks*

From the results shown in Table 2, it is obvious that the specific gravity for all of the formulated inks were very similar, all around 1.0 g/cm^3.

The surface tension of each sample was measured with three replications, and the average value was calculated. The results of surface tension (ST) are shown in the Figure 1.

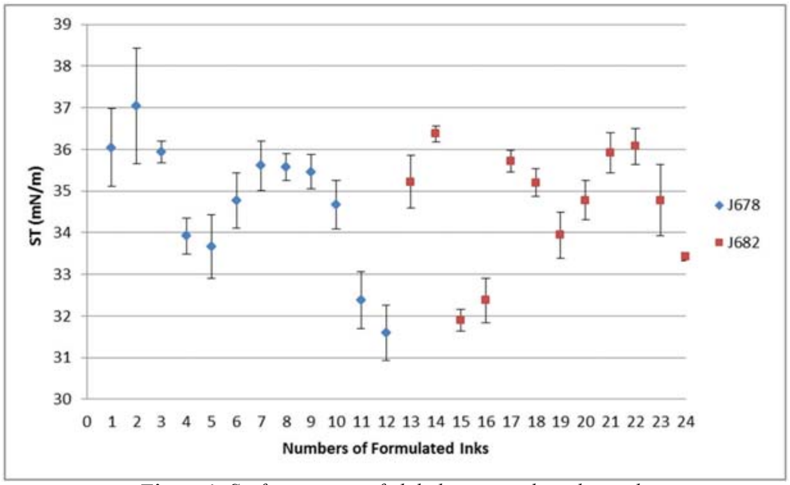

Figure 1: *Surface tension of phthalocyanine dye ink jet inks*

Figure 1 shows that the surface tensions of the different formulated water-based inks all fell within the range of around 31 to 37 mN/m.

Figure 2 shows viscosities for all twenty-four formulated inks. Each one was measured three times and the results below are the averages of these measurements.

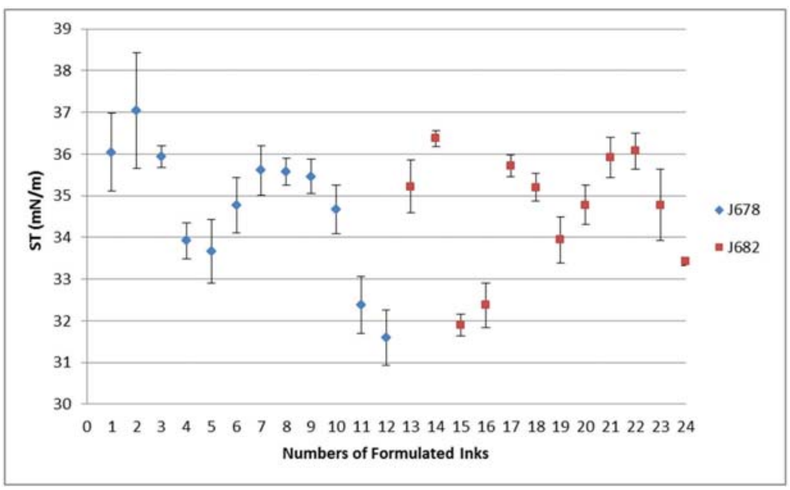

Figure 2: *Viscosity of phthalocyanine dye ink jet inks*

From the results shown in Figure 2, it is obvious that the viscosity of all inks is in the range 2.29-2.81 cP. Viscosity increases with the addition of Joncryl resins J678 or J682, but both imparted a very similar viscosity to the inks.

Based on the results of density, surface tension and viscosity, the equation Z=1/Oh [$Oh = \sqrt{We}/Re= \eta/(\gamma\rho\ a)$ ½] [Derby, 2011] was applied to calculate the Z number. The results are shown in the Figure 3.

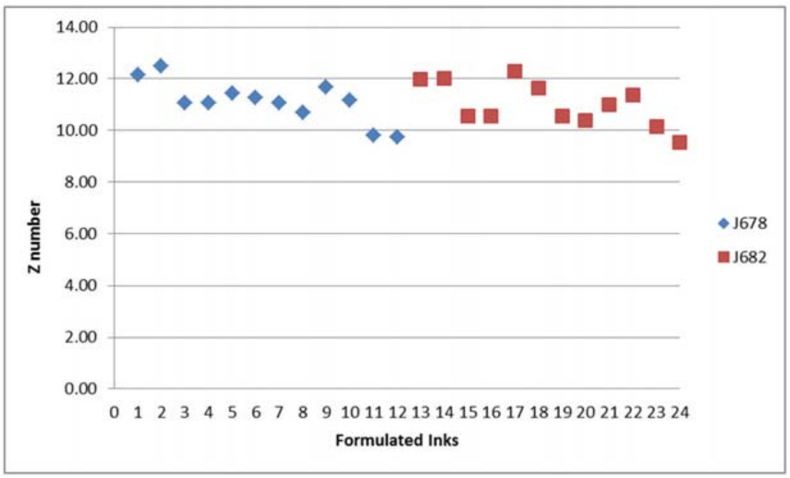

Figure 3: *Z number of phthalocyanine dye ink jet inks*

From Figure 3 it is obvious that the Z number decreases with the increasing content of both Joncryl resins J678 and J682. Also, all the Z numbers are in the range 9 to 11, thus they fall into 2 to 14 range as required, which means all the formulated ink jet inks should be jettable.

Before the formulated inks were printed with the Dimatix Material Printer, it was necessary to check the contact angle of inks on both PET and silver ink (SI). The time point that a drop contacted the substrate for about 20s had been chosen when measuring the contact angle. At this point, the curve for contact angle was stable, marked as 20s in results. The time point could help to determine which formulated inks could wet the substrate and spread well.

The contact angle (CA) of each ink was measured three times and the average was calculated. Figure 4 shows the differences in contact angles at the 20s time point on both PET and Silver ink for the twenty-four formulated inks. In Figure 4, the different water-based resins are shown separately.

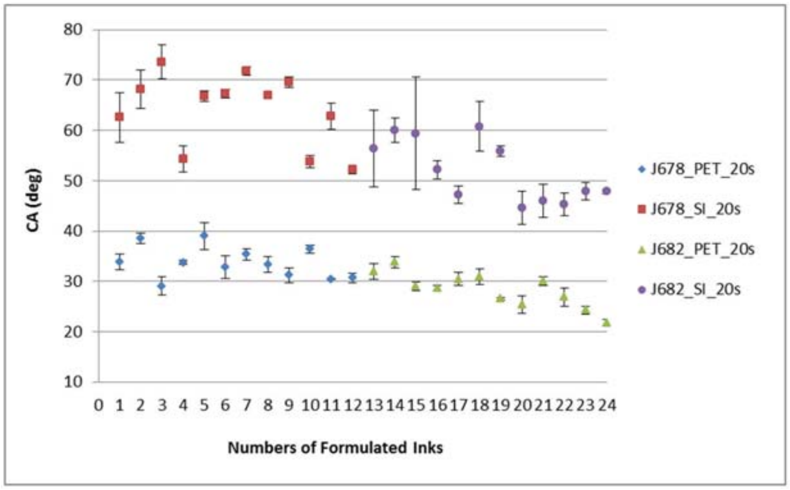

Figure 4: *Contact angles of phthalocyanine dye ink jet inks*

Figure 4 shows that the contact angles on PET are lower than the contact angles on the Silver ink no matter which resin was used. The water-based inks formulated with the J678 had higher contact angles with PET and with silver printed layer than inks formulated with resin J682.

The Z number showed that all of the formulated inks could be used in inkjet printing, because they were in the jettable range. The samples that had lower contact angle on both PET and silver ink were chosen for printing. The two samples (5% J682+12% IPA and 2.5%682+15%IPA+1%EG) were chosen to check the insulator property.

As a first layer, the silver ink was printed on PET. The printed sample is shown in Figure 5.

Figure 5: *Silver ink layer on PET*

The conductivity of the silver ink was 1.5 Ω/□.

Then the selected two formulated ink samples were printed separately with the Dimatix Material Printer. Figure 5 shows the printed results of the 5% J682+12%IPA ink formulation.

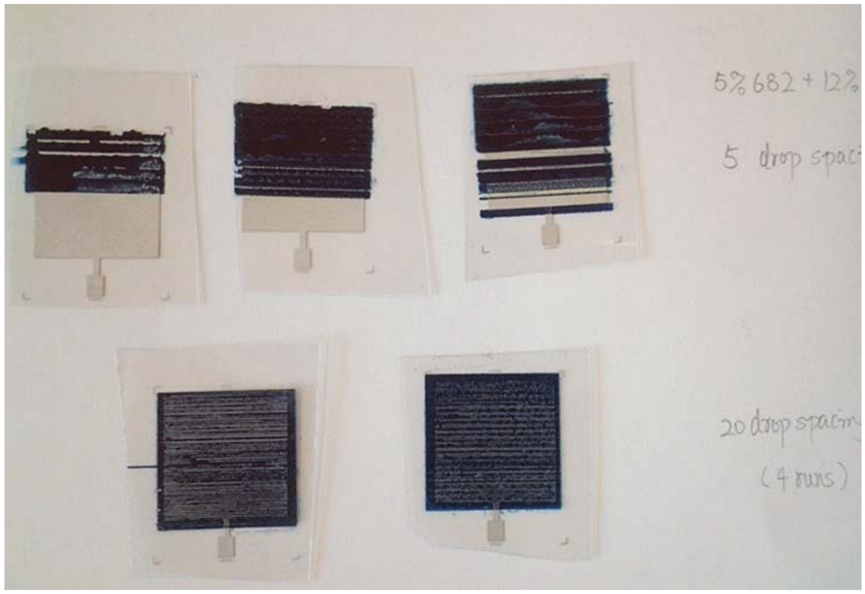

Figure 6: *5%J682+12%IPA printed using Dimatix*

Two digital square bitmap profiles were designed. One used 5 drop spacing (5µm between two drops); the other one used 20 drop spacing (10µm between two drops). When printed using the 5 drop spacing profile, it was very hard to control the cleaning time, and the lower frequency caused the nozzle to get blocked quickly, and even after cleaning, the nozzles were still blocked; but higher frequency generated a huge waste of ink. At the end of printing, the nozzle clogged after two cleaning cycles. The results of printing at the 5 drop spacing are shown in the top row at Figure 6; the frequency was changed from low to high (from left to the right).

The squares in the bottom row of Figure 6 were printed with a 20 drop spacing, which had a lower resolution. Because of the lower resolution (higher drop spacing), printing repeat of four times had been chosen for one sample in order to make sure that the ink covered the whole square.

It was found that the phthalocyanine ink does not spread well and cover the whole area of the silver ink layer, no matter if 5 drop spacing or 20 drop spacing was selected. However, based on the results of the tests, it can be concluded that the 20 drop spacing was much easier to control than the 5 drop spacing.

In order to have the ink spreading well on the substrate, especially on the silver ink, a UV Oven treatment was employed to increase the surface energy of the substrate. 5 min and 10 min time treatment was chosen and both of them included 5 min cooling time. Afterwards, the 20 drop spacing profile was selected to print four times again. The results are shown at Figure 7.

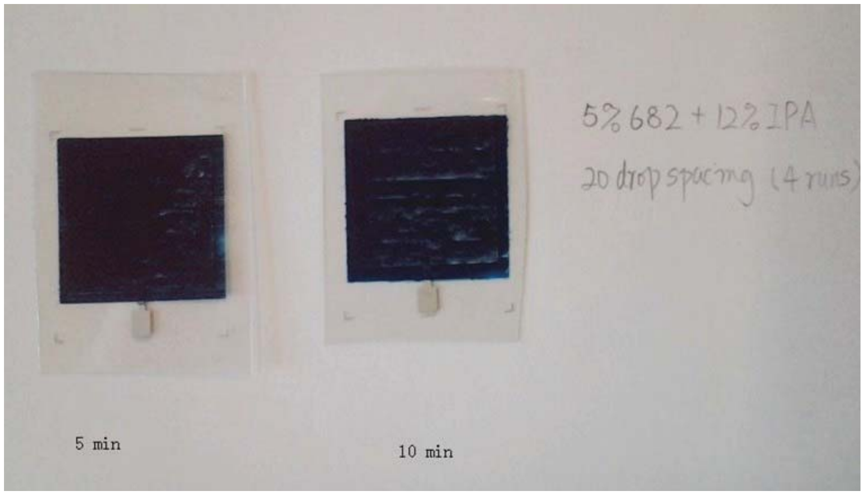

Figure 7. *Insulator layer after UVO treatment, ink with 5% J682+12%IPA*

It is clear that after the UVO treatment, the integrity of the printed layer is enhanced (Fig.7). The layer is significantly more uniform and covers the silver layer more consistently than without UVO treatment (Figure 6). When comparing the two treatment periods, 5 and 10 min UVO treatment, the results of the 5 min UVO treatment are better (Figure 7 left), because the ink coverage is more uniform.

Ink with 2.5% J682+15%IPA+1%EG was printed similarly to ink with 5% J682 and 12% IPA. Figure 6 shows the results printed using 20 drop spacing profile without UVO treatment.

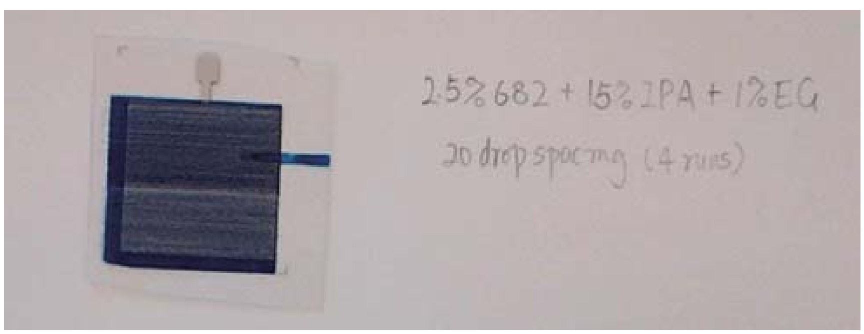

Figure 8. *Insulator layer printed with 2.5% J682+15%IPA+1%EG*

Figure 8 shows that the print result is similar to the one achieved with 5% J682+12%IPA, just slightly more uniform. The silver layer was then treated for 5 min with UVO treatment (Figure 9) and 10 min UVO treatment and printed with phthalocyanine ink (Figure 10).

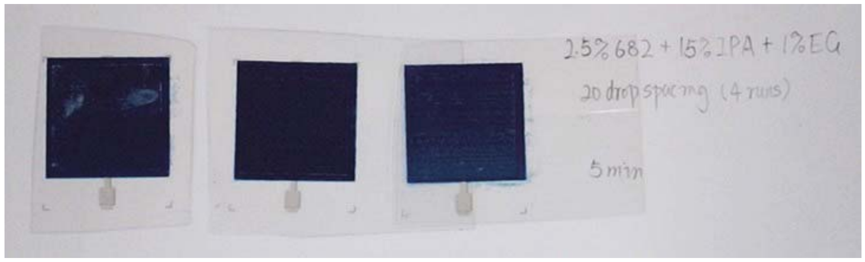

Figure 9. *2.5% J682+15%IPA+1%EG after 5min UVO treatment of silver layer*

Figure 9 shows that the print results are much better than without UVO treatment, especially the middle one. The ink spreading was very uniform and it covered evenly the whole silver ink layer.

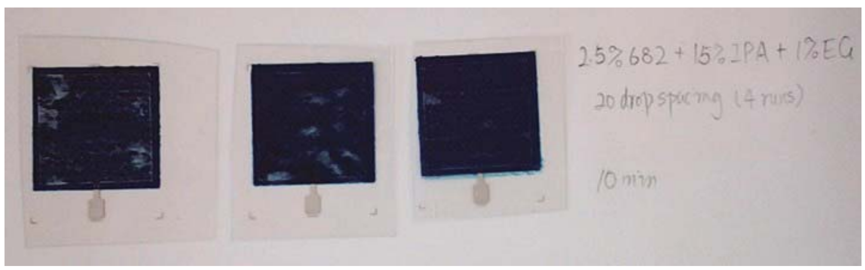

Figure 10. *2.5% J682+15%IPA+1%EG after 10 min UVO treatment of silver layer*

Figure 10 shows print result after 10 min UVO treatment. It is obvious that silver layer after 10 minutes of UVO treatment has worse coverage ability than the same layer after 5 min UVO treatment. It is possible that the layer was rougher than the one after 5 minute UVO treatment

The surface energies of the silver ink with the 5 min UVO treatment and 10 min UVO treatment rere measured by contact angle measurement instrument FTA200 and calculation. The surface energy of silver ink with 5 min UVO treatment was 45.51mN/m and the surface energy of silver ink with 10 min UVO treatment was 53.48mN/m.

The roughness of the silver ink after 5 min UVO treatment and 10 min UVO treatment was measured with a Bruker Contour GT white light interferometer microscope. Table 3 shows the roughnesses of the silver ink after the 5 min and 10 min UVO treatment.

	Roughness (μm)
5 min UVO treatment	1.12
10 min UVO treatment	2.20

Table 3: *Roughness of silver ink with 5min and 10min UVO treatment*

From the results shown in the Table 3, it is obvious that the silver ink layer with 5 min UVO treatment is much smoother than the silver ink layer with 10 min UVO treatment. Figure 11 and Figure 12 show the differences of the two treated surfaces.

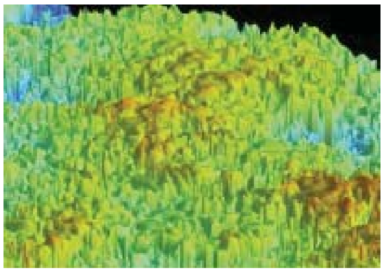

Figure 11. *3D of silver with 5min UVO treatment*

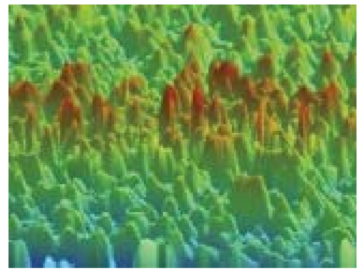

Figure 12. *3D of silver with 10min UVO treatment*

he results of the roughness measurements explain why the formulated inks printed on the 5 min UVO treatment silver ink resulted in better ink coverage.

After these prints were done, the third layer of silver ink was printed on the phthalocyanine ink layers. The insulator property was measured after printing, which showed that the two conductive silver inks connected with each other. It is possible that the silver layer printed using screen printing process has spikes and valleys created when lifting the screen, which create pinholes in the next layer of phthalocyanine ink. The microscopic images of printed results of formulated inks were analyzed with ImageXpert.

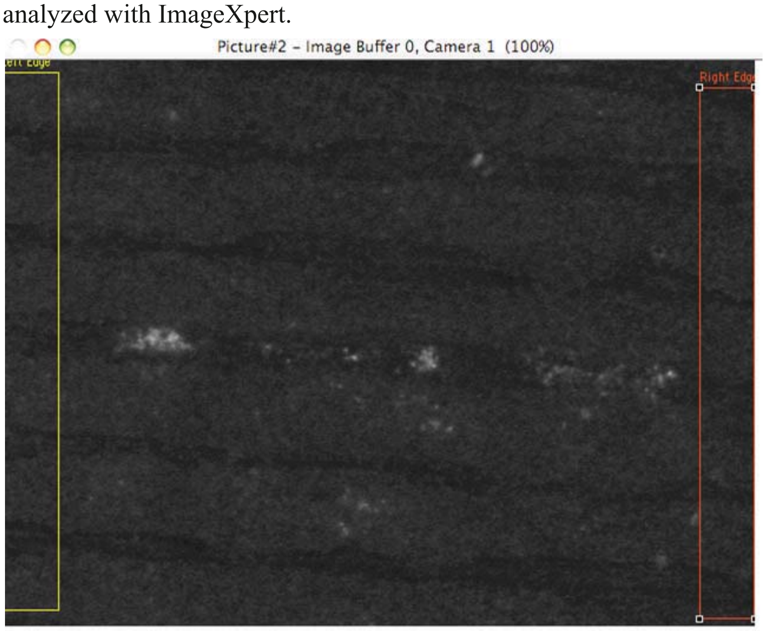

Figure 13. *Micro image of printed results for formulated inks*

The microscopic image (Figure 13) shows tiny white spots not covered by phthalocyanine inks, which most likely enable the bottom silver layer ink connect with the top layer silver ink directly and interfere with capacitor properties.

In order to resolve the pinhole problem, repeated runs (six and ten repeated runs) were carried out using the 20 drop spacing profile. Surfactant (Carbowet 300 surfactant, Air Products) was also added into ink formulations. These did not help to resolve the pinhole problem.

In order to find out the reason, which caused the pinhole problem, the thickness of silver ink layer and formulated ink layer was measured by Bruker Contour GT, White Light Interferometer instrument. Table 4 shows the thickness of silver ink layer and formulated ink layer (using 20 drop spacing, single run).

	Thickness (μm)
Silver ink layer	4.20
Formulated ink layer	0.25

Table 4: *Thickness of silver ink layer and formulated ink layer measured by WYCO*

The results (Table 3) show that the thickness of formulated ink layer is very low. The roughness of the silver ink layer with 5 min UVO treatment is 1.12 μm (Table 3), which means 4 repeated runs, even 10 repeated runs of formulated ink are not sufficient to cover the spikes within the silver ink layer. Because of the pinholing problem, the insulator property test failed. For future work, it is suggested that the silver layer be calendered to level the peaks. Also, the gravure printing process is suggested to print the silver ink, in order the get a smoother layer than that achieved by screen printing.

Conclusion

In this work, the inkjet inks were formulated and Z numbers were calculated to predict the jettability. It was found that all phthalocyanine based formulated inks had the Z numbers in the jettable range of 2-14. Selected phthalocyanine inks were printed and tested for the insulator property. In order to achieve proper wettability of PET substrate and printed silver layer, the contact angles of both PET and silver ink layers were measured. The best inks, which were most compatible with the two layers, were chosen to be printed by Dimatix Material Printer. The results of contact angle measurement showed that the inks with acrylic resin Joncryl J682 were more suitable than those formulated with J678. The inks formulated with resin J682 had lower contact angle, therefore better wetting and spreading ability than inks with J678 resin. Based on the results of contact angle, two inks were selected to be printed and tested for the insulator properties. The two phthalocyanine inks were formulated with 5% J682+12% IPA and 2.5%682+15%IPA+1%EG. When printing these two inks with the Dimatix Material Printer, it was found that 20 drop spacing was better than 5 drop spacing. The 5 drop spacing encountered cleaning problems. The inks were more ready to dry and block in the needle. When the surface energy of the substrate was increased with the UVO treatment, better and more uniform ink films were achieved. Based on the results, 5 min UVO treatment was found to be better than 10 min UVO treatment. None of these treatments were sufficient in removing pinholing defect; neither surfactant could help to resolve it. It was confirmed that the silver layer printed using screen printing process created peaks and valleys in the silver ink layer and the roughness of this layer was larger than the thickness of the next ink jet ink layer, thus proper capacitor functionality was not achieved. Printing on silver layer required prior treatment with UVO cleaner, which also contributed to silver layer roughening, which was confirmed by white light interferometry measurement.

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