Towards Formulating Conductive Nickel Ink for Flexography Printing

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Abstract

Printing methods and conductive inks have brought electronic manufacturing to a new level by enabling production of thin, light-weight and flexible components at high speed, low cost and low waste. The printed electronic market is massive, yet the developments and varieties in ink formulation is very limited. This paper reports an alternative conductive ink for flexography printing. In the formulation, metal nickel sphere particles are mixed with different latexes and acrylic resins in water and ammonia. The optimum photonic curing condition is presented along with electrical response of the ink films.

1. Introduction

Creating electronic devices through printing science goes back to early 2000s (Gamota, 2004). By using functional inks (i.e. conductor, semi-conductor, insulator), it is possible to manufacture electronic devices, called printed electronics (PE), with bendable, rollable, stretchable and/or washable nature on thin, flexible and light-weight materials, such as paper, plastic films and textiles (Willmann, Stocker & Dörsam, 2014; Leenen et al., 2009; Vervust et al., 2012). The projected market growth for PE in 10 years is nearly $74 billion (Das et al., 2017). Although the market is massive, the development and variety in the ink formulation field is limited. Currently, silver, and gold inks are the most common conductive inks being used by PE device designers, because of their high costs, lower cost alternative materials are needed (Leenen et al., 2009; Husovska et al., 2012). Copper inks are popular and have a price advantage, but they are susceptible to corrosion and oxidation (Lim et al., 2012). Even though there are remarkable advancements, there is still a big demand for new ink formulations (Pathak, Pekarovicova & Fleming, 2015; Altay 2016), new product designs and applications (Kirchmeyer,

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Hecker, 2013). To advance PE field, and innovate new products, alternative low cost materials that can be readily scaled to meet the needs of large scale printing operations are needed (Husovska, 2012). Nickel (Ni) is an abundant metal element on earth (Wells, 1943). It is a metallic element that is ferromagnetic at up to 358°C as well as highly conductive and has high resistance to oxidation and corrosion.

Flexography (flexo) printing process has an advantage of being able to deposit a broad range of functional materials on various materials at feature sizes as low as 10 microns. Roll-to-roll flexo presses enable material and handling cost reduction through the gains achieved through its high throughput efficiency that can be integrated into making active packaging, sensors, RFID tags among other applications.

The most common practical approach to an ink formulation is to start working with an existing ink (Lambourne and Strivens, 1999). Therefore, the viscosity of an existing Ni screen ink was optimized to run on flexo proofer in the first part of the study. In the second part, the Ni screen ink was screen printed to investigate optimum photonic curing condition. In the last part, an alternative conductive flexo ink formulation that contains nickel sphere metal particles is reported.

2. Method and Materials

2.1 Rheology measurement and ink optimization by viscosity adjustment

A TA Advanced Dynamic Stress Rheometer AR2000 was used to characterize rheological behavior of commercial inks in response to shear rate. The rate was ranged from 0.1 to 500 1/s at 23° Celsius.

Viscosity adjustment method was used to optimize Ni screen ink (*NovaCentrix HPN-DEV nickel flake: Austin, TX*) by following the procedure published by Faddoul et al. (2012) to match flexo ink nature to print on a flexo proofer. Harper QD proofer was used with a 200cpi/21.7µ anilox for print trials. Flexo plate had 90 and 100% solid patches.

2.2 Screen printing and photonic curing

The Ni ink was screen printed on cover paper (*International Paper C2S 144-lb.: Chicago, IL*) and PET (*DuPont Melinex ST506: Chester, VA*) substrate as a control group. Print pattern was a 1.5x1.5 in. square. Mesh size was 165 threads per inch. A full factorial design was selected to explore optimum single pulse photonic curing condition by using a PulseForge 1200 curing device (*NovaCentrix: Austin, TX*). The voltage, web speed and overlap settings were kept constant at 450 volts, 20 fpm and two, respectively, while varying the pulselength time and mode factors as in Table 1. The difference between the once through and fixed mode is that a sample receive multiple pulse lights in once through mode, while receives one single pulse light in fixed mode.

A Keithley 2400 4-point probe sourcemeter was used to measure sheet resistivity.

Factor	Levels
Pulselength (μs)	0, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 2000, 2600
Mode	once through, fixed

**pulselength 0 represents before curing condition*

***Table 1.** Factor Information*

The resistivity results were corrected based on Haldor Topsøe geometric correction factors.

2.3 Ink formulation

70 nm nickel sphere particles were purchased (*US Research Nanomaterials: Houston, TX*) and mixed with four different commercial binders that listed in Table 2. Ammonia water with a pH of 8.5 was used as the vehicle of the ink.

	Chemistry	Solid level
B1	Acrylic A	34%
B2	Acrylic B + Acrylic C	35.5% + 48%
B3	Carboxylated styrene-butadiene A	55%
B4	Carboxylated styrene-butadiene B	50%

***Table 2.** Binder selection*

Drawdowns were made using 0.05 bird type applicator. After sintering, 1000 pli (pounds per linear inch) nip load was applied twice against the soft roll on a calendering device. A Bruker CounterGT vertical scanning interferometer 3D microscope was used to analyze the thickness of ink film.

3. Results and Discussions

3.1 Rheology measurement and ink optimization by viscosity adjustment

For good handling and on-machine processability, it is important to understand how inks flow/deform under various rates of shear and different temperatures. The science of rheology reveals such information to these changings (Chen et al., 2012) as well as the change in chemical concentration of an ink formulation. While low shear rates represent storage conditions for inks, high shear rates represent press run conditions.

In Figure 1, the viscosities of traditional and functional screen and flexo inks were represented in response to shear rate. Screen and flexo inks had a viscosity value around 1000 and 100 Pa•s, accordingly at 0.1 1/s shear rate. Although they had different viscosity at low shear, the curves were started to overlap around 100 1/s shear rate. This indicates that the screen ink could act like a flexo ink at high shear

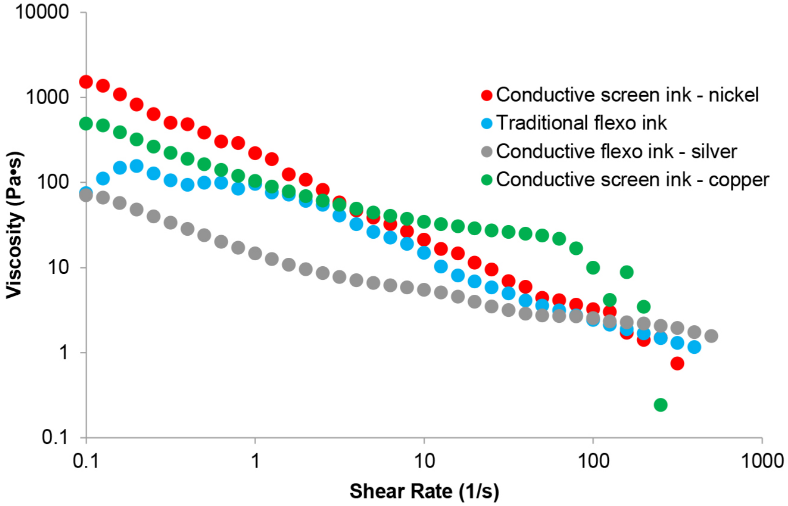

Figure 1. *Ink viscosity in response to shear rate*

rates. It also means that the viscosity of screen ink may be optimized to fit flexo ink curve.

Faddoul et al. (2012) demonstrated a viscosity adjustment method for a screen silver ink that performed well on a flexo proofer. Therefore, the same method was adopted to optimize screen Ni ink. Initially, Ni ink had 62% solid level was reduced to 30% and printed on the flexo proofer. The optimized ink did not perform well on the proofer. Another trial was performed using a flexo silver ink to check the plate quality. Figure 2 represents both print trial results. Silver ink performed well on the proofer, proving that the plate quality was proper. It was concluded that the ink optimization method by Faddoul et al. is not applicable to Ni screen ink. The reason would also be incompatible ink surface tension with the surface energy of

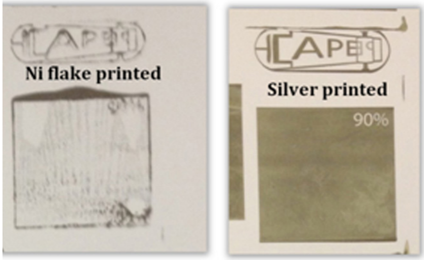

Figure 2. *Print results of the optimized Ni ink (left) and flexo silver ink (right)*

substrate or plate; Ni particles would be bigger than possible to release from the openings on the anilox cells.

3.2 Screen printing and photonic curing

The Ni screen ink was printed on both cover paper and PET to find optimum curing conditions and to use sheet resistivity results as a control group in the ink formulation part. Figure 3 shows the resistivity results of ink films on cover paper. The minimum resistivity of 0.4 Ω/sq was resulted at 2600 µs with the fixed mode, but the ink film was damaged due to burning binder component in the ink (Figure 4). The second minimum resistivity of 0.7 Ω/sq was resulted at 1700 µs with the once through mode, therefore this curing condition was selected to use for ink formulation trials.

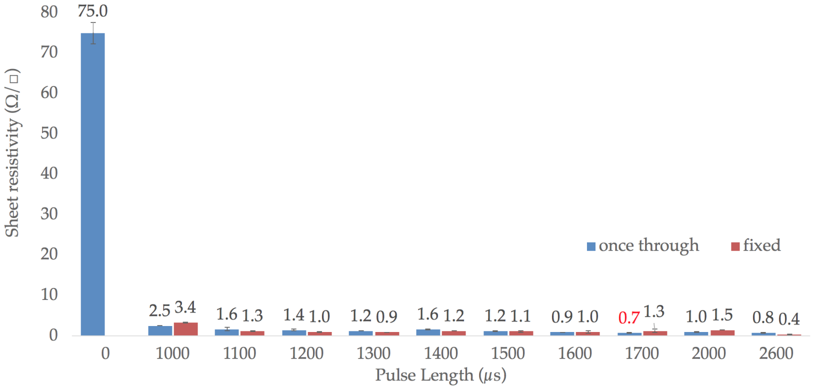

Figure 3. *Ink film sheet resistivity on cover paper*

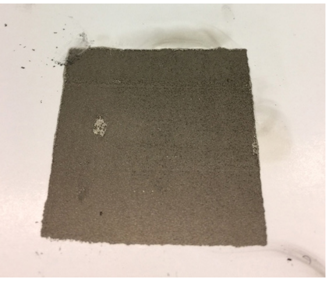

Figure 4. *Damaged ink film on cover paper at 2600 µs pulselength*

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	21	1378.16	65.627	59.13	0.000
Linear	11	1348.13	122.558	110.43	0.000
Pulse length	10	1345.61	134.561	121.24	0.000
Mode	1	2.52	2.521	2.27	0.139
2-way interactions	10	30.02	3.002	2.71	0.011
Pulse length*Mode	10	30.02	3.002	2.71	0.011
Error	44	48.83	1.110		
Total	65	1426.99			
Model Summary					
S	R-sq	R-sq (adj)	R-sq (pred)		
1.05349	96.58%	94.94%	92.30%		

Table 3 *Multilevel factorial design analysis for cover paper*

The regression analysis in Table 3 indicated that the pulselength and the interaction between the pulse length and mode have a significant effect on the sheet resistivity. On the other hand, PET film had shrinking problems and moisture blistering during the photonic curing process (Figure 5 and Figure 6). To further analyze the problem, the same curing conditions were applied to unprinted PET substrate. Shrinking was not observed on the substrate after the curing process. This indicates that the

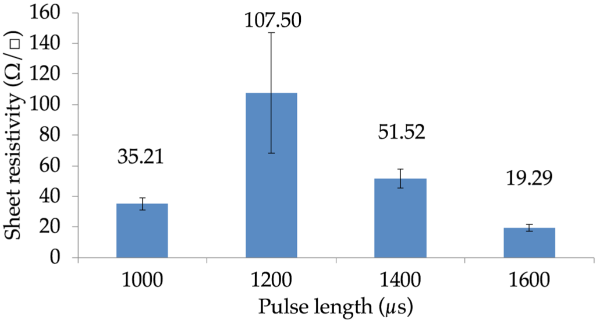

Figure 5. *Ink film sheet resistivity on PET*

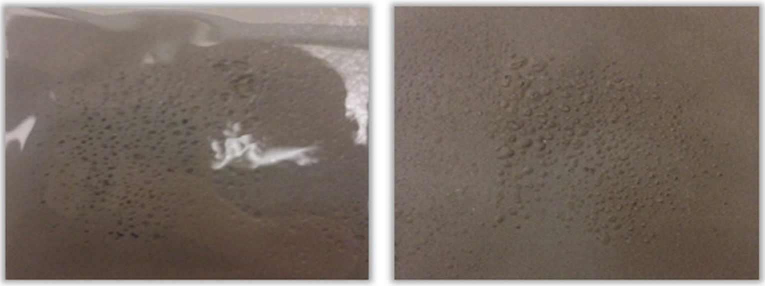

Figure 6. *Moisture blistering on PET film*

interaction at the interface of Ni ink and PET layer would be causing the shrinking problem.

3.3 Ink formulation

70 nm nickel sphere particles were mixed based on 8:1 pigment:binder ratio by using four different binders. Ink drawdowns were applied on cover paper. Due to shrinking and blistering problem, PET was not used in this part.

The sheet resistivity results in Figure 7 shows that the resistivity of inks with B1 and B2 binders were in the kilo Ohm (KΩ) and mega Ohm (MΩ) range. Binder B4 was provided the minimum resistivity of 49 Ω/sq. Calendering was applied in general to increase smoothness, reduce thickness and/or increase gloss characteristics of paper during paper making process. In our case, it was applied for the compression of printed ink film to decrease sheet resistivity. As can be seen in Figure 7, the overall decrease after the calendering was 99.9% for B1; 99.7% for B2 and B4; and 90.9% for B3. The cause for the dramatic resistivity reduction is that the calendering removes voids between the particles in the ink composition and causing Ni particles to more densely pack and connect (Fleming, 2010).

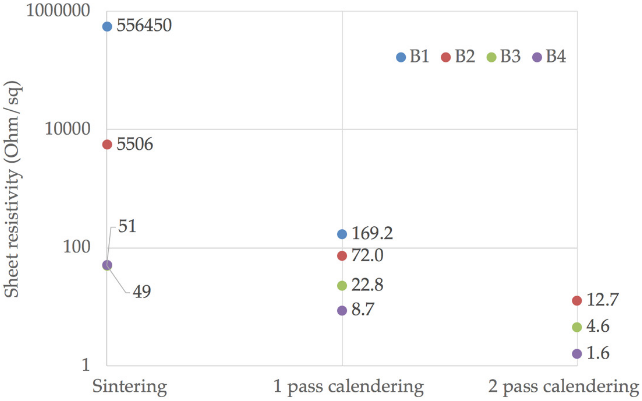

Figure 7. *Ink film sheet resistivity of different binders.*

The calendered ink film thickness was measured to calculate bulk resistivity values,

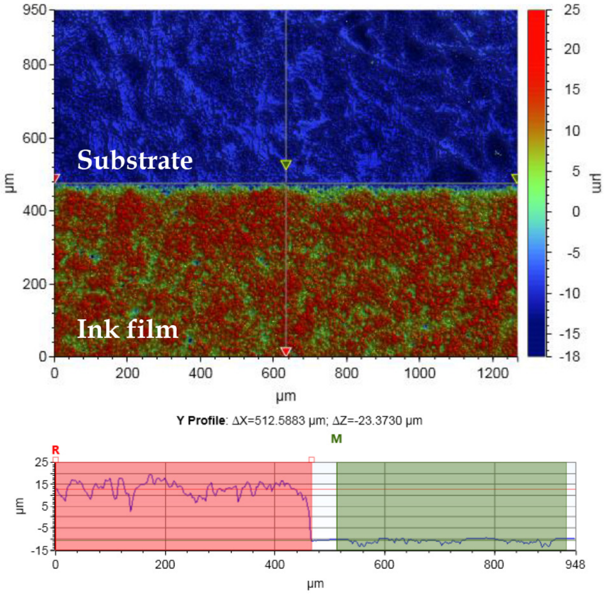

Figure 8. *Profilometry scan of ink film and substrate*

which is a size independent unit. Figure 8 shows an image that gathered from vertical scanning interferometer 3D microscope.

The average thickness and the bulk resistivity values were presented in Table 4. The results indicate that the bulk resistivity of ink formulations was decreased around two orders of a magnitude by changing the binder from B1 to B4.

	Average thickness (µm)	Std. Dev.	Bulk Resistivity (Ω.cm)
B1	3.29	0.67	0.05600
B2	6.65	0.39	0.00800
B3	6.34	0.37	0.00290
B4	2.99	0.28	0.00048

Table 4. *Average ink film thickness and bulk resistivity results*

Figure 9 shows the ink drawdown with binder B4 from flexo proofer print trials. From the result, it can be said that the ink surface tension, the substrate and plate surface energy were not compatible. Next, the ink will be optimized further to

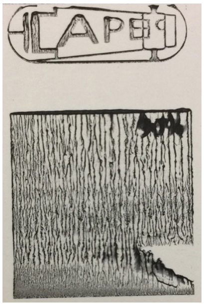

Figure 9. *The flexo proof print trial of the ink with binder B4*

get compatible ink surface tension and substrate or plate surface energy for better printability. New binders will be selected to decrease sheet resistivity.

4. Conclusion

The results show that by using different binder types, nickel ink sheet resistivity can be decreased or increased. Photonic curing can decrease sheet resistivity (or increase conductivity) significantly. Calendering can decrease sheet resistivity and improve electrical property of the ink films. It should also be noted that the ink formulations that show good performance during drawdown may not perform well on a print proofer.

This problem may be overcome by analyzing ink surface tension and surface energy of substrate and plate surface energy.

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