

Screen Printable UV Curing Electronic Inks

*Karen L. Hueston, Laurie N. Kroupa and James S. Tonge
Dow Corning Corporation, Midland MI 48686 USA.*

Introduction

Market analyst, from groups such as NanoMarkets, are predicting the market for printable electronics will generate revenues in excess of \$7 billion in 2010. These values are driven by demand for, RFID tags, photovoltaic's, displays, sensors, computer memory and other printable products [1]. To reach these figures the printable electronic industry must demonstrate the ability to reliably print a wide range of electronic and electrical components, such as displays, power supplies, sound actuators, transistor circuits, sensors, interconnects and the subject of this paper electroluminescent (EL) lighting.

EL lamp are relatively old devices reviewed elsewhere [2] EL lamps are an inorganic capacitor sandwiched between opaque rear Ag and a clear conductive front electrode see Figure 1 for an exploded view.

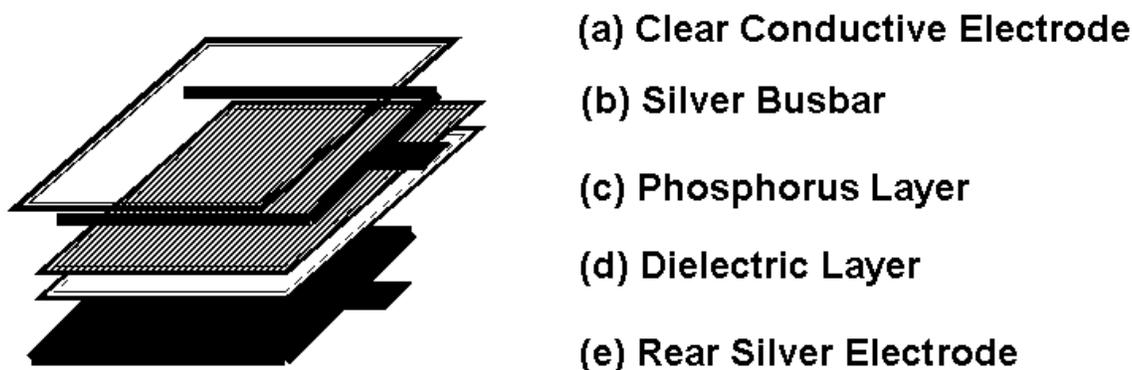


Figure 1 Simplified exploded view of an electroluminescent light.

In early EL lamps, these layers were thermal fused or plasma deposited. These conventional EL lights are subject to failure due to the thermal cycling and the roll pressures used during construction. Both of these processes lead to damaging the integrity of the active layers and supporting circuitry. The damage usually resulted in moisture ingress. The ingress of water leads to the failure of the phosphor particles and is still a major concern in today's EL lamps. Thermal processing also leads to wrinkling and warpage. This non-planarity leads to heterogeneity in the intensity of the light produced by EL lamps and inferior esthetics. To combat these problems the active inorganic and metallic elements of EL lamps are dispersed in a polymeric matrix. This allows EL lamps to be produced by using conventional printing methodologies (screen printing, rotogravure, flexo-, and ink jet printing.). Low temperature cure/dry cycles and thinner traces contribute to faster, more efficient processing, helping to achieve higher throughput rates. Lower cost-of-ownership is achieved by these performance and processing gains. UV curing inks are a mature technology and have been adapted as carriers to the active metallic, semiconductor, and non-metallic particles used in the EL lamps.

Figure 2 depicts a cross-section of a modern EL lamp with a spluttered indium tin oxide electrode on a polyester film as their clear conductive layer front electrodes[3]

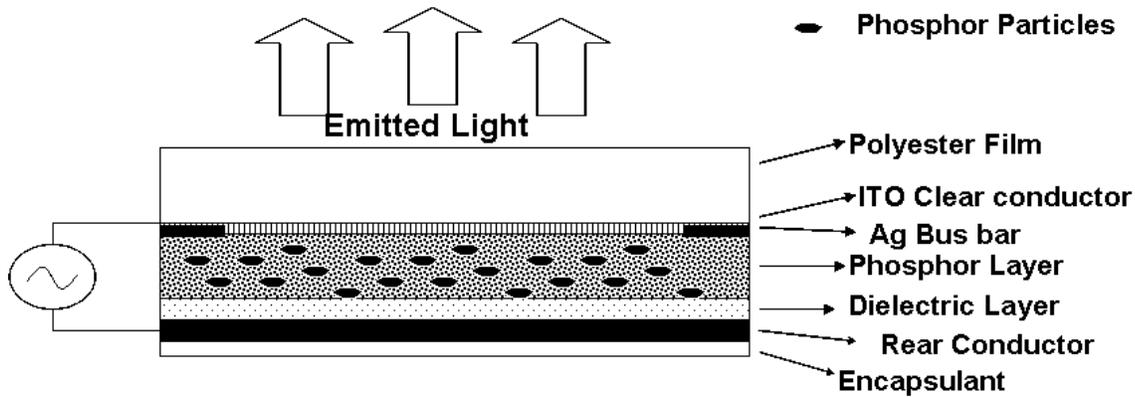


Figure 2 Cross-section of a modern screen-printed EL Lamps

The construction of this type of lamp involves first screen-printing the Ag bus bar onto the ITO coated film, followed by the capacitive phosphorus layer ,dielectric layer, a rear silver electrode, and final protective layer of encapsulant to prevent moisture damage to the lamp. The polyester film serves as a support for the ITO as well as a barrier/protective layer for the device. This arrangement serves in many EL applications, such as backlights in automotive, and portable LCD displays in computers, cell phones and PDA's. The polyester backing is too rigid for the fast growing textile based EL lamps. In textile applications, devices that are more flexible are required. A solution to this problem is to use transfer printing. The device is printed onto a release surface such that on completion it can easily be removed and affixed elsewhere [4]. In Figure 3 we see that these flexible/elastomeric EL lamps have an organic clear conductor [5,6] in an elastomeric envelop.

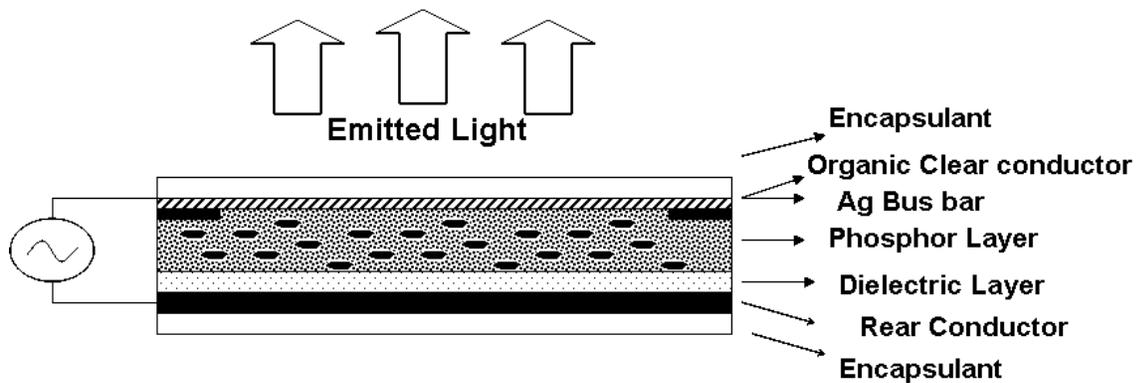


Figure 3 Cross-section of an elastomeric EL lamp.

The printing of a monolithic stack consisting of 10 to 20 discrete layers of >4 different UV inks presents a few potential problems, namely: intercoat adhesion, registration, and embrittlement due to repeated irradiation problems. In its simplest form the elastomeric EL lamp depicted in Figure 3 is constructed

of a base layer, an electrode, phosphor layer, dielectric layer, a transparent organic conductor, Ag conducting bus bars and a protective overcoat. Each of these layers may take as many as 2 to 5 applications to get the required film thickness for operation.

In this paper, we will detail the materials and processing properties of an elastomeric EL lamp in which the clear conductive, phosphor and dielectric layer are already fixed, and we are optimizing the lamp using newly developed Ag inks and encapsulants.

UV Silver Inks.

Highly conducting Ag inks are highly desirable as they reduce the power consumption of the EL lamp and result in higher illumination for a given power level. The more highly conducting Ag inks available are typically thermoset systems and not UV. Heat facilitates the conducting process by increasing the efficiency of the scouring process, and producing matrix shrinkage, both of which lead to direct metallic Ag-Ag interactions and higher current carrying pathways. In order to meet the high conductivity requirements the choice of Ag type/s, loading levels and scouring agents, need to be optimized to achieve direct particle-particle contact. At the 65-80 wt % of Ag loading necessary for the desired resistivity values of ≤ 50 m Ω /square-mil and ≤ 11 m Ω /square-mil little, or no, UV or visible light penetrates the ink surface. UV radical inks where the degree of cure is highly dependent on incident UV flux are ineffective without a secondary cure mechanism. Cationically cured systems, with their inherent living-cure characteristic, are more suited to this application. The cure is initiated in the surface of the ink, and progresses to full cure with time and/or temperature. A small quotient (<35wt%) of the Ag ink formulation is available to optimize UV cure, toughness, flexibility, print quality, and adhesion to a variety of substrates. Table 1 gives the class of materials and their role in the Ag UV ink.

Material	Role
Cycloaliphatic Epoxy	Crosslinking, toughness, viscosity control
Resin	Flexibility and toughness
Cationic initiator	Acid generator, cure speed/ clarity
Photosensitizer	Synergist, cure speed/ clarity
Additives package	Adhesion, conductivity and print enhancers
Ag particles	Conductivity and printability

Table 1 Anatomy of an Ag Ink

Encapsulants

The role of the encapsulant is to provide a flexible, optically transparent, moisture barrier that adheres to multiple substrates and can be printed on top of and cured against. Simple aliphatic backbones, such as EDPM, ethylene butylene-copolymer, butadiene, isoprene, or silicones yield the flexibility and moisture requirement suitable for this application. We chose to work with cationically cured encapsulants with a similar vehicle to the Ag ink described in Table 1. This reduced the number of intermediates and allows a lock and key approach to adhesion. Flexible UV epoxies are derived from

hard cycloaliphatic epoxies formulated with flexible diol's, triol, and hyperbranched alcohols [7] Water pick-up and tensile property testing were used as a primary screening for suitable vehicles. Fine-tuning of the systems took place using adhesion and printability testing.

Printability

In the elastomeric EL lamps studied in this paper, the dielectric and phosphors capacitive layers were supplied as fully formulated inks. These both use the same radically cured vehicle and have excellent printability. There are no suitable clear UV cured ITO inks available to date. The only printable clear conductive inks are those that utilize organic conducting polymer PEDOT[5,6]. The commercial PEDOT materials are thermally cured from an aqueous solution. The cure cycle of PEDOT imposes a thermal shock, wetting and adhesion problems.

As seen by Wells et al, [7] a general physical property profile for the encapsulant and Ag ink vehicle can quickly be derived by routine screening. In this way, 97.5 to 99% of the formulation can quickly be fixed. The most difficult aspect of this application is fixing an additive package that allows the robust printing, and adhesion between these layers.

The EL lamps in this study were constructed via screen-printing. In order to achieve good planarity in the final lamp a heat stabilized silicone coated polyester film is required to compensate for the thermal cure of the organic clear conductor layer. The first stage of construction is to screen print the encapsulant on to a release surface. The low surface energy release film comprises a commercially available silicone coated polyester film. The low surface energy substrate promotes significant de-wetting problems. The standard approaches to solving the problem are to use wetting /surface modifiers, or alternatively to use thixotropic agents to slow down the de-wetting process.[8-10]

The problems with both wetting agents and thixotropes in screen-printing are their propensity to create both macro and micro- foam. To eliminate the foam a defoamer/antifoam is required. Defoamers are also low surface tension materials and like the wetting agents reduce the surface energy of the cured ink. The low surface energy inks reduces print quality and makes it difficult to get intercoat adhesion between successive layers of the same material. This problem is magnified when printing the different active layers shown in Figure 3. The problem becomes one in which you need to wet a low surface energy substrate, but not become a low surface energy film when cured, without forming bubbles. This is a difficult problem to solve without full knowledge of all the ink layers and without the aid of plasma or corona discharge to modify cured ink surfaces.

Experimental

The ink vehicles used in this study comprised cycloaliphatic epoxies crosslinkers and resins. Masterbatches of resin and crosslinker were created using a Hauschild dental mixer. The final ink formulations were also prepared in a dental mixer. The printability of each Ag ink and encapsulant were evaluated using a Forshlund screen printer. The Ag inks were printed through a 230 mesh stainless steel screen see Figure 4. The encapsulant was printed using a 230 polyester mesh with a simple rectangular pattern(5.25 x 3.25 inches). Three printed samples were prepared for each ink. Each sample was printed, cured and printed again to assess printability and intercoat adhesion. Tensile testing was carried out on screen-printed materials.

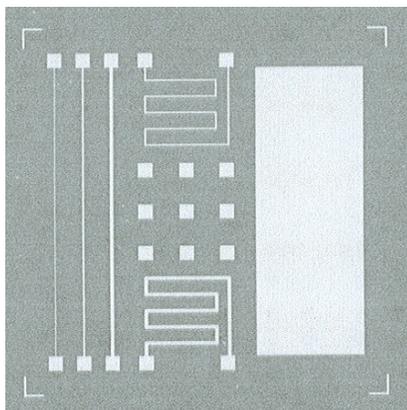


Figure 4 Screen Print Pattern on 230 stainless steel mesh screen

The electrical properties were measured using a ASTM D390-98 on Ag inks drawn down an FR4 board. The cured film thickness was measured with a digital micrometer. The screen printed and drawn samples were cured by UV using a Fusion UV unit with a H bulb at a belt speed of 50 ft/min. The FR4 board “prints” were sent through the UV source twice and then post cured at 80 °C for at least 1 hour. Once cured, volume and sheet resistivity were measured using the FR4 board samples. The solvent wipe test, ASTM D 5402 – 93, was also performed on the FR4 board samples. An Elcometer 1540 cross hatch adhesion tester, used in accordance with ASTM D 3359, was used to assess adhesion. The encapsulants were cured using a single pass (800mJ/cm²) of a fusion H bulb.

Results

In our previous work with thermosetting Ag inks we had observed a general insensitivity of resistivity to vehicle type. Our initial experiments centered on Ag type and vehicle composition. Table 2 shows the physical properties of a series of Ag flakes and powders tested. Table 3 shows the resistivity values obtained for a fixed level of Ag.

Silver Material	Tap density (g/cc)	Particle size (95%)	Surface Area (m ² /g)
Silver Flake A	3.0 – 5.2	30 um	0.30 – 0.85
Silver Flake B	2.6 – 3.6	12 um	0.80 – 1.20
Silver Flake C	3.0 – 4.5	12 um	0.80 – 1.40
Silver Flake D	5.1	5.18	0.83
Silver Flake E	6.7	11.56	0.22
Silver Flake F	3.2 – 5.7	20 um	0.30 – 0.75
Silver Flake G	2.6 – 3.8	12 um	1.15 – 1.75
Ag powder H	5.6	5 um	0.20

Table 2 Silver Flake and Powder products tested in Ag Ink

Silver Material	Resistivity (mΩ /sq-mil)
Silver Flake A	50
Silver Flake B	124
Silver Flake C	160
Silver Flake D	30192
Silver Flake E	2070
Silver Flake F	131
Silver Flake G	226
Ag powder H	938

Table 3 Resistivity of Inks Containing One Silver Product

The Ag flake A was found to give the lowest resistivity at a fixed level A design experimentation was used to assess the suitability of resin/epoxy vehicle combinations at a fixed Ag flake A loading. The results of this test are shown in Table 4

Run	Solvent Wipe	Volume Resistivity (Ω-cm)	Sheet Resistivity (mΩ/sq-mil)	Thixotropic Index (1/10)	Printability
1	5	28.5	148.3	5.44	Good
2	4	42.4	175.1	5.52	Good
3	30	21.2	146.5	5.38	Poor
4	52	21.7	106.4	5.47	Good
5	10	18.8	103.5	4.49	Good
6	29	10.4	45.4	5.91	Good
7	110	8.09	46.3	4.59	Good
8	105	9.38	66.2	4.96	Good
9	55	7.84	42.1	5.15	Good
10	39	7.79	49.4	5.09	Okay
11	88	9.5	59.8	5.58	Good
12	100	18.1	112.7	4.90	Good
13	105	8.94	59.8	5.37	Good
14	2	152	453.1	5.68	Good
15	105	7.13	57	5.12	Good
16	100	9.54	80.1	5.33	Good
17	85	9.97	57.6	5.46	Good
18	100	8.38	59.8	5.73	Good

Table 5 Impact of matrix on Ag ink properties.

It was found that for a fixed level of Ag, the vehicle composition had little impact on volume and sheet resistivity. The greatest correlation in resistivity came to the level of scouring agent in the vehicle.



Figure 4 Mesh Marks on Cured Ag Ink with 75% Ag

Figure 4 illustrates a problem seen in printing thixotropic Ag inks. The screen mesh is retained in the cured Ag trace. The ink fails to flow and level in the 5 to 10 seconds between printing and curing. The large differences in actual film thickness in such cases leads to poor reproducibility in resistance measurements. In order to aid flow out after printing a series of reactive diluents were evaluated; the results are shown in Table 5

Additives	Amount used	Thixotropic Index	Average Resistivity (mΩ/sq-mil)
Epodil 748	1%	4.9	97.3
	1.50%	4.2	43.1
	2%		50.3
	5%	3.2	bubbled
ViscoByk 4010	0.50%	6.3	95
	1%	6.3	66.3
Epodil 757	1%	6.4	92.9
	2%		59.9
	3%		95.9
Epodil 746	1%	5.8	92.7
	2%		62.3
	3%		93.2
Dow Corning DC193	0.50%	7.7	80.9
	1%		63.7
	2%		85.8
Texanol	1%	6	64.6
	2.20%	4.5	86

Table 5 Additives Evaluated to Lower Thixotropic Index.

Most of the additives had no, or a detrimental impact of printability, Epodil 748 gave the biggest improvement in printability of the additives tested.

The use of polybutadiene-based vehicles gave encapsulants with an excellent combination of water vapor barrier and flexibility suitable for this moisture sensitive EL lamp. High molecular weight resins gave desirable elongation and softness properties on cure, but had poor printability and cure rate. Reducing the ink viscosity and increasing the cure rate can be achieved through increased levels of cycloaliphatics epoxies. As can be seen from Figure 5 at higher loadings of the cycloaliphatics epoxy crosslinking agent there is an unacceptable decrease in elongation and increase in hardness. If more conventional polyester/ITO EL lamps were being constructed these low viscosity “harder” encapsulants would be acceptable. As will be seen later, the lower viscosity eliminates the foaming problem seen in the high resin loading materials but increased the de-wet between printed layers. Sulfonium and iodonium SbF_6 photo acid generators gave adequate cure speeds at the 800 mJ/cm^2 H bulb with the chosen vehicle. The iodonium salt was chosen for its lower yellowing of the final lamp. Traditional epoxy trimethoxy silane (Dow Corning Z6040) was used for the adhesion promoter against the inks used in this EL lamp. The first major hurdle in the encapsulant development was the printability on release film.

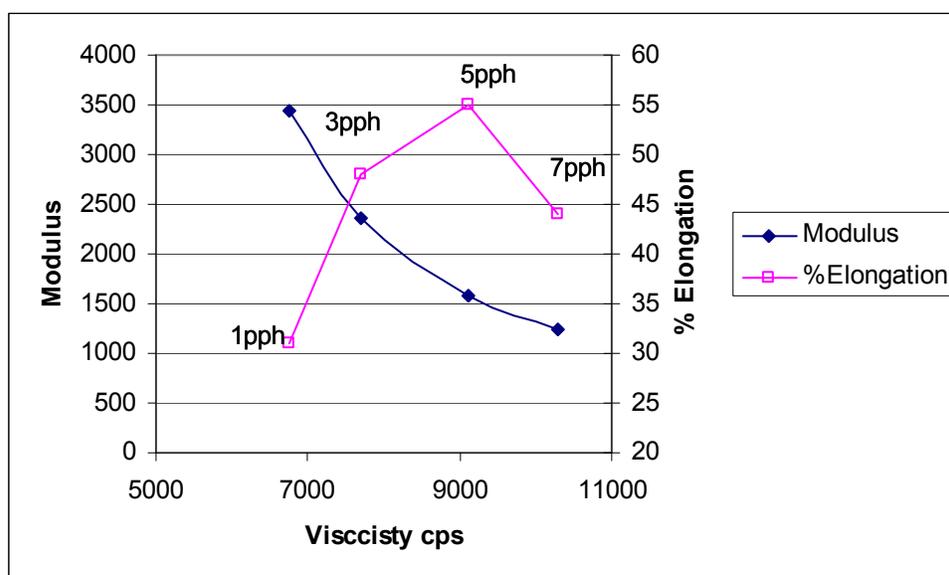


Figure 5 Modulus and % Elongation as a function of viscosity

A 5-mil heat stabilized silicone coated polyester film (FRA353) from Burkhardt Freeman was used as the transfer sheet. This sheet had minimal warp during the $100+ \text{ C}$ heat cure cycle necessary for the organic clear conducting ink, and easy release of the finished EL lamp.

There are few UV curable wetting agents for radically cured inks. The hydroxyl end blocked polyether silicone additives used in aqueous paints additives will cure into cationic systems eliminating migration problems sometimes seen with radical non-reactive additives. Byk UV3500, Dow Corning DC 4-3667, 2-5558, 2-5562 and 2-5211 were found to improve the level of de-wetting on the transfer

sheet, but increased the level of defects due to both macro- and micro foam on printing. In order to remediate the foaming problem defoamers were necessary. The wetting agents and defoamers are both low surface tension > 22 dynes/cm, and lower the surface energy of the cured film. The low surface energy films then caused de-wetting problems on subsequent layers, either of itself, the Ag or capacitive inks, and especially the water based clear conductive layer. The de-wetting was more pronounced as the time between screen-printing and UV cure increased.

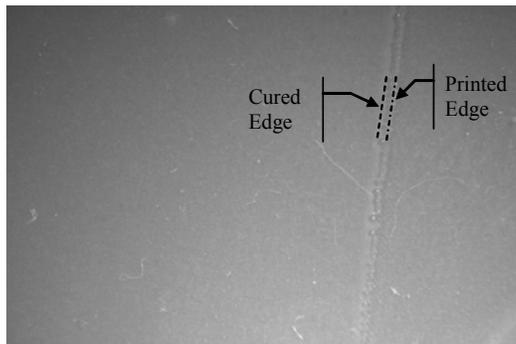
Despite exhaustive combinations of wetting agents, thixotropes, and defoamers a compromise could not be found that gave a consistent, high quality stack of inks necessary for an elastomeric EL lamp. Printing on uncoated polyester films gave acceptable printability when the antagonistic combinations of additives was removed. Reducing the wetting requirements of the substrate does yield larger formulae space. Silicone release coatings are soft elastomeric coatings designed to release pressure sensitive adhesives. The release requirements for UV inks is much lower. A thermal cure release coating which could receive UV inks without wetting agents was formulated and coated on a 5 mil polyester film. Table 6 gives the physical properties of two low viscosity encapsulant formulations used to show the improvement in printability of the release film.

	29-1	29-2
Resin	81.6	78.5
Eoxy Xlinker	14.4	17.6
Cat 28	3.1	3.0
Defoamer	1.0	1.0
Brookfield Viscosimeter		
0.5 rpm	9440	9440
1 rpm	7860	7080
5 rpm	6120	5660
10 rpm	6060	5580
Tensile strength lbf/ins	2726	2858
% Elongation	47.1	34.7
Modulus lbf/ins	1761	2411
Cured with Fusion H bulb 800 mJ/cm ²		

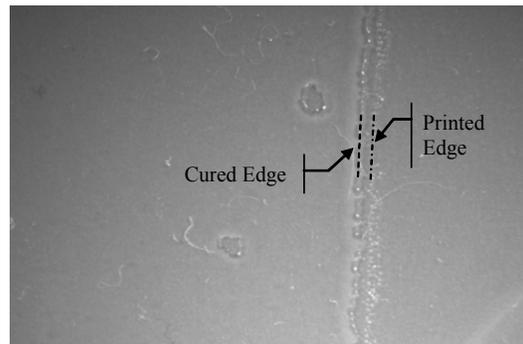
Table 6 Physical properties of encapsulant used for printability studies.



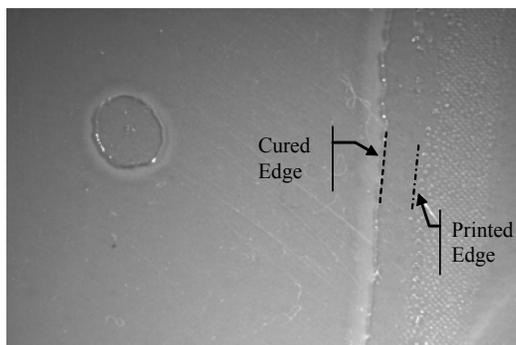
Figure 6 Encapsulant 29-1 on conventional release liner.



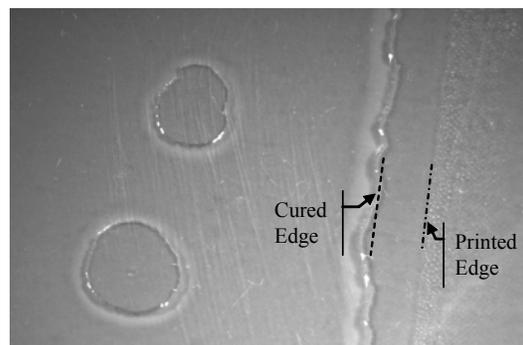
29-1 on Printable release film, cured immediately after print



29-1 on Printable release film, cured 30 seconds after print



29-1 on Printable release film, cured 60 seconds after print



29-1 on Printable release film, cured 90 seconds after print

Figure 7 29-1 on Printable release film as a function of time 0,30,60,90 seconds

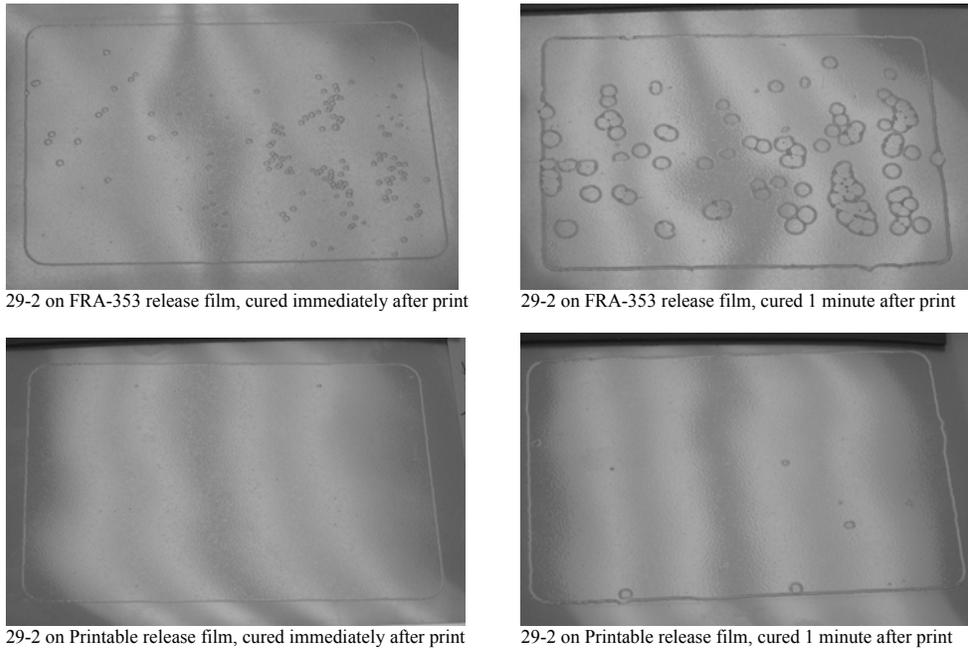


Figure 8 Low viscosity 29-2 encapsulant on conventional and printable release films.

It can be seen in Figure 6-8 the level of de-wetting on conventional release coating even when cured immediately after printing. In Figure 7 the vast improvement in print quality using a printable release surface is evident in the 30 to 60 seconds range. With the lower viscosity version of this formulation 29-2, the window for cure is reduced but superior to the conventional FRA 353 release coating. With a low level of defoamer to eliminate air entrapment during processing and screening a monolithic stack of inks can be sequentially printed to give a robust EL lamp. The removal of the majority of the surface active materials made intercoat adhesion routine with the conventional adhesion promoters and monomer choices.

Conclusion

The main drivers for printable electronic is low cost through high throughput. This is true in the application of EL lamps. The manufacturers of these electronic components and devices are demanding greater flexibility in design to meet the needs of an increasingly portable electronic market. Elastomeric EL lamps have a high degree of flexibility, toughness and water resistance such that these lamps are being applied to garments, which are cleaned in washing machines. It can be seen that with a moderate level of formulae expertise a reasonable working ink can be achieved. The difficulty arises in modifying the inks to fit the manufacturing process. As in the case of the printable release film it is sometimes necessary to create new materials to meet challenges not adequately met by available materials.

References

1. <http://www.nanomarkets.net>
2. "Materials used in electroluminescent displays." Rack, P.D.; Naman, A.; Holloway, P.H.; Sun, S.-S.; Tuenge, R.T. *MRS Bulletin* (1996), 21(3), 49-58.
3. "White polymer thick film electroluminescent lamps and their applications for backlighting liquid crystal displays in portable electronic devices." Zovko, C. I.; Nerz, T. *C Displays* (1999), 20(3), 155-159.
4. "Elastomeric electroluminescent lamp" US 5856030 Burrows, K.
5. Baytron SV3 "Inherently Conducting Polymers" supplied by H. C. Starck Inc, 45 Industrial Place Newton MA 02461 USA. www.baytron.com
6. OrgaconTM EL "Transparent conductive screen printing paste." Agfa Corp 100 Challenger road NJ 07660
7. "Effects of key variables on retortability, flexibility and other physical properties of UV-curable cationic epoxide coatings." Wells C., J.; Braddock, J.. RadTech '94 North Am. UV/EB Conf. Exhib. Proc. (1994), 1 246-58. Publisher: RadTech Int. North Am.
8. "Surface properties of cationic ultraviolet - curable coatings containing a siloxane structure." Sangermano, M.; Bongiovanni, R.; Malucelli, G.; Priola, A.; Pollicino, A.; Recca, A.; Joensson, S. *Journal of Applied Polymer Science* (2004), 93(2), 584-589.
9. "Fluorinated alcohols as surface-active agents in cationic photopolymerization of epoxy monomers." Sangermano, M.; Bongiovanni, R.; Priola, A.; Pospiech, D. *Journal of Polymer Science, Part A: Polymer Chemistry* (2005), 43(18), 4144-4150.
10. "Siloxane additive as modifier in cationic UV curable coatings." Sangermano, M.; Bongiovanni, R.; Malucelli, G.; Roppolo, I.; Priola, A. *Progress in Organic Coatings* (2006), 57(1), 44-49.