

Pushing the Limits of FUNCTIONAL PRINTED INKS

The tests performed here were intended to show how some commonly used functional inks fail when pushed to extremes in heat, humidity, and water in printed-electronic applications.

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As printed-electronics applications continue to expand and merge technologies between traditional, polymer thick-film, rigid/flex-circuit and electronic-assembly applications, the requirements for functional, printed inks are being pushed to new limits. Electrically conductive and resistive inks, UV-curable dielectric insulators, conductive adhesives, UV-curable encapsulants, and others that have been used in more traditional PTF-device manufacturing, such as membrane switches and EL panels, must be able to be adapted to the emerging, and often more stringent, requirements of the latest printed-electronics applications.

New substrates and methods of application require changes to polymers and solvents traditionally used in PTF applications. To do this, it is essential to have an understanding of some of the practical limits these materials have when exposed to harsh environments and how to design devices around the limitations of the functional ink materials.

OBJECTIVE

Using a specially designed circuit configuration (**Figure 1**) that incorporates serpentine patterns, surface-mount pads, and crossover multilayer printed traces that are typically found in PTF printed devices, circuits were printed at three different printing facilities using different combinations of silver inks, UV dielectrics, low-temperature curable-surface-mount epoxies and encapsulants, and carbon inks. The three printing facilities were ECI Screenprint in Thompson, CT; GM Nameplate, Inc. in Seattle, WA; and Dawar Technologies in Pittsburgh, PA.

After printing, surface-mount resistors were placed by Nico-matic LP in Warminster, PA. Final assembly was performed at ECI Screenprint and then product testing was performed at Conductive Compounds, Inc. in Hudson, NH. PET films used as substrates were standardized for all printers, and printers were instructed to use their best manufacturing practices that they would typically use for membrane-switch printing. All inks and materials were supplied by Conductive Compounds, Inc.

PROCEDURE

Different copolymer combinations used in the silver inks included polyester, vinyl, and urethane. UV-curable dielectric insulating inks were urethane acrylate copolymers with matte and glossy finishes, and materials were evaluated as undercured and overcured with a Medium Pressure Mercury Vapor (MPMV) UV lamp. Surface-mount epoxies were two-part, low-temperature polymer systems typically used in PTF manufacturing, and epoxy evaluation was done with various ratios of part A to part B to investigate effects of incorrect mixing on polymeric properties.

Because the materials selected are widely used in all areas of PTF-device manufacturing and have passed the rigors of appliance, medical, and automotive testing, it was necessary to push the conditioning and testing to further limits to force failures within the functional inks to try to see which component(s) of the inks would fall out first under adverse conditions. Typical conditioning of test samples were:

- 85°C, 100% Rh, 1000 hours
- Immersion in water at 40°C for seven days
- 150°C bake at ambient Rh until failure

Mechanical and electrical properties of test circuits were measured both before and after exposure. Two levels of testing were employed on the circuits and functional ink materials. First, testing and inspection of the circuits was performed using the following criteria:

- Point-to-point electrical resistance on silver and carbon ink traces
- Low-voltage resistance across 500 ohm surface-mount resistors
- Destructive AC high-voltage-breakdown test through crossover multilayer patterns
- Visual inspection of circuit materials and surface-mount joints

Second, the functional ink materials were analyzed using sophisticated laboratory equipment to try to determine how the materials

changed physically during testing and how these changes might lend themselves to potential failures in a printed electronics application. Below is a list and description of the test devices used as applicable:

THERMOGRAVIMETRIC ANALYSIS, TGA, measures weight loss very accurately at specified temperature ranges. This can be used to evaluate solvent and volatiles coming off of a material or at elevated temperatures up to 1000°C it is possible to burn off all polymeric material, leaving behind metal and inorganic fillers.

FOURIER TRANSFORM INFRARED SPECTROSCOPY, FTIR, gives a unique fingerprint of a polymer material by exposing it to a scan of the full wavelength infrared spectra. At different frequencies of IR, different combinations of atoms on a molecule will absorb the IR energy, so the fingerprint scan shows IR absorption by a polymer at different frequencies of energy. If a polymer undergoes any chemical changes at all, the FTIR scan will be different.

DIFFERENTIAL SCANNING CALORIMETRY, DSC, measures the heat flowing into or out of a very small sample as it is heated by the instrument. This allows accurate measurement of properties such as melting points, activation time for epoxy curing, and crystallization points. The DSC can measure this by adding heat to a polymer or by exposing the polymer to specific bands of UV energy for UV-cured polymers.

THERMOMECHANICAL ANALYSIS, TMA, measures the expansion of a material accurately as it is exposed to heat. It can also measure the deflection of a fixed, constant weight into a polymer material as it is heated. This allows properties such as coefficient of thermal expansion (Cte) and glass-transition temperature (Tg) to be evaluated. This allows us to understand how functional inks and materials will work in an assembly as the device is heated and cooled and the various materials it contains expand and contract at different rates.

TENSILE/ELONGATION testing allows studying of the mechanical strength and elongation of materials. This testing is valuable not only as a benchmark to compare different materials, but also to look at the effects of undercuring materials and exposing them to heat and/or moisture.

SCANNING ELECTRON MICROSCOPE, SEM, allows us to look at functional ink materials at exceptionally high magnifications—as high as 100,000x. This lets us see effects such as packing efficiency of filler materials and whether there is any evidence of fusing of the filler materials.

RESULTS

The test results showed some expected and surprising results. Starting with an analysis of the performance of the UV curable, screen-printable dielectric/insulator inks, results indicated the need for two-pass applications of these materials to achieve reliable electrical insulation between two layers of conductors. Two different industry-standard acrylate function dielectric formulations (matte and glossy) were paired with silver inks made using more common polyester and vinyl copolymers to see if any interactions would show up during testing.

Because the crossover-voltage test was destructive and failure ranges varied significantly, the results were tallied by percentage of failure of test samples at high voltage. Notice that the figure has two legends—one print pass and two print passes, yet there is only one set of bars on the chart for the two print passes. This is because every single sample of the one print pass dielectric failed at significant-

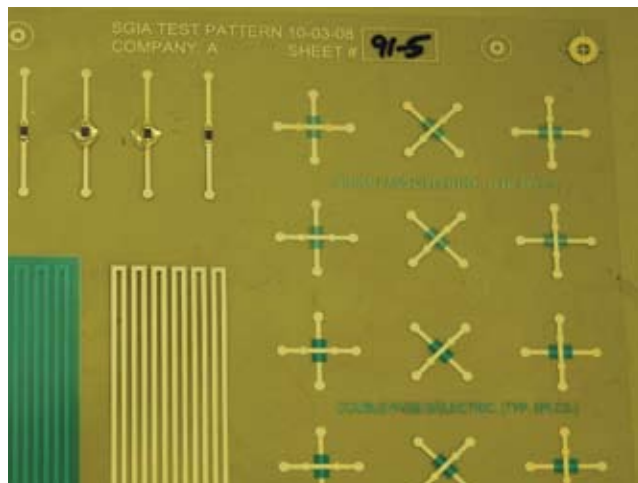


Figure 1
This specially designed circuit configuration incorporates patterns, pads, crossovers and traces typically found in PTH printed circuits.

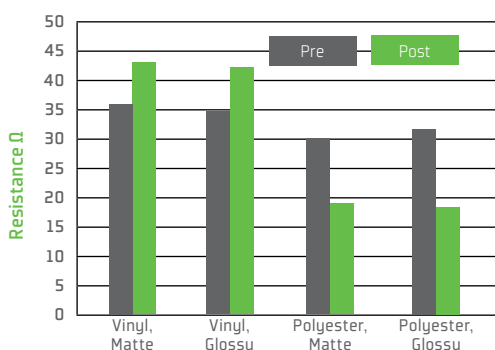


Figure 2
The effect of heat and moisture on conductive inks and UV dielectrics when exposed with and without graphic overlay materials laminated onto them.

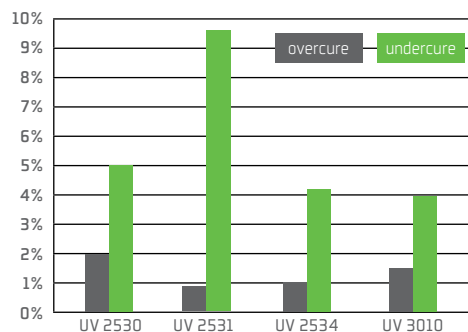


Figure 3
The weight loss percent by TGA of several different industry-standard UV materials.



Figure 4
A typical vinyl copolymer silver ink pattern before and after heat and humidity exposure

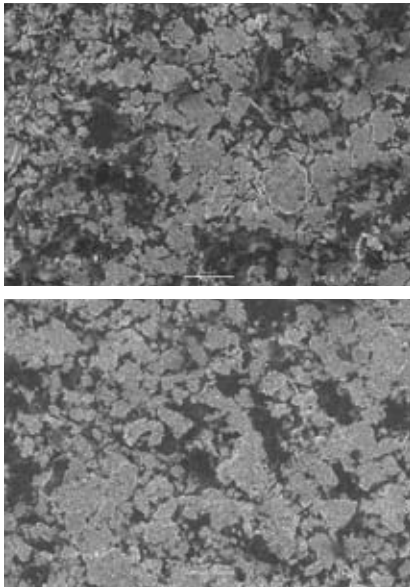


Figure 5
A SEM surface scan of the two ink samples indicates that the surface of the silver particles do not appear to have undergone significant oxidation.



Figure 6
The base polymer used in the ink before and after humidity exposure

ly low voltages when tested. This reinforces the accepted industry standard of printing two layers of dielectric to build up to a final thickness of between 0.001-0.0012 in. total thickness rather than printing a single layer only to save materials and processing times.

The first results showed the effects of heat and moisture on conductive inks and UV dielectrics when exposed with and without graphic-overlay materials laminated onto them, as well as the effect of using dielectrics for protection of printed circuitry instead of overlays only. When a vinyl copolymer and polyester copolymer silver conductive ink are paired on a test circuit with and without a PET-film overlay material laminated to the circuit surface, both the vinyl

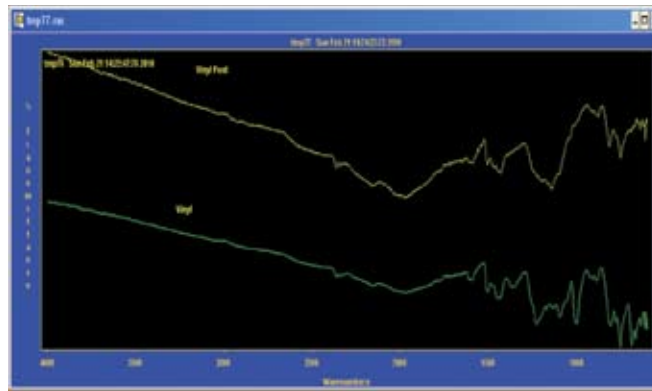


Figure 7
An FTIR scan of the polymer before and after exposure shows that the vinyl copolymer has undergone a significant chemical change in response to high temperature and humidity exposure.

and polyester inks show that even with laminated overlay film protection, the resistance of the ink traces increased greatly after heat and moisture exposure, presumably due to moisture wicking between the overlay and circuit substrate and causing swelling within the conductive ink polymer. **Figure 2** shows the effect of heat and moisture with these same two conductive inks, but with matte and glossy UV dielectric covering the ink traces. Note the dramatic improvement to the polyester based conductive inks, and the slight improvement to the vinyl inks.

This illustrates one of the reasons why vinyl-based conductive inks are not used for high-reliability printed-electronics applications. Vinyl copolymers do not have the long term stability with respect to heat and other factors that polyester copolymers and other thermoplastic polymer materials used to make conductive inks do.

Our final data with respect to UV-curable dielectric/insulator inks address the issue of undercuring. Undercuring UV materials is probably the single largest factor with respect to crossover joint failure and surface-mount component placement. It is possible to cure a UV material to the point where it will marginally pass a cross hatch/tape adhesion test on a substrate, but the material will still be very vulnerable to moisture and solvent attack, as well as degradation from long term heating. **Figure 3** shows the weight loss percent by TGA of several different industry standard UV materials, including acrylate functional urethane insulating inks, cationic epoxide insulating ink, and acrylate functional surface mount component attachment.

Undercuring was accomplished by increasing belt speed to minimize time under the UV lamp until a level of approximately

10% undercuring, as verified by DSC analysis, was achieved. In all instances, the appearance of the undercured materials would pass standard crease and/or cross hatch tape adhesion testing. However, TGA analysis shows a dramatic increase in weight loss from volatiles on all undercured UV materials compared to those cured optimally. This is due to the fact that when undercured, many of the liquid polymer components are left unreacted in the dielectric film, so they can be removed much like a solvent can by heating. If these components have not reacted completely, this means that the hardened film created by the UV curing process is not optimized and is much weaker, leaving it prone to moisture or solvent attack.

To illustrate this point, the percentage of elongation (stretch) of the component encapsulant and acrylate urethane matte and glossy dielectrics was evaluated on an Instron for both optimally cured and undercured configurations. Results showed a drastic difference in performance for undercured material vs. optimally cured for all three materials. Again, this indicates that unreacted polymer remains in the system and the crosslink density of the cured polymer is not optimal, leaving it prone to moisture and solvent absorption as well as heat degradation over time.

Figures 4 – 7 illustrate a common misconception regarding silver conductive inks. Sometimes discoloration in these inks over time is attributed to silver oxidation, and there are concerns about electrical performance degradation over time because of oxidation. Even when completely surrounded by polymer binder in a conductive ink formulation, metal particles will gradually oxidize on their surfaces over time. The oxides that form on the surface of silver and

gold particles remain highly conductive compared to the oxides that form on other metals such as copper or aluminum. For this reason it is necessary to use the more expensive metals when formulating conductive inks.

Even when exposed to ambient temperatures over time, many conductive inks will undergo a slight discoloration. This is more pronounced with vinyl and some urethane copolymer inks than with polyester or some other types of thermoplastics. A common perception is that this discoloration (usually a brownish or yellowish light coloration) is due to metal oxidation. **Figure 4** shows a typical vinyl copolymer silver ink pattern before and after heat and humidity exposure. Note the light brown coloration after exposure. **Figure 5** shows a SEM surface scan of the two ink samples, indicating that the surface of the silver particles do not appear to have undergone significant oxidation. **Figure 6** shows the base polymer used in this ink both before and after heat and humidity exposure. There is a dark discoloration of the polymer after exposure. An FTIR scan of the polymer both before and after exposure (**Figure 7**) shows clearly that the vinyl copolymer has undergone a significant chemical change in response to the high temperature and humidity exposure.

The final data sets presented focus on the surface-mount aspects of printed electronics. Because of the unique requirements of PE applications, often the substrates used are extremely thin and flexible, and cannot be exposed to high temperatures. Because most of these substrates are polymeric, adhesion of the surface-mount epoxy can be difficult. Temperature limitations of these polymeric substrates require that the vast majority of surface-mount applications in PE use two-part epoxy adhesives, which are able to cure at very low temperatures but have the disadvantage of short pot life (working time) after mixing.

One of the frustrating aspects of trying to analyze surface-mount failures in printed electronic applications is that often the failure shows up as a latent defect, meaning that it passes testing after manufacturing but then shows up as a failure sometime after the customer receives it. Often the factors that contribute to this (incorrect curing of conductive epoxy, improper component placement, incorrect mixing of epoxy, and improper ink trace design) cannot be isolated and identified after manufacturing.

It is nearly impossible to properly analyze a PE surface-mount joint to investigate means of failure. Often you will find a failed surface-mount joint, but the surface mount component sitting close to the failed joint does not fail, and often will even withstand an aggressive flex/crease test without failing. For this reason, it is essential to follow good manufacturing practices as recommended by suppliers in order to minimize the impact of these factors on potential surface-mount failure.

Because of the potential for joint failure when attaching LEDs, resistors, or other components onto flexible thin films, it is advised to use center-stake adhesives such as one-part cyanoacrylates and clear, UV-curable encapsulants to cover the component completely after it has been surface mounted to the substrate. **Figure 8** shows the results of four different construction methods after long-term immersion in hot water with respect to the number of extreme (out of spec) readings obtained when measuring resistance through a surface-mount joint and across a discrete resistor. The four construction methods used were conductive epoxy only, conductive epoxy with center stake adhesive, conductive epoxy with clear UV encapsulant

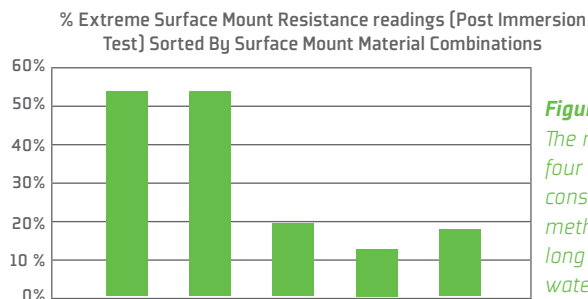


Figure 8
The results of four different construction methods after long term hot water immersion

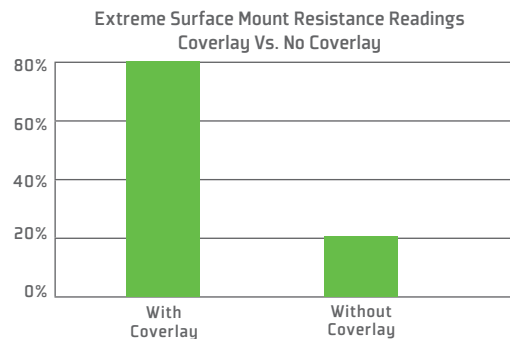


Figure 9
The effect of providing some protection to the surface-mount component and joints

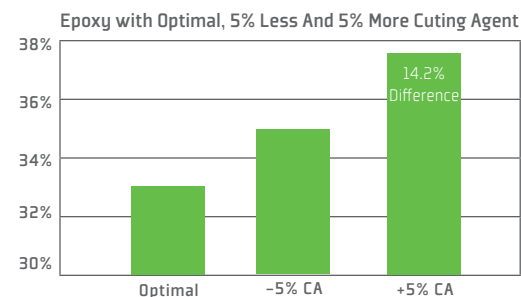


Figure 10
The effect of a common two-part conductive epoxy adhesive that has an abundance of curing agent added and a shortage of curing agent

only, and conductive epoxy with center-stake adhesive and clear UV encapsulant. Note the dramatic improvement in surface-mount joint reliability on the two construction methods that use the clear UV encapsulant to seal and protect the component and surface-mount joint from moisture.

Figure 9 further illustrates the effect of providing some protection to the surface-mounted component and joints by comparing the number of failures on surface-mounted components both with and without a laminated polymer film overlay to protect them during long term water immersion.

A common cause of surface-mount joint failure in printed electronics is incorrect mixing of resin to hardener. Most epoxy formulations require precise mix ratios with a tolerance of $\pm 1\%$ by weight to optimize the mechanical properties of the conductive epoxy. Careless or incorrect weighing errors can easily push this tolerance out to $\pm 5\%$ or more. **Figure 10** shows the effect of a common two-part conductive epoxy adhesive that has both an abundance of curing agent added to it, and a shortage of curing agent. For this test, an optimal mix was prepared, as well as a mix with 5% less curing agent

and 5% more curing agent. The samples were cured to completeness, and the TGA was used to evaluate weight loss at very high temperature.

Figure 10 shows the actual TGA scan to the left, and then a table of weight loss of the three different epoxies to the right. Note that the two configurations with less and more curing agent showed a significantly higher amount of weight loss during burn off in the TGA than the sample that was weighed and mixed correctly. This shows that if these two part epoxy materials are not weighed and mixed correctly, surface-mount joint integrity will be compromised because there is a lot of volatile, unreacted polymer in the materials that over time will act as solvents and begin to leach out of the material.

To capitalize on the rapidly emerging opportunities within printed electronics, it is essential that manufacturers learn some of the material science behind these inks and have access to analytical equipment that can help them explore and understand the limits of the materials. Printed electronics continues to have a stigma of the Wild West attached to it, but collaborations between suppliers, printers, and OEM manufacturers can help push the boundaries of what functional ink materials and substrates are capable of accomplishing. 🍌



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