 

# The Electrostatic Printing of Microstructures for Flat Panel Displays and Printed Wiring Boards

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## Abstract

Functional materials configured as liquid toners are printed on a variety of surfaces for various manufacturing processes. The materials include metal toners, resistor toners, high K dielectric toners, phosphors and ITO. The substrates printed upon include glass, bare and coated metal, polymeric film and even paper. A fixed configuration electrostatic printing plate is used in most manufacturing applications though traditional photoreceptor plates can be used if electronic addressibility is desired.

Results with a pure silver toner printed on both glass and paper will be reported. Examples of passive electronic components such as resistors, capacitors, and even inductors that have been electrostatically printed with liquid toners will be shown. Near term goals for the future will be discussed.

## Electrox's Electrostatic Printing Process

There are three key elements to the electrostatic printing process:

1. The Electrox electrostatic plate[1,2]
2. Functional materials configured as liquid toners
3. Non-contact or gap transfer in which toner particles are transferred by an electric field across a gap of the order of 50 to 150μ to the receiving surface[3]

The steps of the process are best illustrated in the following figures. Figure 1 shows the plate-making step. A photopolymer layer is coated on an electrically grounded substrate. The substrate can be metal, metallized polyester or polyimide film, or even glass made conductive with an indium tin oxide coating (ITO). The photopolymers typically vary in thickness from 10μ to 50μ. The photopolymer is exposed to UV radiation in the 300 to 400nm region which causes exposed areas to undergo a chemical change. This raises the electrical resistivity of these regions significantly so that they can store charge for a useful period of time. The plate-making step is now complete; there is no chemical or aqueous processing of the plate.

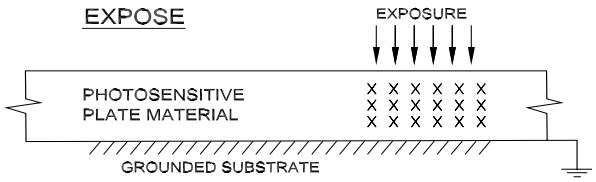


*Figure 1. Plate Making*

The plate is sensitized by corona charging it. The resulting surface potential for a typical 37μ thick plate is from 500 to 1000 volts. After a short period of time the unexposed regions of the plate self discharge due to their relatively low electrical resistivity. We now have a traditional latent electrostatic image. The latent image is processed by development with an electrophoretic liquid toner

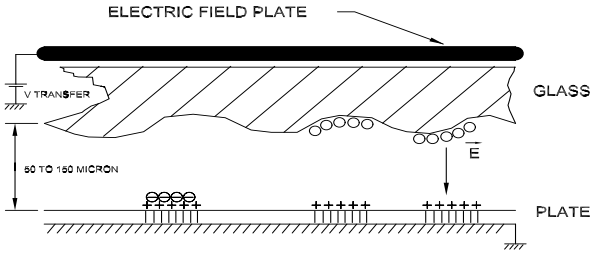


*Figure 2. Toner Transfer Across a Gap*

Figure 2 shows the transfer step wherein the toner is transferred across a finite mechanical gap to a receiving glass plate by an electrical field created by the electric field plate on the other side of the glass driven to a suitable potential. An alternate scheme not shown in Figure 3 is to corona charge the other side of the glass with a charge of polarity opposite that of the toner . Figure 3 shows a highly irregular surface, not an exaggeration. This is a particular advantage of electrostatic printing over other printing or deposition techniques. The toner travels the gap following the parallel electric field lines and it does not disperse as a function of distance between glass and plate. Therefore high resolution images, true to their design, can be deposited on the glass substrate, even if it has imperfections or a relief structure already on it. We have also printed on metal

plates, polymeric films and paper. An example of printing on steeply relieved metal surfaces is the printing of images on U.S. coins.

## Toners I: Composites vs. Solid Form

Electrophotographic toners are typically resins with 5 to 10% by weight of colorant material. The resin provides the mechanical functions of bonding the colorant to the paper and protecting it from aging effects. For manufacturing applications you want the toner to be a solid functional material with no resin. Silver filled resin have been around for decades but their resistivities are too high to perform most electronic circuit functions. Their effective resistivities are a factor of 30 to 60 times that of the pure metal.

A composite capacitor or inductor material ($BaTiO_3$ for, the capacitor dielectric and $Fe_3O_2$ for the inductor) has similar problems. Assuming a 50% fill volume of the resin by the pigment, the end results are disappointing. One achieves a capacity improvement of 2X over the pure resin layer. In the case of the inductor or transformer one effectively achieves an air core device of one half the actual physical dimension with the ferrite filled resin inductor material, not enough to be interesting. This is why solid form, resinless toners are desired when printing electronic conductors or components.

## Parmod™ Materials to Print High Performance Electronic Components

### Conductors

Last year in Toronto[4] we presented the results of printing Parmod™ silver liquid toners to produce electrical conductors as fine as 40 microns in width on glass and 100 microns on polymer substrates. The chemistry of Parmod™ is such that the printed images can be cured to pure metal traces at a temperature that is compatible with conventional polymer-based printed wiring board substrates. The conductors printed on polymer was cured at 220°C for three minutes and had an electrical resistivity four times that of bulk silver, approximately the same as "thick film" pastes which are cured on ceramic substrates at temperatures 600°C higher for an hour. The conductors printed on glass and cured at 400°C for five minutes had essentially the conductivity of bulk silver.

In the past year, additional work has been done with the silver toner to produce circuit components and circuits as described below. The bulk of the materials R&D has been devoted to the extension of the Parmod™ chemistry from metals to oxides. The objective of this DARPA-funded program[5] was to provide materials that could be used to print passive components such as resistors, capacitors and inductors as well as the conductors to connect them together. In future programs we plan to make the most promising of the new materials into toners.

### Resistor Compositions

A significant effort was devoted to silver-palladium oxide resistor mixtures, which are a relatively small step out from the metallic compositions that had been developed previously, but the most useful results were obtained with pure oxide systems for resistors. Preliminary experiments with ruthenium oxide were abandoned when it was found that the oxide could react spontaneously with the organic Parmod™ constituents. Better success was obtained with doped indium tin oxide compositions.

The electrical properties of the ITO-based inks can be controlled through variations in the ink composition. As Figure 3 shows, the resistivity can currently be varied over 3 orders of magnitude between <100 and 10,000 Ω/sq/mil. At 10,000 Ω/sq/mil we can print resistors which cover 75% of those normally used in electronic circuitry in a square format and 98+% of the requirement in a 1x10 format[6].

Higher values are possible, but have not been tested at this point. Our objective is a resistivity range up to 1,000,000 ohms per square per mil. To date we have covered more than half of the desired range with a controllable resistive material.

Currently a temperature of >350°C is necessary for complete curing of the resistive material. It would be desirable to reduce this temperature. A possible solution to this is the application of laser annealing to reduce the required temperature. These films consolidate well, and have good adhesion to glass. They should adhere well to other substrates as well, but due to the high temperature currently required, other substrates have not been tested thus far.

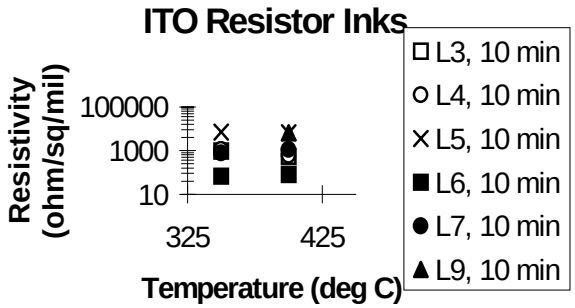


*Figure 3. Resistivity vs.curing temperature for various ITO inks*

### High K Dielectrics

We have found that mixed ferroelectric compositions function better than pure compounds as printable, high permitivity-dieletrics. Lead titanate additions increased the dielectric constant to more than 100 compared to 60 for pure barium titanate. Because lead titanate crystallizes at about 470°C versus 750°C for barium titanate, it is easier to get it to provide a matrix with a high permittiviy. The only drawback is that lead titanate has a maximum dielectric constant of about 300. The majority of the conversion of the barium titanate is completed by 400°C, but weight loss is seen up to 600°C. The lead titanate converts completely by

about 300°C. Since the dielectric properties are dependent on the crystallinity (long range order) of the material, the lower crystallization temperature of the lead titanate material means that at 350-400°C, the lead titanate material formed should have "longer range order" than the deposited barium titanate material, and thus have better properties.

The difference between pure barium titanate and lead titanate/barium titanate seen in SEM images is in the connectivity of the barium titanate powder particles. In the barium titanate only ink (I-11), the particles appear sharp and distinct from other particles, indicating few interconnections. Whereas the lead titanate/barium titanate ink shows a "merging" of the particles so that each particle is not completely distinct from the particle next to it. The lead titanate appears to be sticking the barium titanate particles together better than the barium titanate itself. The lead titanate is also sticking the barium titanate particles together better than polymer binders. The best polymer-based high K dielectric formulations of which we are aware have a dielectric constant of approximately 60. The preliminary MOD-based compositions we have made so far provide an advance of a factor of two in the permittivity available from printable dielectric materials with ample room for further improvement as this new technology matures.

### X-ray Powder Diffraction Analysis of Lead Titanate/Barium Titanate Films

X-ray analysis on a lead titanate/barium titanate film was obtained from Rutgers University. The results indicated that the sample was 98-99% tetragonal barium titanate (as it should be due to the high concentration of barium titanate powder). A minor phase most likely due to PbO was seen. The lattice parameters of the barium titanate were $a_o$=3.9965 A., $c_o$=4.0213 A., and c/a= 1.0062. The c/a ratio is somewhat low compared to the literature value, 1.0098. If this were due to lead titanate going into solution in the barium titanate, the c/a ratio would be larger. Due to the apparent presence of PbO, the reason for the change in the c/a ratio may be due to the titanium going into solution with the barium titanate. There is no evidence of an amorphous phase, so the solvating of the titanium by the barium titanate is the best current explanation.

### Electrostatically Printed Silver Capacitors

Capacitors were made using lead titanate/barium titanate ink as the dielectric and electrostatically printed silver as the top and bottom electrodes on a glass substrate. The capacitors worked well giving capacitances in the range of 1-10 nF. This is the first example of a capacitor made completely from Parmod™ materials. Data on the dielectric constant and dissipation factor from 1-100 kHz are shown below. Dielectric properties as a function of cure conditions are shown in Figure 4.

The range of dielectric constant at 300°C suggests that cure temperatures above about 350°C will be necessary to obtain reproducible performance with these mixtures. Further optimization is expected to lower this temperature.

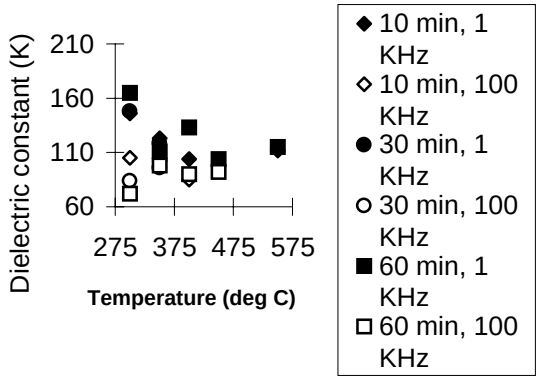


*Figure 4. Lead titanate/ barium titanate ink. Dielectric properties at various curing temperatures and times, measured at 1kHz and 100 kHz*

**Dielectric Constant and Dissipation Factor Data for Lead Titanate/ Barium Titanate Printable High K Dielectric**

| Cure Temp (°C) | Cure Time (min) | Thick-ness (mil) | 1kHz K | 1kHz DF | 100 kHz K | 100 kHz DF | Break-down Voltage (V) |
|---|---|---|---|---|---|---|---|
| 300 | 10 | 1.3 | 146 | 0.21 | 105 | 0.07 | >24 |
| | 30 | 1.3 | 148 | 0.35 | 84 | 0.17 | >24 |
| | 60 | 1.3 | 165 | 0.56 | 72 | 0.39 | >24 |
| 350 | 10 | 1.2 | 123 | 0.12 | 102 | 0.06 | >24 |
| | 30 | 1.2 | 119 | 0.13 | 96 | 0.10 | >24 |
| | 60 | 1.6 | 111 | 0.07 | 98 | 0.05 | >24 |
| 400 | 60 | 1.4 | 133 | 0.21 | 90 | 0.17 | >24 |
| 450 | 60 | 1.2 | 104 | 0.03 | 92 | 0.09 | >24 |

Breakdown voltages were greater than 24 Volts for films of approximately 25 microns thickness, but in thinner films approaching 10 microns, the values were about 5 V. The main problem that remains is to improve the quality of the thin films so that a higher capacitance can be obtained with an acceptable breakdown voltage.

## Examples of Electrostatic Printing of Electronic Packaging Structures and Components

Silver toners were printed on 2.25mm thick soda lime glass and even on thick paper stock. The latter was thermally processed at 230°C for 2 minutes to reduce the silver toner particles to solid silver, on glass forty microns wide lines with sixty microns spaces were demonstrated; on paper 75μ lines/ 75μ spaces were shown. A five turn inductor will be shown that consists of four layers; a bottom layer of Ag metal, two layers of ferrite toner and a top layer of Ag metal with excellent conformability to the first layer of metal. Resistors will be shown which are two layer parts; metal end electrodes with a straight stripe of resistor toner overlapping the ends.

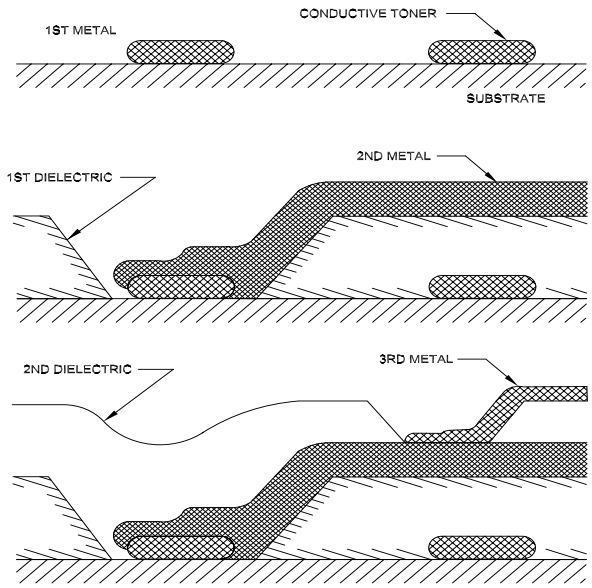


*Figure 5. Printed Wiring Board Manufacturing*

Figure 5 shows the order in the printing of multi-layer printed wiring boards. A bottom layer of metal conductors is printed on a suitably insulating substrate. Then a patterned dielectric layer of low dielectric constant is printed to support the second metallic layer of conductors. Note the low dielectric constant is needed for maximum signal propagation velocity, very important for very high speed processors.

Next the second metal layer is printed and note the through hole connection to the first layer. Further layers are added as necessary.

## Conclusion

This paper has presented information on non-contact imaging for printing electronically functional materials to produce electronic components. The process has demonstrated the capability of printing silver conductor patterns as fine as 40μ on glass and 75μ on paper with conductivity comparable to bulk silver. The technology has been extended to oxides as well as metals for printing integral resistors and capacitors. The potential exists for creating complex circuits with embedded passive components by digital imaging technology for maximum manufacturing flexibility and speed.

## References

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4. "Electrostatic Printing of Parmod™ Electrical Conductors", Kydd, P.H.; Richard, D.L.; Detig, R.H. NIP-14, Oct. 18m 1998.
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## Biography

**Robert H. Detig, President, Electrox Corporation**

Robert Detig has 30+ years of experience in the field of electrophotography. He has extensive experience in every aspect of the electrographic imaging process. He was awarded a Ph.D. in Electrical Engineering from Carnegie Mellon University, Pittsburgh, Pennsylvania.

**Paul H. Kydd, President, Partnerships Limited, Inc.**

Paul H. Kydd founded Partnerships Limited as an independent applied research laboratory in 1983. Since 1994 the primary focus had been on the development of the Parmod™ technology under DARPA sponsorship. Dr. Kydd received a Ph.D. in Physical Chemistry from Harvard and attended the Advanced Management Program at the Harvard Business School.

**David L. Richard, Partnerships Limited, Inc.**

David L. Richard began working at Partnerships Limited in 1996. He has specialized in the chemistry and metallurgy of the silver Parmod™ Liquid Toner, and the development of printable resistor and high K dielectric materials. He was awarded a M.S. in Chemistry from the University of Illinois, Champaign/Urbana.