

# Electrostatic Printing of Functional Liquid Toner Materials on 3 Dimensional Objects and Thick Glass Substrates

*Robert H. Detig*  
*Electrox Corporation*  
*Denville, New Jersey, USA*

## Abstract

The printing of functional toner materials on glass substrates presents unusual problems due to the thickness of normally useful glass (1 to 3 mm) and its surface irregularities. Technical issues relating to printing on "flat" glass will be described. Alternately, we will describe electrostatic printing on steeply relieved surfaces like plasma display panel ribs and even US silver coins. Here surface heights extend to 150 to 200 micron.

Liquid toner materials include high density glass frit, solid silver metal toners as well as phosphor toners. Of particular interest are the resinless silver metal toners. A rationale for establishing a "zeta potential" charge on a solid metal particle will be described. The mechanism for sintering a mass of silver metal particles into a solid, useful electrically continuous pattern will also be described. Glass frit toners for printing micro structures for flat panel displays will be described as well as toner for decorating glass and ceramics products.

## Introduction

Electrostatic printing uses traditional liquid toner materials for printing on a variety of substrates; paper, polymeric film, metal and glass. The toners use traditional Isopar diluents and industry standard charge director materials, only the toner particles itself (metal, glass, phosphor, etc.) are new to the technology aspect of the equation.

## The Electrostatic Printing Process

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 photopolymers, both liquid and dry film, typically vary in thickness from 10 $\mu$  to 50 $\mu$ . The photopolymer is exposed to UV radiation. This exposure 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.

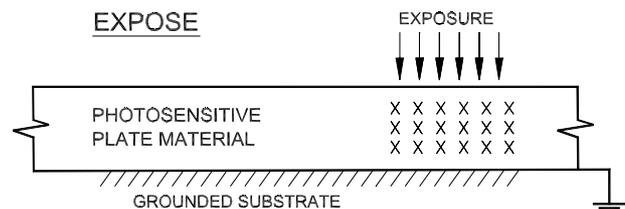


Figure 1. Plate Making

The plate is sensitized by corona charging it. The resulting surface potential for a typical 37 $\mu$  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 usual development means with an electrophoretic liquid toner.

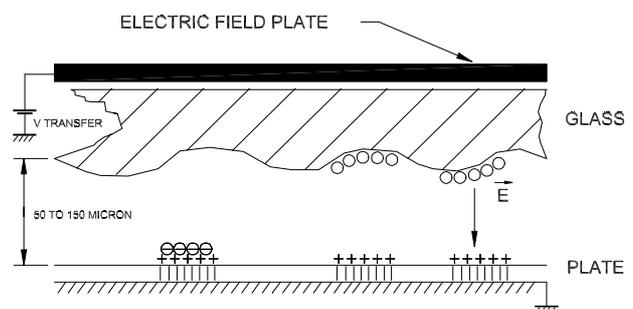


Figure 2. Toner Transfer Across a Gap

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. 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. An example of printing on steeply relieved metal surfaces is the printing of images on U.S. coins.

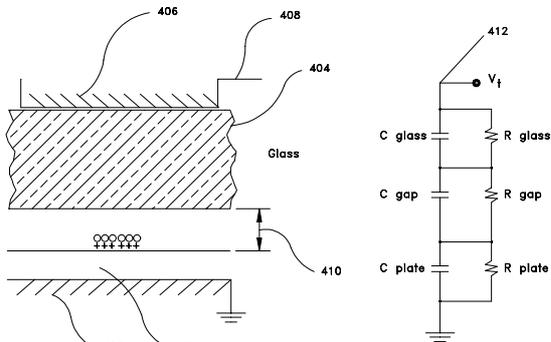


Figure 3. Transfer Process and Electrical Equivalent Circuit

### The Toners

The toners are functional material configured as normal "zeta potential" toners. For metals, glasses and phosphors this presents new challenges. For applications where high temperature processing is expected, glasses and phosphors can be coated with a thin resin material which can be "burned-off" in a subsequent bake out step. For metals which need to be free of resin which would interfere with electrical conductivity, resin coatings are to be avoided.

Paralec LLC of Rocky Hill, New Jersey has formulated a resinless metal toner consisting of a solid silver particle coated with a silver organo metallic compound.<sup>1</sup> This coating serves two functions:

1. It acts as a charge control agent and forms the acid/base couples with the charge director material dissolved in the liquid toner diluent.
2. After toner drying, where the diluent is evaporated, the silver toner particulate structure is sintered. During this step the silver organo metallic decomposes into "atomic" silver thereby "fusing" adjacent silver particles together.

This decomposition reaction occurs at a relatively low temperature of 230°C for 2 minutes. On an inert surface like glass the sintered silver metal structures are conductive but have no adhesion to the glass. Raising the fusing temperature to the 430°C range causes the silver to diffuse into the structure of the glass and provide superior adhesion.

### The Transfer Process

Necessarily, when printing on 3 dimensional objects toner transfer occurs across a finite mechanical gap which if filled with toner diluent.

Figure 3 shows a mechanical schematic of the transfer process and an electrical equivalent circuit which allows one to calculate the voltage division across

the three elements (glass, gap, and printing plate) during the transfer process.

### Electrical Conductivity of the Glass Versus the Conductivity of the Gap Liquid

The most critical issues are the conductivities of the liquids in the gap versus the glass as this determines the voltage division between glass and gap. If most of the voltage appears across the glass and very little across the gap between plate and glass, no toner will transfer. This is best illustrated by some examples.

Printing plate consists of a photopolymer of 10 to 50µ thickness connected to electrical ground. Receiving glass plate is typically 0.5 to 3.0 mm thick and is backed by a field electrode connected to the transfer voltage supply. It is separated by a mechanical gap from the printing plate. The equivalent circuit for this structure is shown to the right.

### A Glass of Interest is Electroveere ELC-7401

Electroveere ELC-7401 is made in Switzerland by Erie Scientific. If charged and then the voltage decay measured it shows a decay time constant of 5.6 seconds which calculates to a resistivity of  $9 \times 10^{+12}$  ohm · cm. Typical ranges of toner bath conductivities are of the order 10 to 100 pico mho/cm  $10^{+11}$  to  $10^{+10}$  Ω · cm resistivity). There is one caveat to be disclosed. The charging test with the glass is a dc test and measures the flow of electronic charges through the glass, while the measure of toner conductivity is an 18 hertz test that measures back and forth flow of electrons, ions, and charged toner particles.

Now applying electromagnetic theory to the glass/gap structure initially when a step function of voltage is applied the voltages divide capacities between the elements, glass, gap, and plate. Since the imaged areas of the plate are highly resistive they can be disregarded for short periods of time. Since the glass is thicker than the gap, typically 10 to 100 times, and it's dielectric constant is 6.7 versus 2.1 of the liquids in the gap, the voltages divided preferentially across the glass with little across the gap. If the conductivity of the gap fluids is higher than the glass this situation will worsen the time and transfer will be inhibited.

Table I Glass Types of Interest in the Electronics Industry

Type	Soda Lime	Electroveer	St. Gabian CS77	Corning 7059
Uses	bottles/ glazing	microscope slides, solar cells	plasma display	AMLC D
Strain Pt	511°C	513°C	587°C	593°C
Resist.	$14 \times 10^{+12}$	$9 \times 10^{+12}$	-----	$10^{+15}$
Dielect Const.	6.7	6.7	6.8	5.84
Time constant	8.33 sec	5.6 sec	-----	550 sec

With time, the voltages divide resistively between glass and gap. If the conductivity of the gap fluids is higher than that of the glass, practically all of the voltage is across the glass and none across the gap. If toner had transferred, it will back transfer due to the image charges on the printing plate. This, in fact has been observed.

#### Conductivity of the Diluent Used to Fill the Gap

Typically when a printing plate is imaged excess toner fluids are very effectively removed by a "reverse roller" that scavenges liquid containing random background particles; the result being a almost dry plate. Now the plate and glass are placed in proximity with each other and the gap between them filled with fluid. If one fills the gap with clear Isopar (conductivity less than 0.15 pmho/cm) the toner charge may be reduced by the lack of charge director is the clear Isopar. If one fills the gap with Isopar plus charge director with a conductivity of 20 pmho/cm, the voltage division between glass and gap suffers. Again the demands of maintaining charge on the toner particles versus the conductivity of the gap fluids conflict. Conductive Isopar in the gap is desired but may not be possible if the glass has very high electrical resistivity.

#### Mounting Techniques for the Printing Plate and Glass

To preserve the fidelity of the toner image on the plate the transfer electric field must be everywhere normal to the plane of the plate and undistorted on the edges. And since we are transferring to glass with a resistivity of the order of  $10^{+12}$  to  $10^{+16}$  ohm · cm the mounting and holding of the plate must be consistent with these resistivities, i.e. these fixtures must be of materials substantially higher in resistivity. Even with the most conductive glass (lowest resistivity of  $10^{+12}$  ohm · cm) some typical engineering materials, like cotton filled phenolics or poly acetals (Delrin of DuPont) may not be adequate for the job. For instance, Corning 7059 or 1737 glass is typically used for liquid crystal display panels for lap top computers. They have a resistivity of the order of  $10^{+16}$  ohm · cm. A cotton filled phenolic resin material would not be inadequate. Teflon™ type materials with resistivities of  $10^{+18}$  are needed.

Also the conductivity of the bath can cause problems around the edges of the printing plate. Since the substrate of the plate is electrical ground, the conductive gap filling liquids might distort the electric field near the edges of the glass/plate assembly if they can contact electrical ground causing distorted image transfer. Further discussion of the issues can be found in PCT patent application #PCT/US99/ 23612<sup>1</sup>

Figure 4 shows a  $40\mu$  wide line of silver metal toner printed on 2.25mm thick soda lime glass. The spacing between lines is  $60\mu$  for a line to line pitch of  $100\mu$ . The toner was heated to  $430^\circ\text{C}$  for about 2 min to allow it to diffuse into the glass for proper adhesion.

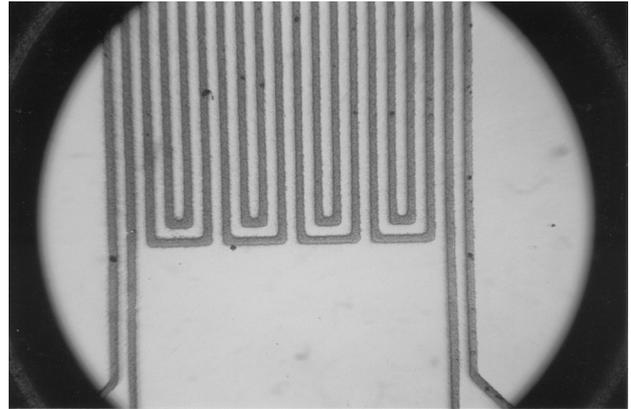


Figure 4. Silver metal toner printed on soda lime glass

#### Printing on 3 Dimensional Objects

Figure 5 shows the printing of an Indigo black toner on a US coin. This is a dramatic demonstration of the ability of liquid toners to be printed on 3 dimensional surfaces. An even more dramatic example is shown below. Figure 6 shows the cross section of the back plate of an A-C color plasma display panel. The back plate consists of glass ribs (202) that are 100 to  $150\mu$  high. Phosphor (206) needs to be printed on the bottom and walls of the trenches formed by the ribs. Figure 7 shows an example of a back plate with phosphor toner printed on every 3<sup>rd</sup> trench. In the next two printing steps the 2<sup>nd</sup> and 3<sup>rd</sup> color phosphor (red-green-blue) are printed in alternate trenches.

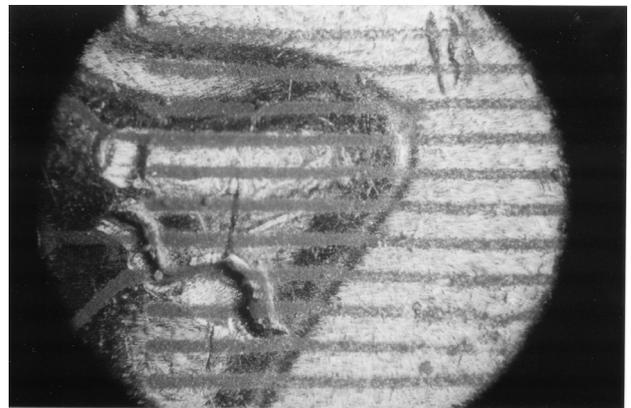


Figure 5. Indigo black toner on US coin

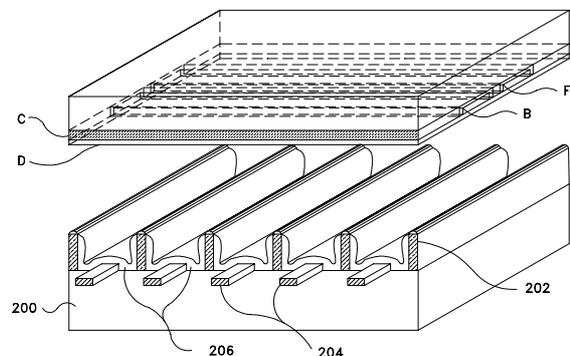


Figure 6. Cross section of back plate

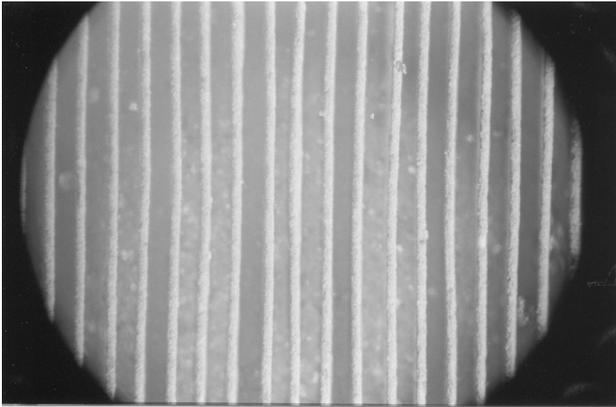


Figure 7. Phosphor toner printer in the trenches of a plasma display panel.

### Conclusions

Electrostatic printing is a useful manufacturing tool with its ability to print on 3 dimensional objects and thick layers of glass. In addition metal lines of commercial interest (40 to 50 $\mu$ ) can be printed on the same glass surfaces.

### References

1. Kydd et. al., US# 6,153,348, November 28, 2000.
2. Detig, WO 00/21690 or PCT /US99/23612

### Biography

Robert H. Detig founded Electrox Corporation in 1992 to apply electrographic imaging technology as a manufacturing tool for various industries. He has some of the basic patents relating to the polymeric electrostatic printing plate. He has extensive experience in all aspects of the electrographic imaging process going back to his early years at Xerox. He pioneered the concept of functional toners made of high density materials like metals and glasses to be used in manufacturing process.

He was awarded a PhD in Electrical Engineering from Carnegie Mellon University in Pittsburgh, Pennsylvania.