 Copyright 1998, IS&T

Electrostatic Printing of Parmod™ Electrical Conductors

Paul H. Kydd and David L. Richard
Partnerships Limited, Inc., Rocky Hill, New Jersey
and
Robert H. Detig
Electrox Corp., Newark, New Jersey

Abstract

A new family of liquid toners has been developed to print conductive traces on printed circuit boards by a digital printing technology. The new toners are based on Parmod™ technology which has been developed to enable low cost production of printed circuits by a simple print-and-heat process. The novel feature of these printable materials is that they cure to pure metallic conductors in seconds at a temperature low enough to be compatible with polymer-based printed circuit substrates. The resulting circuit traces have high electrical conductivity and are solderable. The use of conventional printed circuit substrates and the speed of the process permit high-production, low-cost roll to roll processing.

The extension of Parmod™ technology to liquid toners provides two major additional benefits: 1) It provides a major increase in resolution for production of advanced technology high density interconnect structures, and 2) It permits direct digital printing of circuits from CAD files with no intermediate tooling requirements. The latter capability realizes the goal of total CAD/CAM integration and the ultimate in manufacturing flexibility. This paper discusses the characteristics of Parmod™ technology, the performance of the liquid toners based on it and some applications of the technology which can be foreseen.

Introduction

PARMOD™ is a family of materials that can be applied by virtually any printing process and thermally cured in seconds at a temperature low enough to be compatible with conventional polymer-based printed circuit substrates. The basic technology can be applied to conductors, resistors, dielectrics, ferroelectrics and ferrites to permit production of a variety of electronic components by a simple print-and-heat process at very low cost. The bulk of the research and development to date has been on compositions for printing pure metallic conductors, primarily copper, silver and gold. Preliminary product formulations are now being tested in major applications.

The printing technologies used to date have been those conventionally used in the thick film electronics industry, namely screen printing and stenciling. Some preliminary tests have been done with gravure printing which promises to be of great interest in high production applications.

There is a major incentive to proceed to digital printing to permit rapid prototyping of electronic assemblies and to minimize inventory requirements for circuit boards. A successful demonstration of printing Parmod™ under digital control has been carried out with an Asymtek dispenser. Modern electronic packaging , however requires higher speed and higher resolution than the dispenser can offer.

A substantial program has been undertaken to develop Parmod™ ink jet inks. This has been moderately successful, but still higher speed and resolution is desired. Electrostatic printing, either directly computer driven as in a laser printer, or optically mediated as in a xerographic copier, is the ultimate process for high resolution and high speed.

The development of a successful Parmod™ toner for electrostatic printing imposes an additional set of constraints and requirements having to do with the printing process. These include the state of subdivision, stability and static electrical charge of the toner particles, as well as their ability to convert to well-bonded electrical traces. A considerable effort was devoted to developing a conventional dry toner. Conductive images could be made this way, but the toners had undesirable properties and the process was awkward and inefficient.

A literature survey of electrostatic printing technology suggested that liquid toners offered far more promise than dry toners for this application because they offer high resolution in very simple equipment and have much more latitude in composition than dry toners. The fact that they depend on an organic dispersant which has to be evaporated was not felt to be a major limitation in an industrial environment in which the printing process replaces far more objectionable etching and plating operations.

Liquid Toner Technology

Liquid toner technology[1] features very high resolution due to toner particles which are 3 microns or less in size. It has been developed for high quality four-color proof printing and other high-resolution applications. Liquid toners consist of a colloidal suspension of pigmented or dyed resin particles in an insulating liquid dispersant with charge control agents (charge directors) which charge the particles to stabilize the suspension.

The dispersant liquid is typically a hydrocarbon liquid of low viscosity and relatively low volatility. Highly branched C_{10}-C_{13} alkanes such as Exxon's Isopar series are used. The charge directors are typically ionic surfactants and metal soaps added to the resin particles. Addition of surfactants to the suspension of particles results in the creation of inverse micelles which charge the particles by proton transfer. Proton transfer from an acidic inverse micelle to a basic particle for example, results in a positively charged particle and a negatively charged inverse micelle.

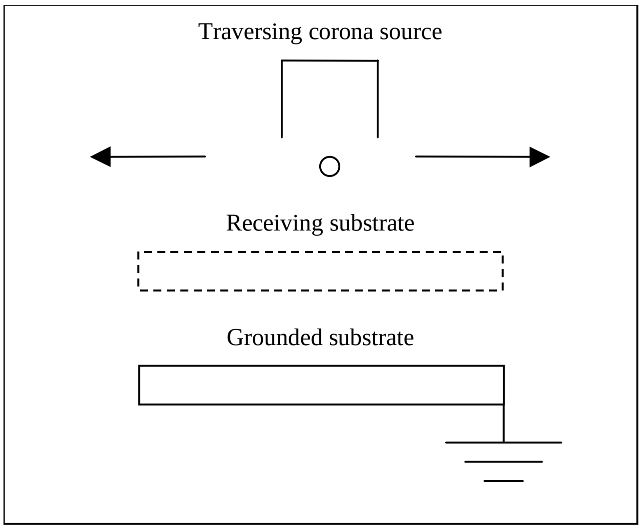

Figure 1. Electrostatic Printing Schematic.

Electrostatic Printing

The liquid toner development described here was carried out with an electrostatic printer shown schematically in Figure 1 which was supplied by Electrox Corporation of Newark, New Jersey. The Electrox printing process works by applying an electrostatic charge to a photoimaged layer on a grounded substrate, essentially an electrostatic printing plate. The substrate can be prepared by analog optical imaging as in a xerographic copier or by digitally controlled laser imaging as in a laser printer. A translating corona source produces a charged latent image on the substrate. The liquid toner is then applied to the substrate, and after a few seconds the excess toner is washed away using the alkane dispersant, leaving an image that has been developed by electrostatic attraction of the charged toner particles to the oppositely charged image areas.

The image can be transferred to a receiving substrate to decouple the final product from the latent imaging process, particularly where it is desired to make multiple products from a single image, or where it is desired to apply the image to a substrate which is not suitable for electrostatic application of toner. An example of the latter situation is applying a redistribution pattern of very fine conductors to a pattern of pads and insulators on an existing printed wiring board.

To perform image transfer, a transfer substrate is placed over the image on the grounded substrate using spacers to create a gap, which is filled with the alkane dispersant. The corona is again passed over the sample to provide an electrostatic transfer field. Under the influence of the transfer field, the toner is transferred through the solvent in the gap to the transfer substrate. The substrate is then carefully removed from the printing plate with the transferred image on its surface. The alkane solvent is allowed to evaporate, and the sample is cured in air to give a conductive metal image on the substrate.

Liquid Toner Development

Fifty-five liquid toners for printing silver conductors based on PARMOD™ technology have been formulated and tested. The basic constituents of these toners are a finely divided silver metal particle and a charge director (CD), dispersed in a C_{10}-C_{13} alkane dispersant vehicle. Different liquid toner properties can be obtained by variation of the silver particle size and/or type. The variation of concentration and type of CD can also change the toner's properties. By using an optimized combination of components, a liquid silver toner has been developed with the desired printing, transfer, and curing properties.

The critical requirement in preparing satisfactory PARMOD™ liquid toners is to create a suspension of charged silver particles that will print an electrostatic image. The key to accomplishing this is to find a CD that will give the silver particles either a positive or negative charge and allow for a variation in the conductivity of the suspension. Control of the suspension conductivity allows for fine tuning the printing properties. Enough CD must be present to charge the particles sufficiently without overly raising the conductivity of the suspension. If the suspension is too conductive, it will simply "wash" away the particles from the image. The important properties which govern printability include the number of silver particles put down on the image, the "adhesion" of the particles to the image which has to do with both the amount of charge on the particles and the conductivity of the suspension, the elimination of oppositely charged particles, and the ability of the printed particles to be transferred.

Silver Powders

Silver flake with 10 μm average particle size was used for much of this research. The relatively large size of the silver particles was believed, in part, to be the cause of poor resolution at the edges of the image. By decreasing the particle size, the edges of the image become smoother. A 50 nm silver particle was synthesized so that the particles were coated with a charge director augmentor as they formed. This powder produced very satisfactory images.

Charge Directors

An optimized charge director was formulated with the silver flake and also with the coated silver nanopowder. The silver flake toners printed very nice images, but, as with the previous silver flake formulations, the edges of the image were rough. These two toners did print well at higher

 Copyright 1998, IS&T

suspension conductivities of 7.0 and 6.6 pmho/cm respectively and were stable with time. Toner E-43 formulated with the coated silver nanopowder and the optimized CD was the best performing toner tested during this study. It printed very sharp images, with the particles adhering very well. The suspension conductivity could be raised as high as 7.5 pmho/cm without interfering with the printing properties. This toner fits all the necessary requirements to be used as a liquid toner.

Curing a Printed Image

Once an image has been printed,it can be cured at 220°C in air for 3 minutes, to form a continuous, conductive metal trace, as shown in Figure 2. The properties of the best such samples are reported in Table 1. The thickness of these traces was measured by cross-sectional optical microscopy and also by profilometry. When the 10 µm silver flake was being used, the thickness of the trace was about 6 µm. When the 50 nm coated silver nanopowder was used, the traces were found to be about 1.5 µm thick. A 125 cm long trace that was 0.396 mm wide, (3156 squares) gave resistance values of as low as 90 Ω with volume resistivity values as low as 5.7 µΩ-cm compared to 1.6 µΩ-cm for bulk silver.

Transferring the Image

Once acceptable PARMOD™ toners were available, the effort was focused on the transfer of the toner image to desirable substrates. The substrates of interest were various kinds of glass, G10/FR4 epoxy glass boards, polyimide or coated polyimide, and various other high temperature (200-260°C) polymer substrates. Although toners may print well, they do not always transfer well. While most of the toners made were tested for transfer properties, only the best two were extensively studied for use as a transferable toner. Both of these toners used the coated silver nanopowder for the silver particles.

Images printed with toner E-43 transferred very well. The complete layer of toner on the printed image was transferred to the substrate. The resolution of the transfer varied greatly depending on the substrate. Very sharp, high-resolution transfers could be made to various types of glass, Tyvek, anodized aluminum, and copper substrates. Transfers to polymer substrates such as polyimide, polyester, Tedlar, silicone rubber, and G10/FR4 epoxy glass were less successful. The image would transfer very well, but after a few seconds, the particles could be seen coming off the image and dispersing over the surface of the substrate.

The high resolution images transferred to glass using toner E-43 were then cured to give a conductive silver trace shown in Figure 3. The cured metal properties of these samples are shown in Table 1. The samples on glass were cured at 400°C in air to give good silver adhesion to the glass surface based on the Scotch tape test. The resistivity values obtained were as good as 1.7 µΩ-cm. Although the resolution on polyimide was in question, it was determined that if cured at 350°C in air, good adhesion was obtained and resistance values similar to the glass samples were obtained.

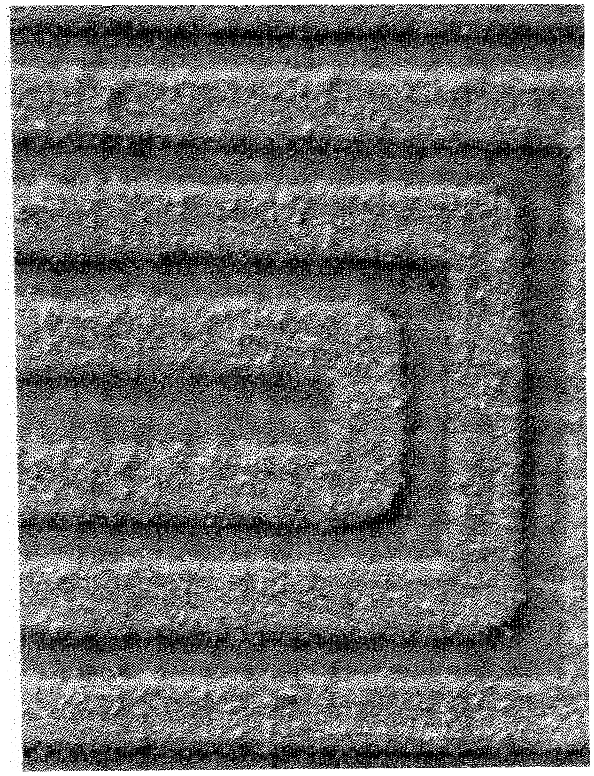

Figure 2. Cured silver image on polymer substrate. 100 micron lines and 50 micron spaces

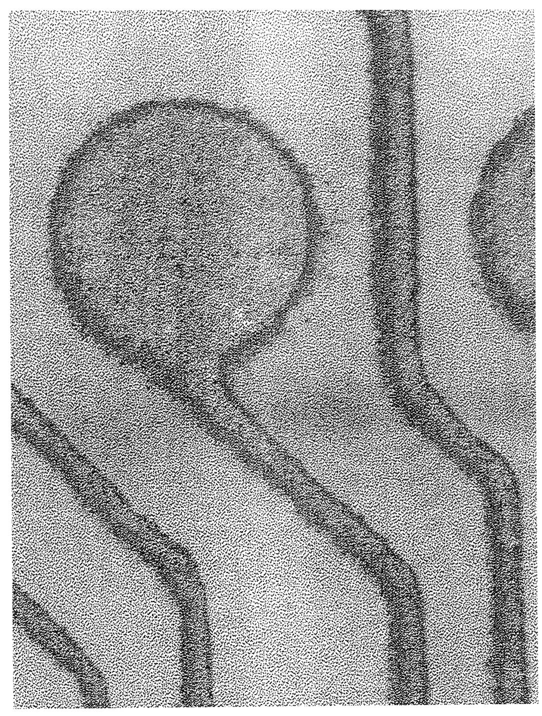

Figure 3. Electrostatically printed silver PARMOD™ image transferred to glass and cured. The lines are 40 microns wide.

 Copyright 1998, IS&T

Table 1. Cured Properties of PARMOD Liquid Toners

Toner/ Conduct. (pmho/cm)	Substrate	Cure Temp/time (°C/sec)	Ohms per 125 cm	Cross Sect. Area (cm^2)	Resistivity ($\mu\Omega$-cm)
E43/ 3.90	Polymer	"	97	$7.92*10^{-6}$	6.1
7.5	"	"	235	"	15
2.9	"	"	350	"	22
E43/ 2.70	Glass	400/300	115	$3.17*10^{-6}$	2.9
2.70	"	"	67	"	1.7

Conclusions and Applications

The goal of developing a PARMOD™ based liquid toner that could be electrostatically printed, transferred, and cured to give a high resolution, highly conductive trace has been achieved. A major program has been proposed to apply this technology to metallizing high density interconnect structures and microvias. The object is to create the ability to match the capabilities of advanced printed circuit manufacture to the rapidly accelerating demands of the semiconductor industry for ever finer features and ever greater numbers of I/O connections per chip.

Another major application area is metallizing silicon devices themselves. The distinction between ICs and the interconnect structures on which they are mounted is blurring as interconnect capabilities become finer and direct chip attachment is more common.

A final major application area is direct digital printing of passive components such as resistors, capacitors and inductors as well as the conducting circuitry. Parmod™ chemistry can be adapted to create toners to produce silver palladium and other resistive compositions as well as ferrites and ferroelectrics. The goal of circuits created totally by printing technology is achievable.

Acknowledgement

This work was supported by the Defense Advanced Projects Agency under Contract N00014-95-C-0354. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the DARPA or of the U.S. Government.

References

1. Schmidt, S.P.; Larson, J.R.; Bhattacharya, R.; Handbook of Imaging Materials, A..S. Diamond, Ed. Marcel Dekker, NY, 1990, Chapter 6 “Liquid Toner Technology”

Biography

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

Paul H. Kydd founded Partnerships Limited as an independent applied research laboratory in 1983. The company has pursued research in a variety of chemically related technologies for government agencies and private clients. Since 1994 the primary focus had been on the development of the Parmod™ technology under DARPA sponsorship. A new company, Parelec, LLC, has been established to commercialize the new technology. Dr. Kydd received a Ph.D. in Physical Chemistry from Harvard and attended the Advanced Management Program at the Harvard Business School