Partnerships Limited, Inc

Waste Minimization in Circuit Board Manufacturing by PARMOD™ Technology

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by

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In Phase I of this SBIR Contract the feasibility of producing well-consolidated, well-bonded silver conductors by a simple print-and-heat process was demonstrated. The objectives of Phase II have been to extend this PARMOD™ technology to copper conductors and to electrostatic printing.

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Successful copper ink formulations and oven treating conditions have been found which very nearly equal the performance of silver inks. A major increase in our understanding of the chemistry of the process has provided an entirely new class of PARMOD™ formulations with superior performance and potential for future improvement.

A much improved approach to electrostatic toner materials based on liquid toner technology has been demonstrated. The ability of this technology to produce high resolution circuits quickly over a large area should provide opportunities in high density interconnect applications.

These achievements have been the basis of further development and evaluation in selected markets. A Dual Use application to prototyping printed wiring boards and metallizing vias is under active development with the U.S. Army. PARMOD™ liquid toners for metallizing microvias and high density interconnects in advanced technology PWBs and multichip modules have been proposed for demonstration in an industry-wide consortium. Low-cost, high-volume production of flexible printed circuits is being developed for specific applications.

Notice

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Comparison of High Density Circuit Fabrication Costs

List of Symbols, Abbreviations and Acronyms

DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
DTA	Differential Thermal Analysis
FEP	Fluorinated Ethylene Propylene (Teflon®)
FTIR	Fourier Transform Infrared spectroscopy
MOD	Metallo-Organic Decomposition
ROM	Reactive Organic Medium
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetry Analysis
Torr	Unit of pressure (one mm mercury column)
ppm	parts per million

mil	0.001 inch
micron	0.001 millimeter
mm	0.001 meter
cm	0.01 meter

Summary

The objective of Phase I of this SBIR contract was to demonstrate the feasibility of printing thick film electrical conductors on conventional polymer-based printed wiring boards. The approach was to develop the thickness of a printed image by powder coating with a Metallo-Organic Decomposition (MOD) compound. These compounds have been shown to decompose to high quality metal deposits at temperatures low enough not to destroy the substrate (1).

In Phase I, the solution to the problems of poor pattern definition and thin deposits was to add metal powders to the mixture of MOD compound and an organic vehicle to create a paste or ink which would consolidate into well-bonded pure metal conductors on oven treatment. These formulations have come to be known by the name PARMOD™. The silver compositions whose feasibility was demonstrated were the equal of conventional thick film silver compositions, but at an oven treating temperature approximately 500°C lower. Potential users of this technology who were contacted during Phase I made it clear, however, that its full potential could only be realized by extending it to copper conductors and improving the resolution of the printing process still further. These challenging but high impact objectives were chosen for Phase II.

Most of the Phase II effort has been spent on achieving successful copper conductors. This is complicated by the fact that copper reacts with the oxygen in the air, so that an appropriate atmosphere must be chosen to avoid carbon deposition from the organic constituents on the one hand, or conversion to copper oxide rather than copper metal on the other. Fortunately, it has proven possible to deposit good quality copper conductors in an atmosphere based on pure nitrogen.

The morphology of the particulates in the copper PARMOD™ mixture has been the key to achieving consolidation to high conductivity traces in seconds. The metal content has been optimized to lower the processing temperatures to 260°C , which is compatible with conventional epoxy-glass substrates, as well as the more expensive polyimides.

The particulates only consolidate in a Reactive Organic Medium (ROM). The work done in Phase II has demonstrated a variety of effective organic compounds and has provided guidance on the most suitable ones for various applications.

To achieve higher resolution than conventional screen printing used with thick film pastes, liquid toner compositions have been developed for electrostatic printing. This process has demonstrated the ability to produce patterns of 125 micron lines and 50 micron spaces as long as 56 cm and 50 micron lines and spaces at shorter distances.

Introduction

The manufacture of printed circuit boards is a seven billion dollar industry in the U.S. Virtually every electronic device includes one or more circuit boards to support and interconnect integrated circuits and discrete components. The printed circuit industry is also the source of significant hazardous waste problems. Printed circuits have historically been produced by photoetching copper-clad, glass-reinforced epoxy boards or polyimide films with acid in a subtractive process, producing several hazardous waste streams.

Several technologies have been developed for direct additive printing of circuits with minimal waste. The most common of these is silk screening of thick film paste, as in preparation of hybrid circuits on ceramic tape. These require firing at temperatures of 600-1000 C, and are not compatible with circuit board manufacture using conventional polymer-based substrates. The use of conducting polymers or metal-loaded epoxy adhesives as printing inks could circumvent this problem, but these have electrical conductivities less than 3% of that of bulk metal at best and they are nonsolderable.

Metallo-Organic Decomposition as a Solution

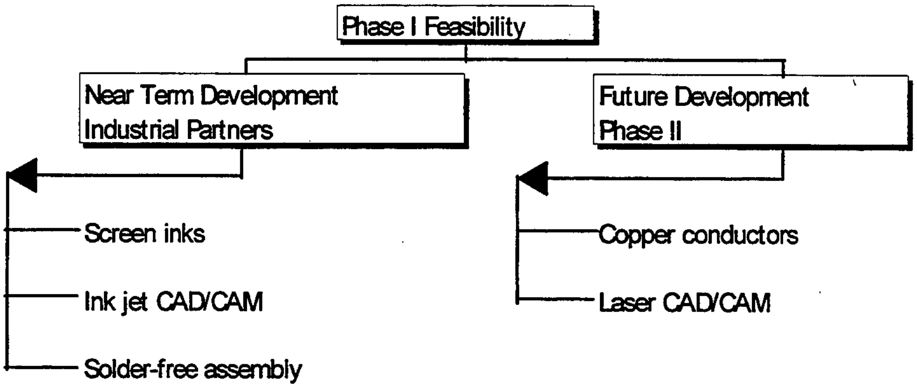
The new technology developed in this program which can realize the objective of fully additive circuit production is based on mixtures of Metallo-Organic Decomposition (MOD compounds and metal powders. These mixtures have been given the trade name PARMOD™. The MOD constituent decomposes at a low temperature to provide pure metal which acts to bond together the metal powder in a well-consolidated electrical conductor. The result is to bring the processing temperature of conventional thick film technology down by approximatley 500°C and allow it to be used on conventional printed wiring board substrates. This process is the optimum method of circuit board manufacture from an environmental standpoint. It eliminates all the wet chemistry associated with photolithography. It eliminates the use of etching and plating solutions to remove more than half of the original copper laminate and to configure the metal conductors. The only sources of emissions or wastes will be the small amount of solvent in the ink and the decomposition products of the MOD compound, which are carbon oxides and light hydrocarbons.

Results of Phase I

The results of the Phase I program, which demonstrated the feasibility of the PARMOD™ technology with silver, have been described in the Phase I Final Report (2). Early tests with silver neodecanoate confirmed that this MOD compound did indeed decompose cleanly and quickly to metal at an acceptable temperature, but the compound melted before it decomposed and tended to spread out into a thin layer with very poor definition. The solution to this problem was the addition of silver powder or silver flake to provide good definition and additional metal for thicker conductors. A U.S. Patent (3) has been granted on the basic concept of metal powder mixtures bonded by additional MOD-derived metal.

Phase II: Problem Definition and Technical Objectives.

The activities needed to capitalize on the success of Phase I have been separated into near term developments to be pursued with industrial partners and long term, high risk research activities with high potential returns to be pursued in Phase II.



The objectives of Phase II have been to extend the PARMOD™ technology demonstrated in Phase I to copper conductors and to xerographic printing.

The questions to be answered were:

1. How to overcome the divergent requirements of maintaining a high enough oxygen partial pressure to remove the organic material while maintaining a low enough oxygen activity to prevent formation of copper oxide rather than metallic copper.

2. How to foster the consolidation of "nascent" metal from MOD decomposition with preexisting particulate metal powders which is the heart of the PARMOD™ technology. This conversion of particulate material to a well-consolidated dense metal at temperatures far lower than the sintering temperature is critical to all conductor applications, and was poorly understood. For copper it was undemonstrated.

3. How to create toner particles with the characteristics required for successful xerographic printing. These include the state of subdivision, stability and static electrical charge of the particles, as well as their ability to convert to well -bonded electrical traces. Thus the development of a successful toner imposed an additional set of constraints and requirements having to do with the printing process.

Methods, Assumptions and Procedures

Sample Circuit Preparation

Ink Paste Preparation

The ink components are mixed in a glove box to minimize exposure to air. This premix is then removed from the glove box, and roll milled for at least 30 minutes to completely homogenize the ingredients. Using a minimal gap setting between the rolls, the roll milling disperses the individual ink components. The milled ink is stored in a foil package in air or in a plastic syringe.

Thermogravimetric Analysis (TGA)

Ink samples were evaluated using thermogravimetric analysis in order to determine the temperatures at which they decomposed, as well as the effect of the atmosphere on the decomposition process. A sample of known weight is deposited on an Al_2O_3 substrate, which is then put onto a Cahn microbalance. The sample is heated at a controlled rate, and the sample weight change is recorded as a function of time or temperature.

Screen Printing

As-received samples of substrate (either polyimide film or epoxy-glass) are washed in methanol. The ink is screened onto the substrate in air using a screen with an emulsion thickness of 0.02 – 0.04 mm and a screen size of 280 mesh. A polyurethane squeegee is used to deposit the ink through the screen and onto the substrate with a snap off of approximately 1-mm.

Air Oven

Silver inks, which are usually oven treated in air, were treated in a 22x30x25 cm radiant furnace made of insulating board with a Calrod heater in the top. The oven has provision for supporting two 7.5 cm square samples on stainless steel wire racks with a central thermocouple to measure the temperature. The oven is operated in batch mode usually in a six minute heating cycle with one minute at the chosen temperature.

Belt Furnace

Some copper samples and silver samples have been treated in an RTC Corp. radiant belt furnace at BOC Group Technical Center with provision for a nitrogen atmosphere. Measured flows of hydrogen and/or oxygen could be added to the atmosphere, and the two could be combined over a catalyst to generate a measured water vapor concentration. The belt speed was adjusted to give a heating time of 6 minutes with at least a minute at maximum temperature.

Tube Furnace

A tube furnace with a 56-mm ID quartz tube is used to heat treat the sample circuits in a carefully controlled atmosphere. The isothermal zone is 7.5 cm long. The atmosphere is provided by a gas delivery system capable of providing controlled volume flows of air, N2, H2, H2O, or mixtures. The sample is attached to a 1-cm diameter stainless steel tube that can be slid in and out of the furnace. A thermocouple is inserted through the end of the tube to the position where the sample is attached to the rod. The end of the thermocouple touches the middle of the sample.

The general procedure for heat treating a sample circuit is to bring the furnace to the desired temperature, with the reaction gas flowing through the quartz tube at approximately 1 liter/minute. The sample, which is mounted on a sample holder, is inserted into the furnace opening and is allowed to equilibrate for 1 minute. The sample is then inserted into the isothermal zone. At the end of the heat treatment, the sample is removed from the isothermal zone and allowed to cool in the process gas to ambient temperature, after which it is removed and evaluated.

Water vapor is added to the atmosphere by passing the atmosphere through a tube filled with water, the temperature of which is precisely controlled. A gas switching valve and separate gas supplies allows the gas flow to the reactor to be switched from dry to wet and back again instantaneously. Hydrogen is added during the cool down phase.

Infrared Furnace

A Five Star Electronics infrared furnace (25 cm x 30-cm hot zone) is used to heat-treat larger sample circuits. A brass reactor with 20-cm diameter glass windows is used to isolate the circuits, and the same gas delivery system used for the tube furnace is used. Circuits up to 18 cm in diameter (or equivalent four sided circuits) can be processed in the reactor. The reactor sits on movable drawer, which is mounted on tracks that allow the reactor to be easily moved in and out of the reactor. A thermocouple is inserted into the gas outlet, and the tip of the thermocouple touches the underside of the sample.

The general procedure for heat treating a sample circuit is to insert the sample into the reactor and the reactor is "buttoned up", isolating it from the ambient atmosphere. The gas flow is initiated through the reactor, and the reactor is slid into the furnace. The sample is held at ambient for 1 minute to allow the atmosphere to flush sufficiently to remove oxidants. The same temperature profile and reaction gas makeup used in the tube furnace are used in the IR furnace. At the end of the run, the reactor is removed from the hot zone and the circuit is allowed to cool to ambient in the flowing gas, after which it is removed and evaluated.

Sample Circuit Evaluation

Resistivity Measurement

The electrical resistivity of the sample circuit is one of the most critical properties. It may be determined approximately by measuring the resistance of a circuit trace of known length, width and thickness. Because measuring the thickness of the trace is difficult, most measurements have been made using the length, width and mass of the trace, assuming the density of the deposited metal to be equal to the bulk density. A more accurate method is prescribed in IPC method 2.5.13. A rectangular trace of length l_1 is applied to a substrate and weighed. The resistance R is measured between two points on the trace separated by l_2. A digital multimeter is used to measure the resistance The resistivity is then given by $\rho = R\ Wt/\ l_1\ l_2$ in gram ohms per meter squared. This method substitutes accurate determinations of mass per unit area, length and resistance for a very difficult measurement of the thickness of thin, rough traces. The IPC method has been used for the measurements of resistivity shown in Figures 1.2 and 1.4 of this report.

Sample Consolidation - The Tape Test

The tape test is an indication of the degree of consolidation of the metal deposited on the substrate. A piece of Scotch tape is pressed onto the surface of the circuit trace using enough fingertip pressure so that all of the air bubbles are removed and good contact is made between the tape adhesive and the metal trace. The tape is then peeled off the surface at approximately a 90-degree angle. In the case of extensive consolidation, the tape will be clean. Generally, there is a correlation between the tape test and the sample resistivity. The better the resistivity, the cleaner the tape test.

Peel Strength Test

While the tape test is a qualitative test of the degree of sintering in the metal of the circuit, the peel strength test determines the failure mechanism, and it is a quantitative measure of the strength of the metal/substrate or intrametal bond, depending on the failure mechanism. Straight 3 mm and 1-mm wide strips of the metal screen-printed and heat treated on a flexible polyimide substrate are used in conjunction with an electronic force transducer with a variable speed vertical drive.

The sample circuit is glued metal side down onto an aluminum plate with epoxy. When the epoxy cures, the outside edges of the strip are scored, concentrating the lifting force on the metal conductor. The plate containing the sample is mounted, sample side up, and the end of the test strip is gripped by vise jaws directly above the sample which are connected to the force transducer. As the transducer moves upward at 5 cm/minute, the force required to pull the test strip away from the metal is measured. A 90-degree angle between the substrate strip and the sample plate is maintained while the substrate is being pulled. By dividing the observed force by the strip width, the peel strength in N/m (lb./in) can be determined.

Pull Test

In a related test using the same force transducer, samples were prepared by soldering 8-mm diameter brass rivets to copper PARMOD™ sample pads. Samples on rigid epoxy-glass and polyimide-glass boards were used as is. Samples on Kapton® FN were cemented to rigid boards with high strength epoxy. The rivets were pulled off the board vertically, and the force required is reported in Newtons per square meter in Figure 1.3.

Solder Leach Test

To determine the stability of PARMOD™ circuit traces in a solder bath, the heat-treated sample circuit is immersed in a solder bath at 260°C for 20 seconds. Prior to immersion, the edge of the sample is coated with a flux to facilitate the uniform deposition of solder onto the metal surface. The sample is stable if after removal, the circuit trace is intact, and it can withstand the tape test or the peel strength test. If the metal trace has been removed from the substrate while in the solder bath, it is considered unstable and a failure. Upon removal, the trace may be covered with solder, indicative of a clean metal surface. If the trace is intact but is not covered with solder, it is likely indicative of a contaminant on the surface of the metal. This does not constitute a solder leach test failure, however.

Optical and Scanning Electron Microscopy

To determine the microstructure of samples, optical and scanning electron microscopy were used. A pad from a typical sample circuit was mounted in cross section in an acrylic binder. The sample was polished using sandpapers of 120 grit, 240 grit, 400 grit, and 600 grit in succession. The finishing polish step was done using Al_2O_3 powder suspensions of 5μm, 1μm, and 0.1 microns. Mounted samples were examined by SEM and by optical microscopy. A Hitachi atmospheric SEM at the BOC Group Technical Center was operated with an environment of approximately 10 Torr water vapor. This is used to neutralize space charge and provide clearer images. This environment also provided a relevant atmosphere in which to investigate the decomposition of the samples in real time with video imaging. The SEM was equipped with a hot stage which could achieve temperatures up to 400°C. Still pictures at various magnifications by SEM and optical micrography were used to investigate the average grain size, the degree of consolidation, and to determine if voids are present in the heat treated samples.

Scanning Electron Microscopy (Field Emission SEM)

The components of PARMOD™ inks are micron and submicron-sized, and as such, require high resolution scanning electron microscopic techniques in order to observe differences in the level of consolidation. The Ceramics Department at Rutgers University has a field emission scanning electron microscope which is capable of 50-100 angstrom resolution, and this facility was utilized to discern differences in the consolidation process.

Sample circuits which could not be removed from the substrate were prepared by mounting in cross section in an acrylic binder. These samples were wet polished using sandpapers of 120 grit, 240 grit, 400 grit, and 600 grit in succession. The finishing polishing step was done using alumina powder suspensions of 1 μm and 0.1 μm. The polished specimen was washed with ethanol and dried in flowing air.

Sample circuits which could be removed from the substrate were fractured and the specimen was mounted on a flat holder using adhesive coated carbon tape such that the fracture surface could be observed. These samples were very clean, and the best resolution was obtained on these unmounted specimens.

FTIR and DRIFTS

The DRIFTS experiments were carried out on a Bio-Rad FTS 60 FTIR with an internal mercury cadmium telluride detector at the BOC Group Technical Center. The diffuse reflectance seagull apparatus was equipped with a Spectra-Tech Controlled Environment Chamber 0030-100. All of the experiments were conducted using a flow of air, nitrogen or wet nitrogen through the sample chamber, so that any gases formed during the decomposition were swept away with the gas flow. The sample was placed in the sample cup of the seagull apparatus and the controlled environment chamber was sealed. The system was allowed to purge for one hour or until carbon dioxide could not be detected. Spectra were collected with 12 scans and a 1-second interval between spectra. As the spectra were being collected, the temperature was steadily increased at a rate of 3 to 5 degrees C per spectrum collected.

Results and Discussion

Task 1. Extension of PARMOD™ to Copper with a Reactive Atmosphere

Characteristics of Successful PARMOD™ Formulations

Successful copper PARMOD™ formulations have been, the process details have been optimized to cure them to well-consolidated, well-bonded electrical traces. The critical ingredients of the successful mixtures are a Reactive Organic Medium, a bulk copper flake or copper powder and a copper nanopowder with a particle size in the colloidal range below 100 nanometers.

The key to achieving rapid consolidation to pure metal at low temperatures, which is the distinguishing characteristic of PARMOD™ mixtures, is the nanopowder constituent. The proper local chemical environment for consolidation is provided by the ROM, which can be either a Metallo-Organic Decomposition (MOD) compound or the reagent from which it can be formed, for example a carboxylic acid. The copper powder or flake constituent provides the bulk of the metal to be bound together to form the final conductor and gives the conductor good resolution of lines and spaces when printed.

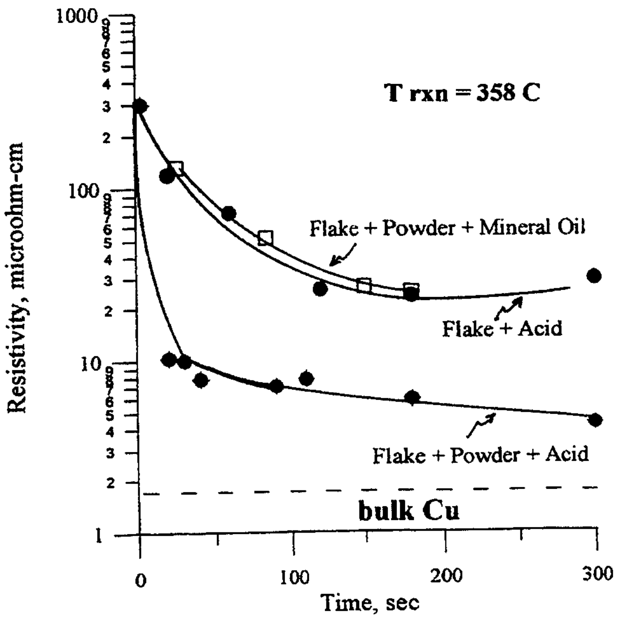


Figure 1.1 Resistivity as a function of cure time for copper-containing inks.

Figure 1.1 shows a plot of electrical resistivity vs. curing time during which the temperature of the substrate reached 358 C for various ink formulations from which components have been systematically eliminated to illustrate their individual effects

When unreactive mineral oil was substituted for reactive carboxylic acid, the resistivity decreased relatively slowly and leveled off at approximately 30-microohm cm characteristic of polymer thick film materials in which electrical conductivity depends on adventitious contact between metal flakes that are not bonded together.

Similarly, when copper flake was mixed with reactive carboxylic acid, but with no nanopowder present, the consolidation was slow and incomplete.

Only when all three constituents were present did the electrical resistivity decrease to a value near that of bulk copper within seconds to provide true PARMOD™ performance.

Temperature-Time Effect on Electrical Resistivity of Copper PARMOD™

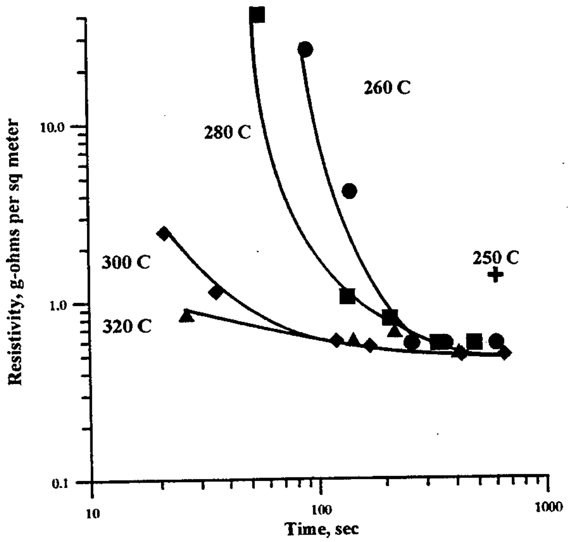


Figure 1.2 Resistivity of copper PARMOD™ as a function of total cure time to reach various temperatures. (IPC Method 2.5.13).

The time at temperature of the circuits produced is critical to defining the electrical properties, as these variables strongly influence the degree of bonding of the copper comprising the circuit. Figure 1.2 shows the resistivity as a function of time at four different temperatures for circuits prepared from ink C-188. The times presented here are the total time in the oven and include the time to get to temperature as well as the time spent at peak temperature. The resistivity was determined by IPC Method 2.5.13. Resistivity is reported as the resistance times the mass of copper divided by the sample and gauge lengths as gram ohms per meter squared. The resistivity of bulk copper in these terms is 0.15 gram ohms per meter squared. A resistivity as low as four times the value of bulk copper can be achieved at temperatures as low as 260° C and in as little as 10 seconds at 320°C.

With the incorporation of more active "wet precipitation" nanopowder particles, time has become a more important variable. With the improved nanopowder, heat treating for longer time and at elevated temperature improves the resistivity of the circuits because the nanoparticles are continuing to consolidate even at lower temperatures (270°C). Larger diameter spherical particles (greater than 1 micron) do not consolidate to a great extent at these temperatures, even after heat treating for at least 10 minutes. This demonstrates the importance of the nanopowder in the overall consolidation process.

Temperature-Time Effect on Adhesion of Copper PARMOD™

Data on the mechanical adhesion of copper PARMOD™ inks as a function of time and temperature is shown in Figure 1.3. As expected, the curves are the inverse of those in Figure 1.2. The pull strength increases with time and temperature in the same way that electrical conductivity (the reciprocal of resistivity) does, and for the same

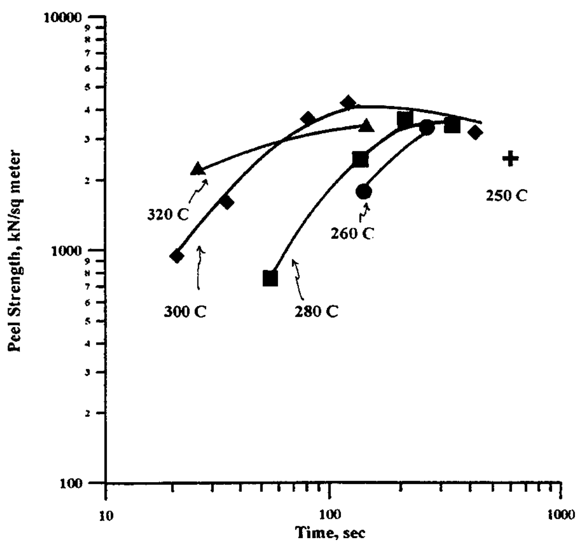


Figure 1.3 Pull strength of copper PARMOD™ on Kapton FN as a function of cure time and temperature.

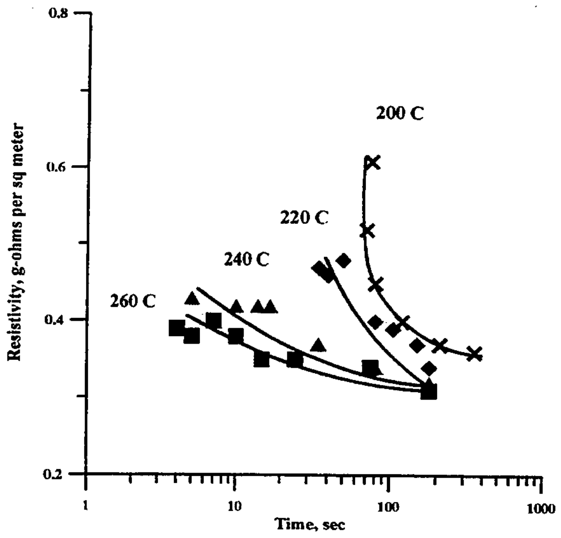


Figure 1.4 Resistivity of silver PARMOD™ as a function of total cure time to reach various temperatures. (IPC Method 2.5.13).

reason. The metal is being welded into a single conductor as the curing process proceeds. A pull strength of 3300 kN/m^2 (3.3 MPa) is equivalent to 500 psi, which is adequate for printed wiring boards.

Temperature-Time Effect on Resistivity of Silver PARMOD™

Comparable results on the effect of cure time and temperature on electrical resistivity are shown for silver ink B-86 in Figure 1.4. Again the resistivity was determined by IPC Method 2.5.13, and the results are presented in gram ohms per meter squared. Pure bulk silver has a resistivity of 0.168 in these units, and it can be seen that the limiting resistivity reached with silver PARMOD™ is approximately twice this value. Silver mixtures tend to cure at lower temperatures and shorter times than copper PARMOD™.

Circuit Thickness Affects Cure Time

Depending on the application, the circuit thickness required may range from 12 microns (0.5 mils) or less up to 100 microns (3 mils). The thickness of the copper circuits printed can be varied by varying the screen parameters (emulsion thickness, mesh size) or by adjusting the level of metal in the ink. There is little or no effect of thickness on the resistivity. The data suggest that the number of metal connections (grain boundaries) per unit thickness does not change with increasing thickness. The thickness does affect the cure time. Thinner copper traces cure significantly faster than thick ones. Thin silver traces cure at substantially shorter times than thicker ones and at somewhat lower temperatures. The surface morphology of silver traces is smoother than copper. Thin traces are smoother than thick ones.

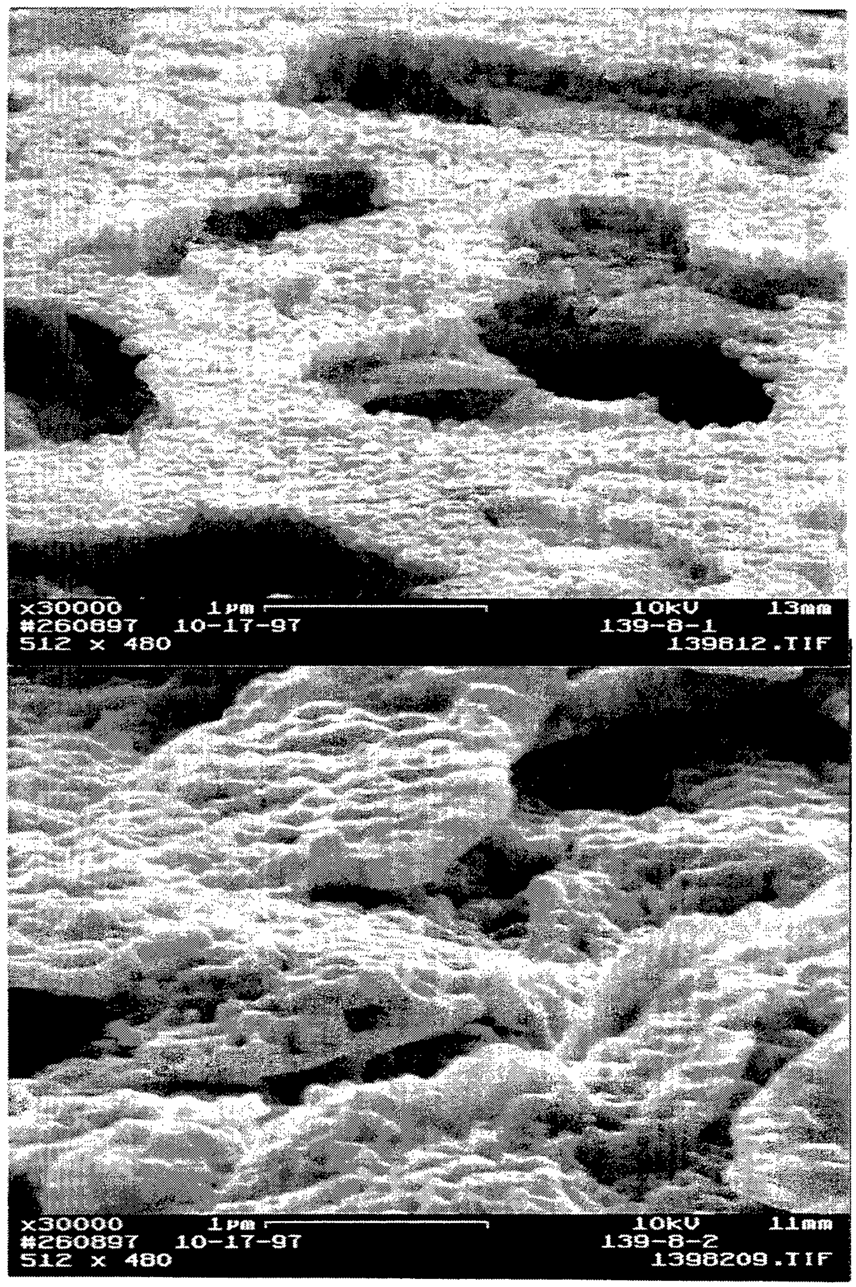


Figure 1.5 Surface of copper Parmod™ heat treated at 350° C for 20 seconds (top) and 5 minutes (bottom).

Effect of Time on Microstructure of Copper PARMOD™

Figure 1.5 shows two copper surfaces at 20 seconds and 300 seconds heat treating time. It can be seen that even at the shortest time the nanopowder constituent of the PARMOD™ mixture is fused to a solid mass. At longer times this process has proceeded to a greater extent. The voids in the surface through which the organic constituents of the mixture vented during the oven treatment can also be seen.

Effect of Temperature on Microstructure

To illustrate the importance of temperature on the consolidation process, the microstructures of copper traces fired at 234°C, 350°C and 586°C for six minutes are shown in Figures 1.6 a, b and c. The micrographs with a magnification of 5000 clearly show that the level of consolidation and bonding is more advanced at the higher temperature. This is shown by the large number of ductile fractures as well as the fact that the individual nanopowder particles are difficult to identify as discrete entities at 350 and 586° C. The microstructure in Figure 1.6 a at lower temperature shows that though the nanoparticles are identifiable as singular entities, there are interconnections between the particles. In all cases, the nanoparticles appear to be well adhered to the bulk copper, which in this ink is a spherical powder. The microstructure will be more thoroughly discussed in the section on Task 2.

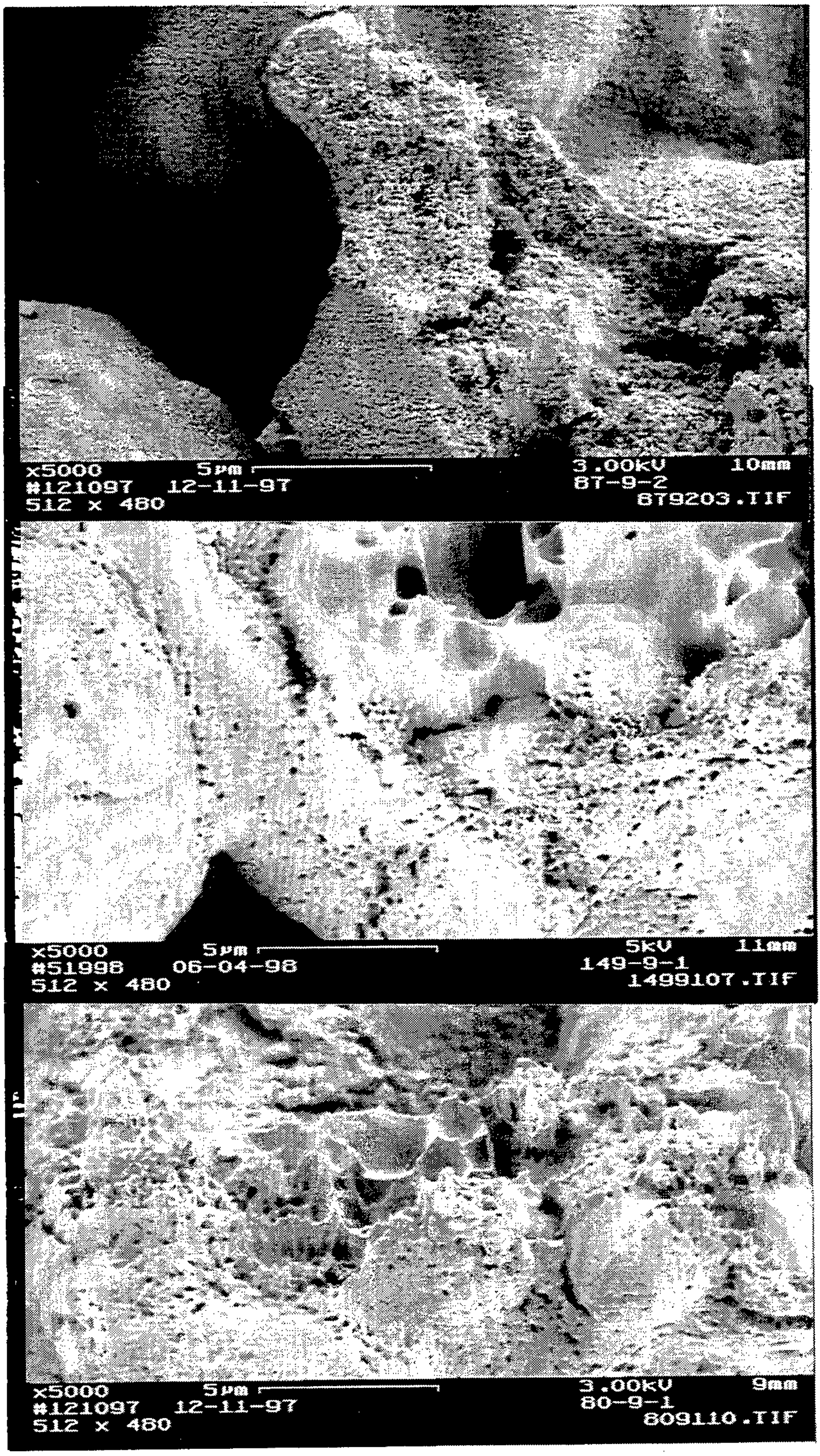


Figure 1.6 a. (upper) Copper PARMOD™ cured at 234 C for ten minutes; b. (center) 350° C for six minutes; c. (lower) 586° C for ten minutes. Magnification 5000.

The time-temperature data extending down to 260°C suggest that copper PARMOD™ inks may be utilized on epoxy-glass substrates, the workhorse of the electronics industry. In fact, copper PARMOD™ does consolidate on epoxy-glass (G-11); however, the circuits do not stick well to the substrate without an interlayer of polyimide. These results will be discussed in the section describing the results on various substrates (Task 4).

Effect of Oxygen

With the appropriate constituents, successful copper PARMOD™ deposits can be cured in an atmosphere with a few parts per million of oxygen, even though thermodynamically this should result in copper oxide rather than copper metal. It appears that the process is dominated by chemical kinetics in the locally reducing atmosphere of the vaporizing and decomposing Reactive Organic Medium (ROM), which is an essential constituent of PARMOD™ mixtures. The ROM can consist of a MOD compound of the metal or of an acid which reacts with the metal to form a MOD compound, or of mixtures of the two. For copper, the acid form is preferable, possibly because the acid reacts with traces of copper oxide to reform the MOD compound and force the decomposition toward pure metal.

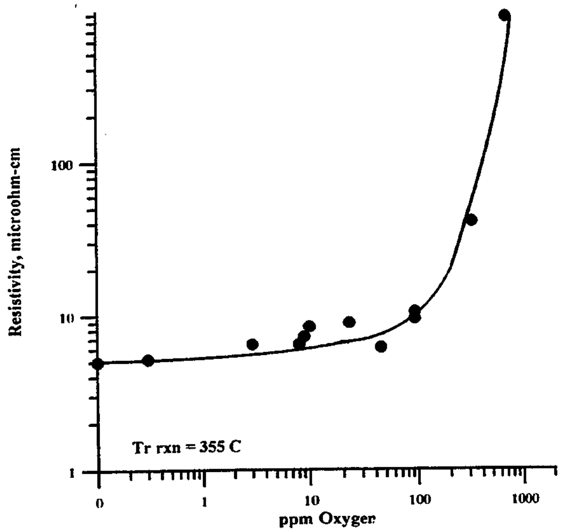


Figure 1.7 The effect of oxygen in the nitrogen atmosphere on the resistivity of copper PARMOD™.

Addition of hydrogen to the heat-treating atmosphere during decomposition of the MOD results in residual carbon being left in PARMOD™ deposits of copper silver and gold, which is detrimental. Once formed, the carbon cannot be eliminated by manipulating the atmosphere or the curing conditions. It is critical to prevent its formation. A mildly oxidizing atmosphere at the proper time is the key in preventing carbon formation.

To determine how much oxygen can be tolerated, an Illinois Instruments Model 6000 oxygen analyzer was used to measure the level of oxygen close to the sample. Figure 1.7 shows a plot of resistivity as a function of oxygen content. Surprisingly, the heat treating process can withstand a significant level of oxygen (up to 100 ppm) with only a minimal effect on the resistivity. At significantly higher oxygen levels, the resistivity increases dramatically. These data suggest that processing restrictions in terms of the gaseous environment may not be as demanding as once thought. However, the level of oxygen will have to be monitored and controlled throughout the process.

Effect of Water Vapor

Water vapor introduced partway through the thermal cure cycle is beneficial in producing good quality copper deposits in a short time. There is an optimum time for the addition of the water. Figure 1.8 shows several runs in which the water was added at various times and the relative humidity were measured with a Vaisala HMI 321 temperature-humidity meter. If the water is added too early in the process (Figure 1.8 a), the result is a dark colored circuit which has inferior electrical properties. If no water is added, the circuits tend to be dark colored and the electrical properties are again inferior. The optimum time for the introduction of water is just after the initial heating stage, as shown in Figure 1.8 (b). When water is included throughout the cycle time including the cool down period, the electrical properties and appearance are not as good as if it is only included in the cure.

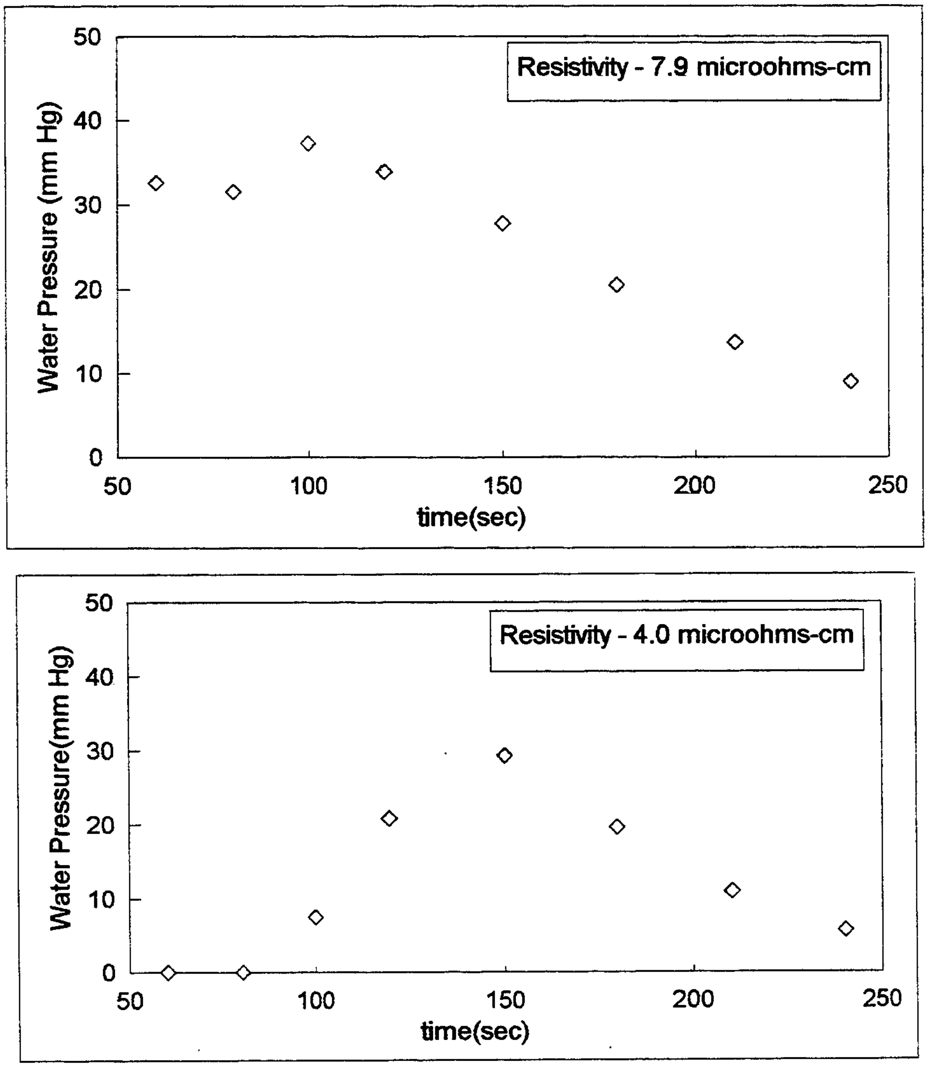


Figure 1.8 a. (upper) water vapor added continuously; b. (lower) water vapor added after initial heating stage.

When water is added at the optimum time, as shown in Figure 1.8 (b), the resultant circuits are clean and bright, with the best electrical properties. The effect of various levels of water addition is shown in Figure 1.9, with 1-3 vol. % water being the optimum for the brightest circuits with the best electrical properties. Up to 10 vol. % water vapor has been added to the system and the resulting circuits still conduct well.

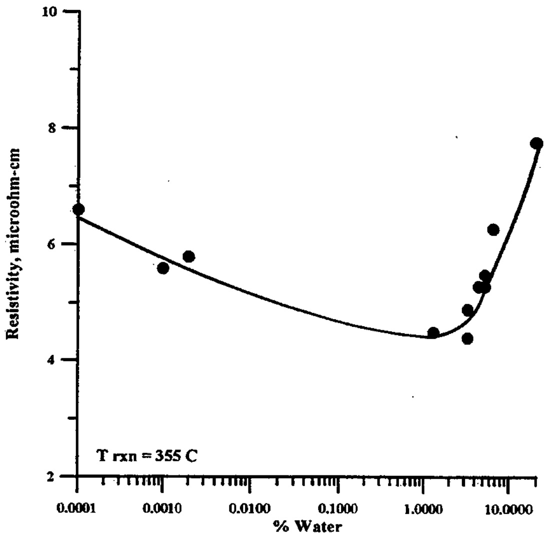


Figure 1.9 The effect of water vapor in the curing atmosphere on the resistivity of copper PARMOD™.

Later Addition of Hydrogen Enhances Circuit Appearance

Hydrogen addition to the extent of ~5 vol. in the nitrogen atmosphere during the consolidation and cooling of copper traces following vaporization and decomposition of the MOD compound results in cleaner and brighter traces, and better electrical properties. The hydrogen likely is acting as a reducing agent in preventing the formation of any copper oxides or their reduction to copper metal. The time at which hydrogen is added is less critical than was observed for water addition; however, hydrogen addition in the initial stages of the curing process is detrimental, as mentioned above.

DRIFTS Experiments

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements have provided guidance on the chemical mechanisms which are taking place in the ROM during cure and on interactions between the ROM and the atmosphere.

Neodecanoic acid by itself vaporizes cleanly at a temperature of approximately 260 C. Silver neodecanoate decomposes cleanly to the acid at temperatures up to 268 C, but forms CO2 at higher temperatures. When the acid is mixed with silver flake and colloidal silver to make a PARMOD™ mixture, a neodecanoic anion is seen in the reacting mixture.

Copper PARMOD™ mixtures show formation of two anions with decomposition to CO2 in pure nitrogen, but only a single anion and no CO2 with added water vapor. The water vapor appears to prevent the decomposition of the neodecanoic acid or facilitate its formation from the MOD compound by hydrolysis. An analysis of the role of the individual constituents in copper PARMOD™ mixtures follows.

Bulk Copper Flake or Spheres

The bulk copper constituent can produce and decompose copper neodecanoate by a reversible reaction with neodecanoic acid, although with the decomposition, Cu_XO, a poorly characterized copper oxide is formed. The fact that the copper neodecanoate can be decomposed to metal even in pure nitrogen indicates that the surface is reactive enough to interact with the neodecanoic acid, but may not be reactive enough to consolidate into a denser mass. The bulk copper probably plays a more important role in the composition as a large mass of copper that provides good conductivity, but needs additional constituents to help bond the flakes or spheres together.

Copper Nanopowder

The copper nanopowder has a more reactive surface, as evidenced by the fact that to decompose copper neodecanoic acid in the presence of the nanopowder, water vapor must be added. The copper neodecanoate is held more strongly to the surface and requires more than heat to decompose it. This more reactive surface than the bulk copper flake may help in the consolidation of the copper flakes and spheres. It seems that the role of the nanopowder is to agglomerate into a matrix around the flakes thus filling voids and providing a conductive path. Further evidence for this will be presented in the discussion of Task 2.

Neodecanoic Acid

The neodecanoic acid reacts with the surface of the bulk copper and nanopowder, removing oxide as well as removing copper atoms as evidenced by the FTIR of the blue solution formed in mixtures of copper and neodecanoic acid at room temperature. The removal of copper from the surface of the nanopowder and the bulk copper may allow for the deposition of this copper in other places and thus help to "chemically weld" the particles together. However, we do not have any direct evidence of the redeposition of the copper.

The neodecanoic acid also acts as an inhibiting agent on the surface of the very reactive copper nanopowder. Without the copper neodecanoate formed on the nanopowder surface, the powder particles would prematurely agglomerate, rather than being dispersed around the bulk copper until the organics are removed and then agglomerating and "embedding" the flakes or spheres in the agglomerated matrix during the curing process.

Cu_XO

Copper oxide also reacts with neodecanoic acid to form copper neodecanoate. However, in the ink compositions during cure, the oxide is generally produced as a result of the decomposition of the copper neodecanoate. This may indicate that the decomposition occurs by breaking the C-O bond rather than the Cu-O bond. The evidence for the organic removal is the loss of the C=O peak due to copper neodecanoate. This indicates the loss of the Cu -O-C bond, but does not indicate which bond is broken. However, the formation of the oxide peaks as the copper neodecanoate is being decomposed indicates that the Cu-O bond stays intact and the C-O bond is the one broken.

Water Vapor

The water vapor allows for removal of the copper neodecanoate organics from the Cu powder. The mechanism of the removal is not clear, except as described in the Cu_xO section above. It may be that water vapor is hydrolyzing the copper neodecanoate leading to the formation of free acid and metal or metal oxide, thereby facilitating a clean, reversible decomposition of the copper neodecanoate. This process can then assist in redistributing the metal between the copper particulates present in the PARMOD™ mixture helping to consolidate them without decomposition of the organics into carbon on the one hand or massive oxide on the other.

TGA Results

The results of the DRIFTS experiments are consistent with thermogravimetric measurements which show an initial weight loss near the boiling point of the acid constituent of the ROM followed by a slower and smaller weight loss up to the peak heat treating temperature as the MOD compound decomposes to metal.

Conclusions

1) The critical ingredients in copper PARMOD™ mixtures are bulk copper powder, copper nanopwder with a particle size of approximately 50 nm and a Reactive Organic Medium (ROM). If any of the ingredients is left out, the properties of the printed and cured circuit traces is degraded.
2) Appropriate PARMOD™ mixtures cure in times measured in seconds to high conductivity metal traces at temperatures as low as 260°C for copper and 220°C for silver.
3) The mechanical strength of the cured PARMOD™ parallels the electrical conductivity as a function of curing conditions. The strength is adequate for printed circuit applications.
4) The electrical resistivity of cured copper PARMOD™ traces is approximately four times that of bulk copper. For silver it is twice the bulk value.
5) Copper PARMOD™ must be cured in an inert atmosphere. Despite the much more stringent requirements estimated thermodynamically, as much as 10-100 ppm of oxygen can be present.
6) Water vapor present during the consolidation phase of the thermal cure promotes the formation of the MOD compound and improves the properties of the final copper traces.
7) Hydrogen added late in the cure process improves the appearance of the copper traces

Task 2. Powder Metal-MOD (PARMOD™) Mixture Approach to Copper

Overview

A synopsis of the major technical milestones in Task 2 is shown in Table 2.1. The four major accomplishments were: the incorporation and optimization of an active nanometer-sized copper powder (nanopowder); substitution of neodecanoic acid for copper neodecanoate as the Reactive Organic Medium (ROM); a dramatic reduction in cost; and the development of an ink which produces a conducting circuit at heat treating temperatures as low as 240°C.

Table 2.1. Copper PARMOD™ Development Milestones

Ink--Metal	MOD/Vehicle	Cost *	Temp ° C	Time min	Resist. μΩ-cm	Adhere Tape Test
C-50--Flake1/Nano	Neo/Bz /α	1.00	350	20	10	bright, powdery
C-136--Flake3/Nano3	NeoA	0.77	360	1	4	bright, clean
C-175—9-Micron/Nano3	NeoA	0.33	360	10	4	bright, clean
C-187—3-Micron/Nano3	α/neoA	0.77	265	10	4.4	bright, clean
C-203—9-Micron/3-Micron /Nano3	α/neoA	0.31	310	6	4	bright, clean

Key

Neo	Copper neodecanoate
Bz	Copper benzoate
Flake1	Copper flake, version 1
Flake3	Copper flake, version 3
Nano	Nanometer sized copper, Vendor
Nano3	Nanometer sized copper, Partnerships
9-micron	9-micron spherical copper powder
3-micron	3-micron spherical copper powder
α	Alpha terpineol
NeoA	Neodecanoic acid

* Cost relative to Ink C-50

The significance of these developments is as follows:

The inclusion of copper nanopowder was the critical ingredient in developing successful copper PARMOD™ formulations which consolidate to pure metal traces in seconds at a temperature far below the conventional sintering temperature of copper, which is approximately 850°C. Several useable compositions were formulated using purchased copper nanopowders produced by vapor phase methods. Still better formulations have been based on colloidal copper produced by a wet chemical precipitation method developed by Partnerships.

The discovery that the MOD constituent, which is responsible for bonding the metal powders into a well-consolidated pure metal conductor, can be made in situ during the thermal curing process permitted the substitution of a low-cost carboxylic acid for the high cost MOD compound in the Reactive Organic Medium, and provided other benefits as well. Several formulations have been developed based on different ROMs and different powder constituents. The best of these were based on neodecanoic acid as the ROM, with mixtures of nanopowder and larger size copper powders providing the metallic content of the ink.

The nature of the interaction between the colloidal powder, the bulk powder, and the decomposing ROM appears to be one in which the ROM deposits directly on the particles "chemically welding" them together. The ROM may be simultaneously dissolving metal or oxide from the finest particles and from the most active surface locations, and redepositing it on larger surfaces of lower energy in a chemical shuttle. High resolution electron micrographs show conclusively that the nanopowder particles fuse to the surface of the larger particles and bond them into a porous but interconnected mass.

The condition of the surface of the bulk copper particles clearly has a major influence on the process. Incorporation of spherical copper powders with no additives on the surface made it possible to reduce the curing temperature from approximately 325°C required for mixtures containing copper flakes and powders with organic coatings on them to as low as 260°C. This major reduction in cure temperature has made it possible to apply copper PARMOD™ to conventional epoxy-glass rigid circuit boards as well as to the polyimide flex substrates used earlier. Because some of these powders are available in bulk at nominal cost, the cost of the resulting PARMOD™ mixtures has been dramatically reduced.

Systematic Studies to Define Ink Component Effects

The most important characteristics of the components in copper PARMOD™ inks are the morphology, size, and surface chemistry of the copper powder components. The morphology and size distribution of the bulk copper directly impacts the packing of the components, and thus to an extent controls the presence and level of voids. The nanopowder has clearly been shown to be the "glue" which, together with the ROM, cements the bulk copper together.

Though very good electrical conductivity has been achieved, there is still a lack of ductility in the copper circuits. This poor ductility is largely a function of the extensive void structure as well as the limited degree of consolidation that is occurring at the relatively low heat treating temperatures. It is postulated that reducing the level of voids will greatly aid in improving the ductility as well as the conductivity by increasing the number of interconnections in the copper. Copper mixtures, unlike silver ones, have very little ability to reorient the powder constituents during the consolidation process. The mixtures exhibit “rigidity”, and the structure laid down in the printing process is carried through to the finished trace.

This distinction between the behavior of copper and silver PARMOD™ mixtures was observed in dynamic SEM videotapes taken of the curing mixtures in an atmosphere of approximately 10 Torr of water vapor. The silver mixture converted from a rough, as-deposited surface to a smooth, featureless consolidated silver between one frame and the next at the 10 second SEM sweep rate. The copper mixture also converted rapidly but to a rough, porous, unconsolidated structure that pulled apart into isolated islands which never changed as the temperature increased further.

Influence of Bulk Copper Morphology

In addition to three types of copper flake, two types of spherical copper powder have been evaluated as shown in Table 2.1. The key variables for these powders are the size, cleanliness (level of adsorbed organic on the surface), and shape. To confirm the importance of at least two of these parameters, experiments were done in which the copper flake was replaced by the low-cost spherical powder. The resulting circuits were very bright and shiny, and the electrical properties were better than the flake-based circuits.

At one time, the flake was thought to be a critical component due to its shape, and indeed flake-based mixtures have shown the ability to produce long traces and large areas without cracking. However, comparison to the results with the spherical powder suggested that the flake has a significant level of organic additives on the surface to facilitate the milling process by which it is made. These organic additives may inhibit the consolidation process. Also, the premise that copper flake would produce the tightest packing in copper circuits was found to be incorrect, largely because the flake does not lie flat. Though the electrical properties of circuits produced from flake-derived inks are acceptable, there are extensive voids in the traces, largely due to poor packing of the flake.

The poor packing of the flake-based inks is depicted in Figure 2.1, which shows SEM micrographs of the cross section (fracture surface) of the circuit traces produced from flake. There is an extensive void structure, similar in size to the diameter of the flake. The nanopowder is also shown well adhered to the surface of the flake, and higher magnification shows consolidation of nanopowder particles within larger clusters.

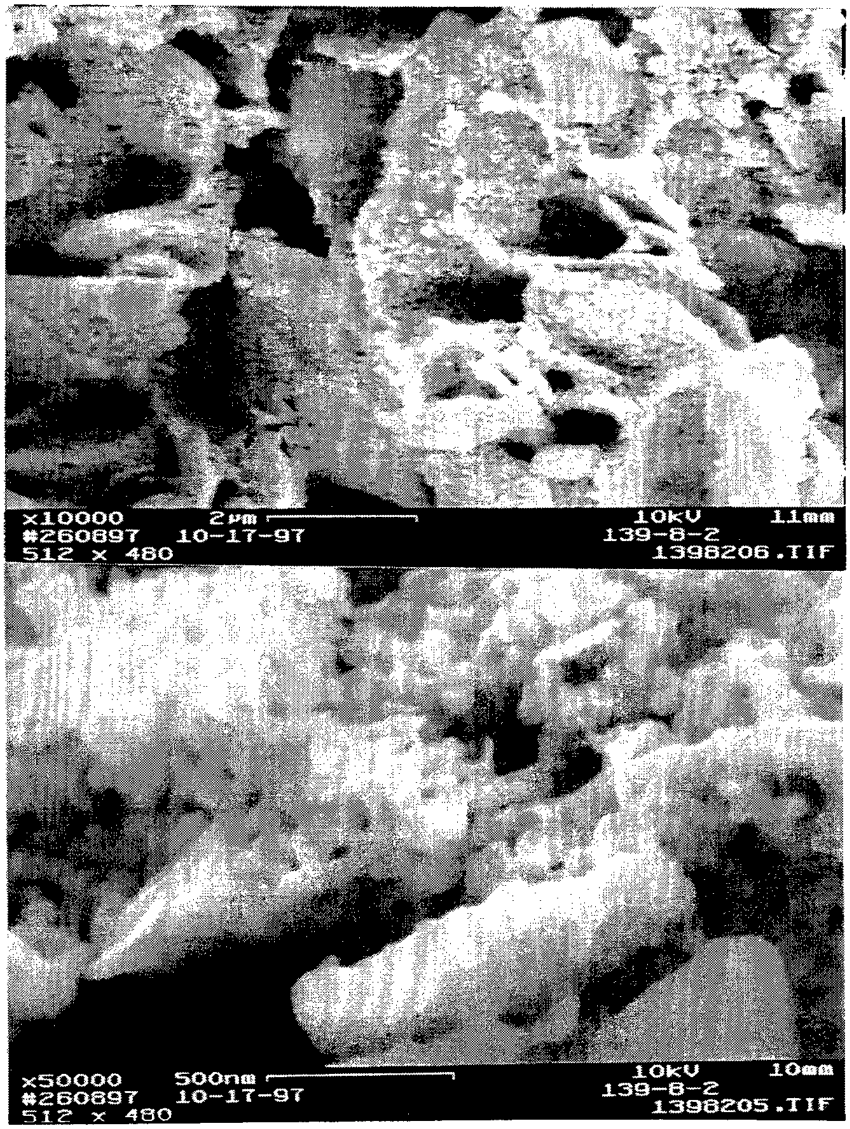


Figure 2.1 (a,b). Scanning Electron Micrographs (SEMs) of fracture surfaces in cured samples of Ink C-136 based on copper flake and copper nanopowder. Magnification 10,000 (a) and 50,000 (b).

What is clear from these micrographs is that the packing of the flake is not two-dimensional. That is, though the flakes are flat, they do not lie flat. This packing configuration is a problem in that the interconnections between the flakes when they do not lie flat are even worse than with spherical particles due to the large flat surface of the flake. The result is an extensive void structure.

Packing of Copper Spheres Improved over Copper Flake

The surprisingly good electrical properties obtained with the 9-micron spherical copper powder shown in Table 2.1 suggested that there might be a significant difference in the microstructure as compared to the flake-based inks. Figure 2.2 confirms that the packing is generally tighter, but that gross voids are still present in the microstructure. Further, the extent of coverage of the spheres by the copper nanopowder is striking as compared to the flake-based ink. The reason for this may be that the spheres have a lower surface area than the flake, and as a result there is relatively more nanopowder to interconnect the spherical powder particles. The surface of the spheres may also be cleaner than the flake due to the processing additives used in milling copper powder to flake. The presence of ductile fracture in the necks of consolidated nanopowder between 9 micron particles is clearly evident. This indicates the formation of solid metal with good mechanical and electrical properties linking the larger particles.

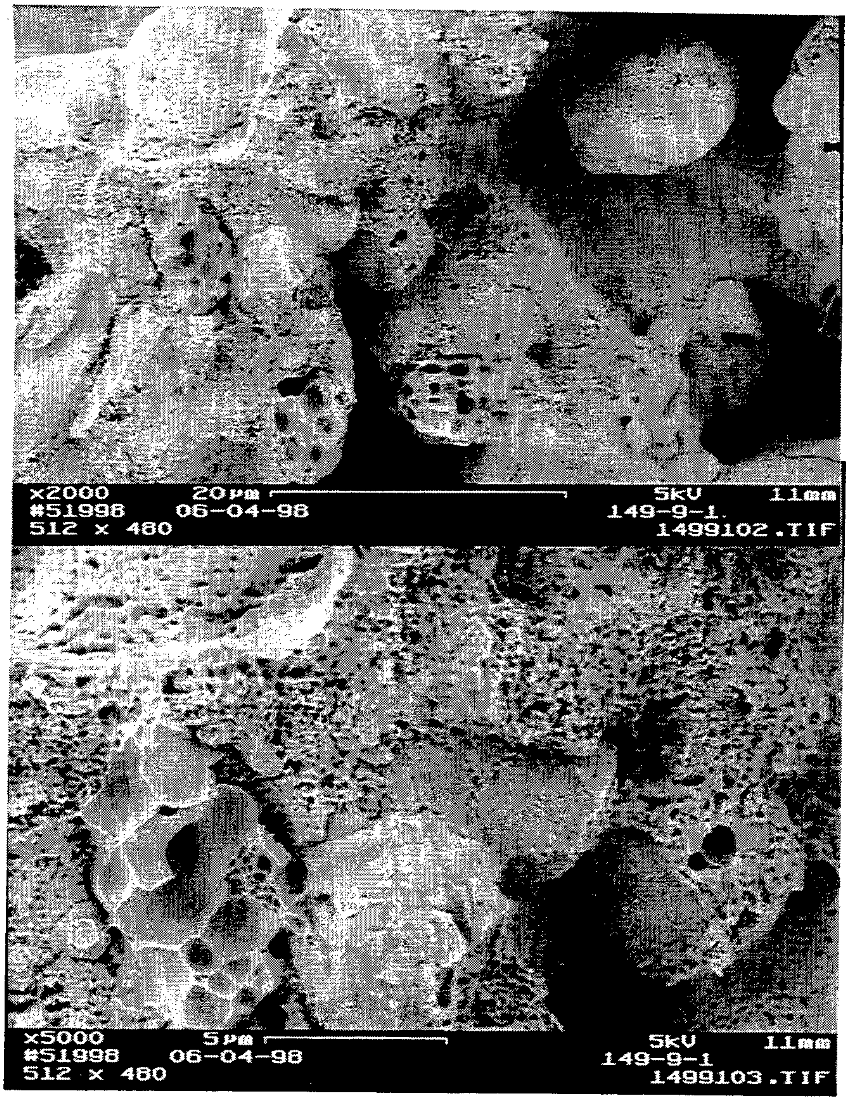


Figure 2.2 (a,b). SEMs of fracture surfaces in cured samples of Ink C-177 based on 9-micron copper powder and copper nanopowder. Magnification 2,000 (a) and 5,000 (b).

Another reason for the enhanced electrical properties may be the reduction in the number of smaller voids that are clearly present in the flake-based ink. Few such voids are present in the spherical copper system, and it is postulated that the reduction in the number of these voids, despite the presence of some much larger voids, enhances the electrical properties of the circuit. Again, the reduction in smaller voids appears to be due to the presence of relatively more nanopowder particles, which can fill the interparticle regions in the bulk copper, as well as better packing of the spherical particles.

A logical extension of these data obtained with nanopowder would be to continue to add nanopowder in order to fill in more of the voids. Unfortunately, continued addition of nanopowder leads to cracking of the circuits, likely due to the large volume reduction associated with extensive consolidation. This illustrates the importance of larger copper particles that provide bulk "building blocks" for the circuit. Further, the larger copper particles provide a better electrical pathway with fewer connections than, for example, sintered nanopowder. The optimum level of nanopowder for the overall consolidation process will be discussed in next section.

Copper Nanopowder A Key Component

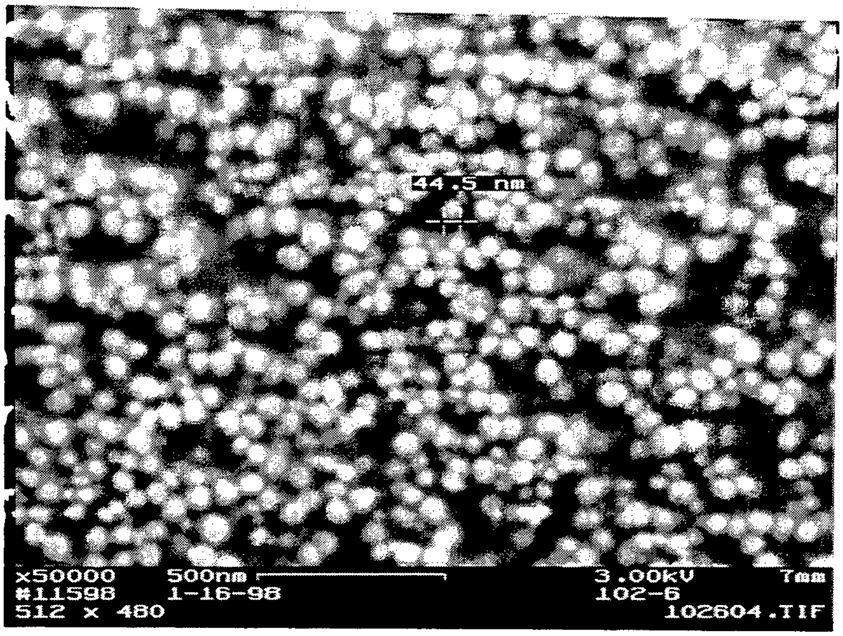


Figure 2.3. SEM of copper nanopowder prepared by wet precipitation. Note the uniform particle diameter of approximately 50 microns and the lack of agglomeration.

The micrographs in Figure 2.2 clearly show that the nanopowder acts to interconnect the relatively large 9-micron copper spheres. What is most striking is the degree of consolidation of the clusters of nanopowder particles. Figure 2.3 shows that the as-synthesized nanopowder particles have a very uniform size of~50 nm, and that they are not agglomerated. In the case of the heat-treated ink shown in Figure 2.2, the single nanopowder particles have agglomerated to an average grain size 4-5 times that of the original nanopowder. As a result, the "glue" holding the bulk 9 micron spheres together has acted to consolidate the ink components, but the metal formed is still not equivalent to void-free bulk metal foil. Without the nanopowder the resulting metal would have very little integrity, since there does not appear to be any sintering occurring between the 9 micron spheres themselves, as one would expect at these low processing temperatures and short times.

Optimization of the Nanopowder- 3 Micron Powder Series

In order to optimize the level of nanopowder, several inks were prepared with varying amounts of the nanopowder as well 9 micron and 3 micron spherical powder. The results are shown in Table 2.2, and the microstructures of the resulting cured samples are shown in Figures 2.4-2.6 and 2.8-2.10

Table 2.2. Effect of Ink Composition on Cost and Resistivity.

	Components, wt. %						
Ink	9-micron	3-micron	Nano	Acid	Terp	Cost*	Resistivity microΩ-cm
3 micron powder with increasing nanopowder							
C-198		84	0	14	2	1.04	8.4
C-199		82	3	15		1.04	6.1
C-187		51.5	31.7	11.5	5.2	1.00	4.2
9 micron and 3 micron copper powder with increasing nanopowder							
C-200	53.6	32.8	3.1	10.4		0.52	5.3
C-203	51.7	30.3	6	12		0.52	4.8
9 micron and nanopowder with increasing 3 micron copper powder							
C-189	54	8.5	24.3	12.2	1	0.48	3.9
C-193	42.2	17.9	25.9	12.1	1.9	0.59	3.9

* Cost relative to ink C-187

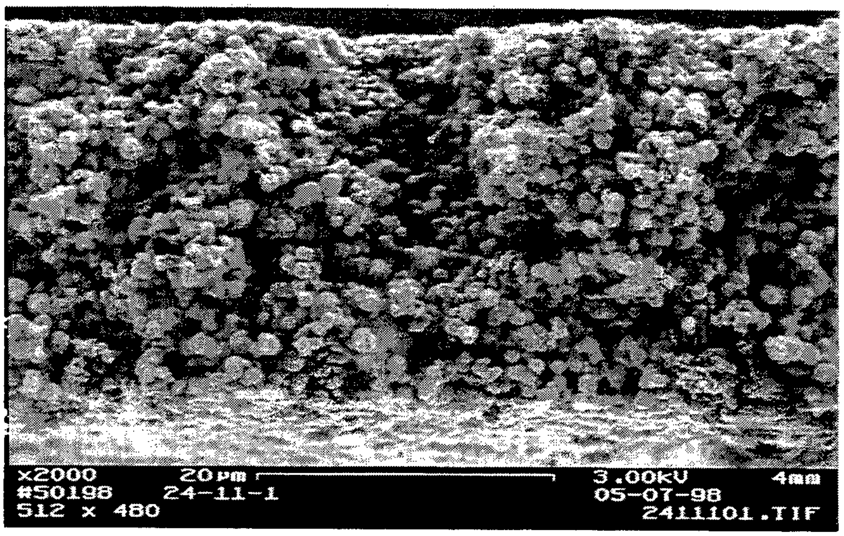


Figure 2.4 SEM of fracture surface in cured samples of Ink C-198 based on 3-micron copper only, cured at 320° C for 200 seconds. Magnification 2,000.

A series of inks was prepared using only 3-micron powder and nanopowder. These microstructures are shown in Figures 2.4-2.6. Some consolidation was observed when no nanopowder was utilized (Figure 2.4, Ink C-198), illustrating the cleanliness of the 3-micron powder and the fact that it is small enough to agglomerate even at this relatively low temperature (320°C). The large voids observed in previous micrographs are not present in the microstructure, as was expected if the nanopowder were a major contributing factor to the creation of such voids. The resistivity was ~8 microohm-cm, which is good, considering that only ROM and no nanopowder was used. The outward appearance of the circuits was very bright copper.

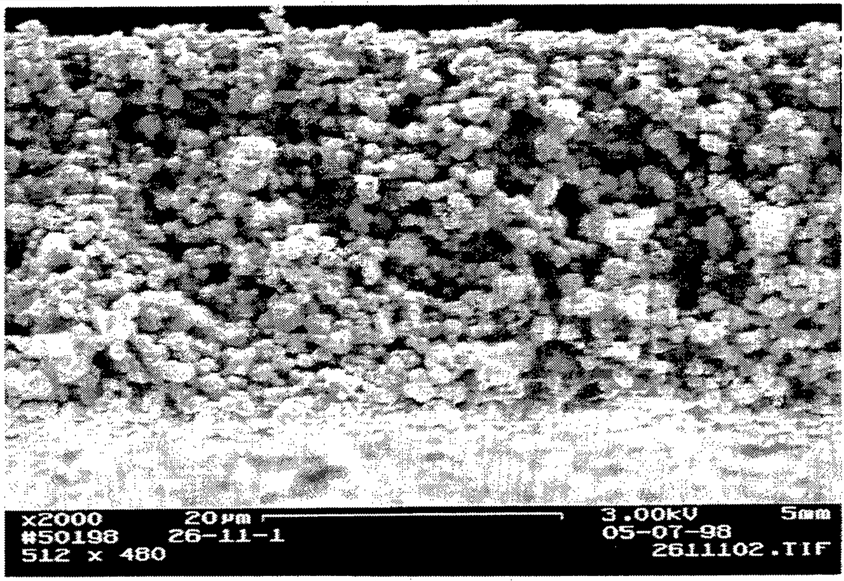


Figure 2.5. SEM of fracture surface in cured sample of Ink C-199 based on 3-micron copper with 3% nanopowder, cured at 320° C for 200 seconds. Magnification 2,000

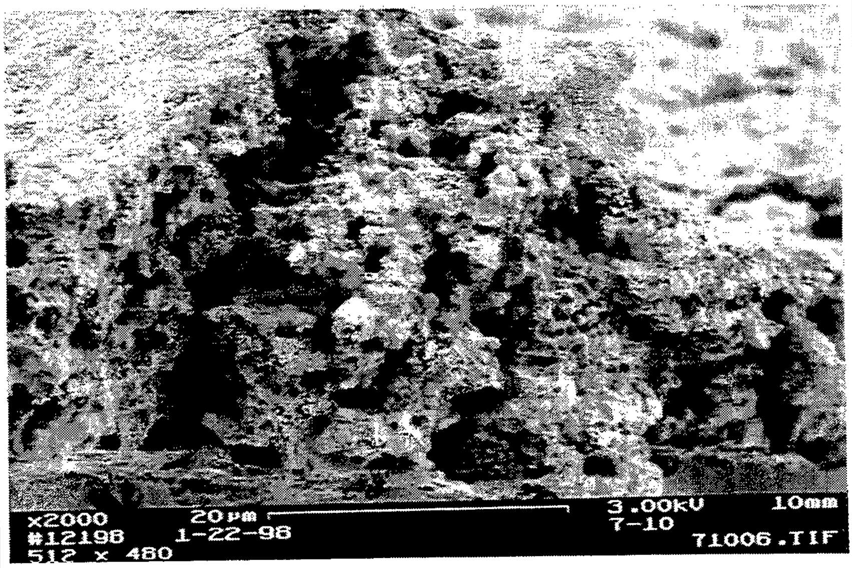


Figure 2.6. SEM of fracture surface in cured sample of Ink C-187 based on 3-micron copper with 31.7% nanopowder, cured at 320° C for 200 seconds. Magnification 2,000.

The effect of the addition of 3 wt.% nanopowder on the microstructure is shown in Figure 2.5 (Ink C-199). More extensive consolidation was observed, and the powder components packed well, with no observable large voids. The resistivity was ~6 microohm-cm, which is better than ink C-198 with no nanopowder, but not as good as inks prepared with more nanopowder. Three wt % of nanopowder corresponds to approximately 5-10 layers of nanopowder on the surface of the 3-micron powder, not enough to fill the smaller voids between individual 3- micron particles. The circuits prepared were again very bright copper.

Figure 2.6 (Ink C-187) shows the dramatic effect of the addition of a significant excess of nanopowder on the microstructure. It is difficult to discern discrete 3-micron particles at lower magnification, though it is clear that there are larger voids in the microstructure. Significant bonding can be observed, particularly between the 3-micron particles where the nanopowder has effectively filled the interstitial voids. The resistivity is very good at 4.5 microohm-cm, and the appearance of the circuit is bright copper.

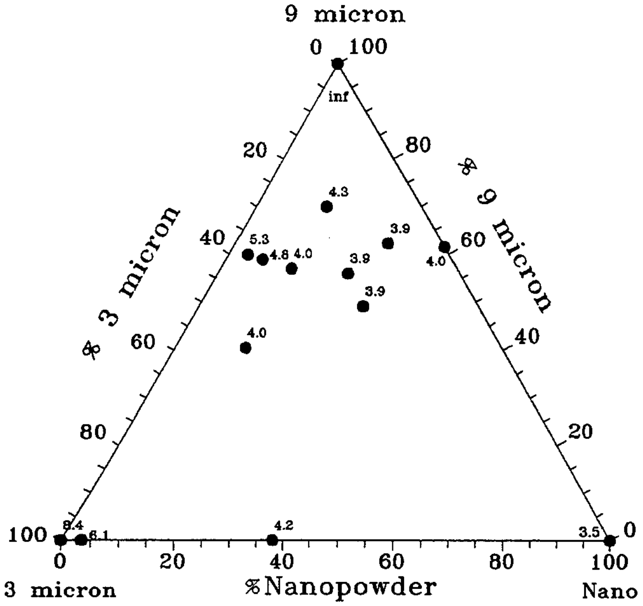


Figure 2.7 Ternary diagram showing the effect of the three copper powder constituents, 9-micron, 3- micron and nanopowder. The parameter is resistivity in microohm-cm.

The effect of systematic addition of increasing amounts of nanopowder is shown in the ternary diagram in Figure 2.7 as the 3-micron-nanopowder leg of the triangle. When enough nanopowder is used to fill the interstitial voids between the 3-micron particles, the micro-structure, which shows extensive bonding between the nanopowder particles, has a positive influence on the electrical resistivity.

While the nanopowder is critical to achieving a well-bonded structure, it is not capable of forming a trace of adequate mechanical integrity by itself, nor will it completely fill the interstices between larger particles in a binary or ternary mixture. The reason for this is not known, although the shrinkage in volume as the nanopowder particles consolidate makes it impossible for them to form an entirely homogeneous structure with a rigid assembly of larger particles to which the nanopowder is fusing. It may be that the nanopowder contributes to this problem by bonding the large particles together early in the consolidation process, locking them into a structure with large internal voids.

Optimization of the Ternary 9-Micron-3-Micron-Nanopowder-Series

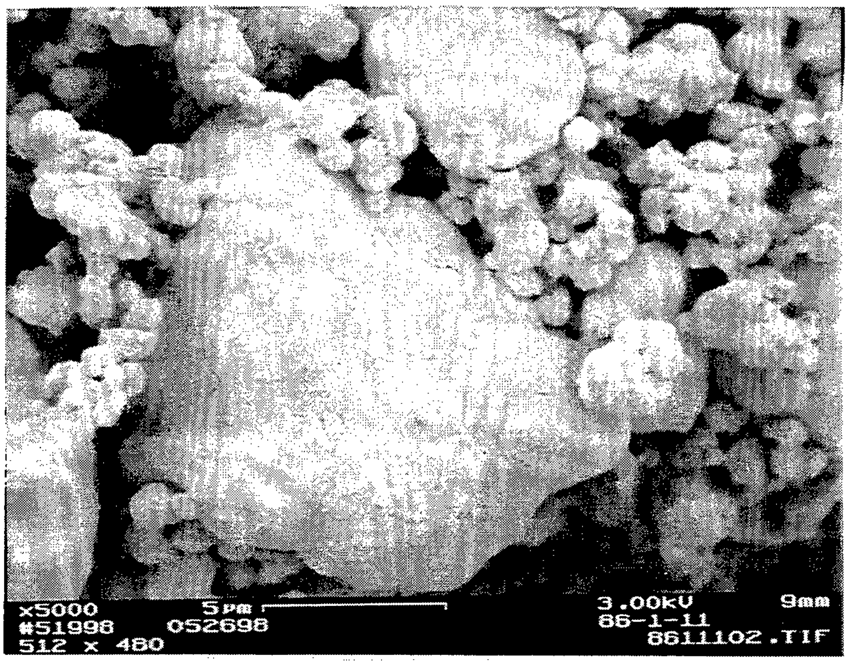


Figure 2.8. Fracture surface in cured sample of Ink C-200 based on 9-micron copper, 3-micron copper and 3.1% nanopowder, cured at 320° C for 200 seconds. Magnification 5,000.

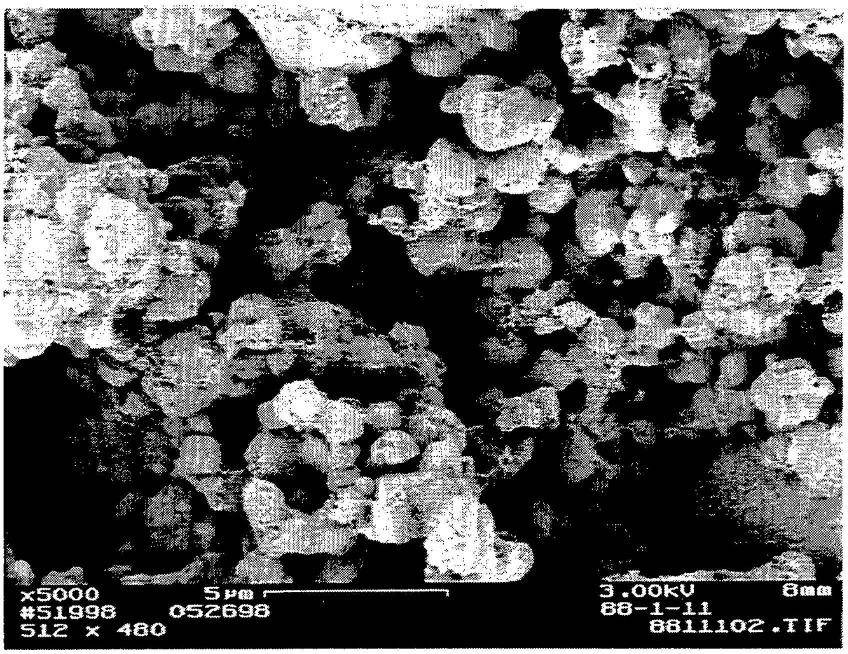


Figure 2.9. Fracture surface in cured sample of Ink C-203 based on 9-micron copper, 3-micron copper and 6% nanopowder, cured at 320° C for 200 seconds. Magnification 5,000.

The incorporation of 9-micron spherical powder with the 3-micron powder and nanopowder reduces the cost of the mixture by more than 50%. Further, the 9-micron spheres provide more bulk and electrical pathways which are comprised of fewer grain boundaries resulting from the bonding of particles. Figure 2.8 shows the microstructure when the three powders are used, with a minimal amount of nanopowder included. There is extensive bonding, however some large voids are present. This contrasts with the results obtained with the 3-micron-nanopowder system where, with a similar level of nanopowder, no large voids were evident. The voids appear to occur adjacent to the large 9-micron spheres, and are likely the result of poor packing around these larger components. The resistivity of 5.3

microohm-cm is slightly better than the circuits produced from the analogous 3-micron-nanopowder ink at 6.1 microohm-cm, and the appearance is bright copper.

Figure 2.9 shows that doubling the level of nanopowder has little effect on the packing, as there are still large voids present. However, the interparticle bonding is improved, as evidenced by the presence of ductile fracture zones between particles. As was observed in the 3-micron-nanopowder system, increasing the level of nanopowder to 25.9 wt % results in better filling of the interstitial voids, and the circuit is well consolidated, as shown in Figure 2.10, with excellent resistivity (3.9 microohm-cm) and bright copper appearance.

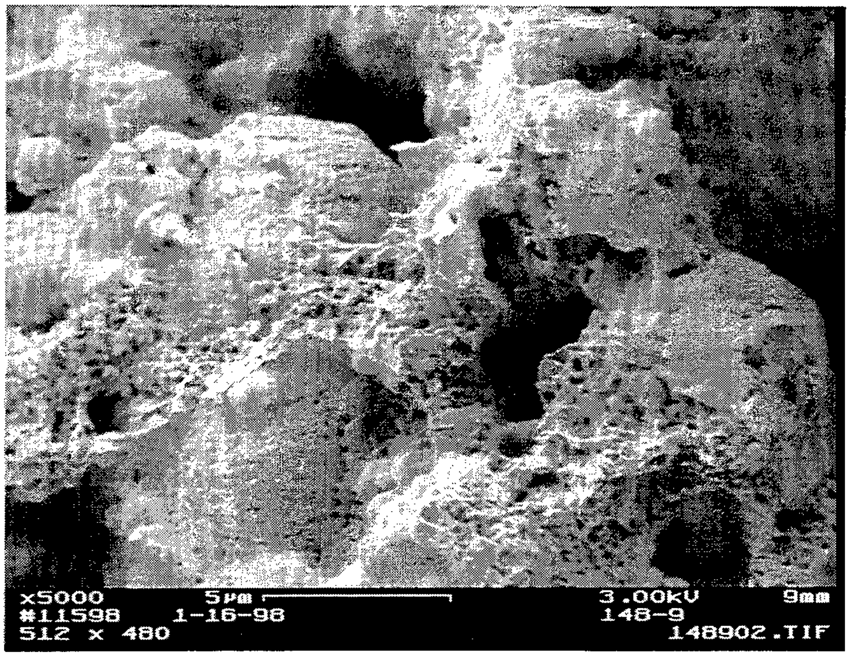


Figure 2.10. Fracture surface in sample of Ink C-193 based on 9 micron copper, 3 micron copper and 25.9% nanopowder, cured at 320° C for 200 seconds. Magnification 5,000.

The fracture surface of this near optimum composition still exhibits large voids. These not only represent an electrical discontinuity, but they are metallurgical weak spots in the circuit. While the metallic structure is better than that with less nanopowder, as evidenced by the large number and larger size of the ductile fracture sites, there is still a serious lack of ductility in the circuit traces as a whole. Further development is in progress to achieve better consolidation and better electrical and mechanical properties. Interaction with the substrate is also critical in achieving rugged and reliable structures. This will be discussed under Task 4.

Alternate Carboxylic Acids

The carboxylic acid which was most extensively used with the best results was neodecanoic acid. One of the steps of the overall curing process is the removal of organic residues from the copper components comprising the circuit. In an attempt to lower the processing temperature, several alternate carboxylic acids of varying chain length were evaluated.

Table 2.3 shows all of the carboxylic acids evaluated. Comparison of the resistivity data shows that none of the alternate carboxylic acids are as good as neodecanoic acid, but the acids structurally closest to neodecanoic acid do yield resistivities which are the same order of magnitude as neodecanoic acid. Circuits derived from the longer chain acids had very poor electrical properties, and consolidation of the metal was poor, as evidenced by the tape test results.

Table 2.3. Summary of Carboxylic Acids Evaluated in the PARMOD™ Process.

Ink #	Acid	Resistivity	Tape Test	# Carbons
C-110	Neoheptanoic	8.4	powdery	7
C-109	2 ethyl hexanoic	9.3	powdery	9
C-111	Oleic	101	powdery	18
C-102	Neodecanoic	6.1	clean	10
C-115	Cyclohexane butyric	14.0	powdery	10
C-113	Tridecanoic acid	15.0	powdery	13
C-116	Stearic	103	powdery	18

Conclusions

1. The key to producing well-consolidated copper traces is the presence of copper nanopowder in a Reactive Organic Medium (ROM).
2. The ROM can be either a Metallo-Organic Decomposition (MOD) compound or the acid from which it can be formed
3. Bulk copper powder is necessary to provide a framework for dimensionally stable conductor traces.
4. Using spherical bulk copper powder constituents improves the packing in the as-deposited ink relative to copper flake. Copper flake does not lie flat after printing, resulting in an extensive void structure.
5. A clean bulk copper surface, free of adsorbed species from the processing of the bulk copper components (e.g., milling spheres to produce flake) greatly enhances the consolidation process, improving the conductivity and appearance of the circuits and lowering the processing temperature dramatically.
6. Copper nanopowder coats the larger bulk copper particles, acting as a "glue" between them.
7. The smaller the copper particle, the faster consolidation occurs, providing the materials are free of adsorbed organics. The interconnecting nanopowder necks between the bulk copper spheres are ductile, but tend to have a void structure of their own related to the rapid sintering of the nanopowder.
8. Too much nanopowder results in a more extensive void structure, apparently because the as-deposited ink does not flow to eliminate the voids.

Task 3. Xerographic PARMOD™ Toners

The objective of Task 3 has been to create PARMOD™-based toner particles with the characteristics required for successful electrostatic printing. Success in this effort will allow PARMOD™ technology to be applied under digital control. Conductive circuit traces can be produced direct from CAD files without intermediate tooling using the equivalent of a laser printer. Electrostatic printing offers advantages in high resolution and in printing speed relative to ink jet printing and dispensing, which are the other candidates for digital printing. The same advantages hold relative to screen printing, which has been used for most of the evaluations in this project. Electrostatic technology can also be operated in a "Xerox copy" mode for still faster production of a given circuit design.

The development of a successful toner 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 particles, as well as their ability to convert to well-bonded electrical traces.

During the first year of the program, dry PARMOD™ toners were synthesized, and a device for coating adhesive patterns with them was built. The results were moderately successful in that a toner image could be deposited and cured to a conductive circuit trace. They were disappointing in that the traces were not of high resolution, and to reduce background, excess toner had to be blown off the surface, which was inefficient and undesirable in a finished machine.

The silver PARMOD™ toner was hygroscopic and difficult to prepare and maintain in a free flowing, finely-divided state. The size reduction was accomplished by cryogenic grinding in liquid nitrogen. The dry nitrogen atmosphere above the toner could maintain the desired size dispersion, if care was used to exclude air and moisture.

In an effort to obtain a more uniform size dispersion, the silver toner was passed through a jet mill with a ten-micron nominal cut off. The toner did in fact pass through the mill, indicating that it had reached the desired size, but when caught in the bag filter down stream of the mill, it had reagglomerated to large, sticky chunks. It would be possible in principle to build a coater based on providing toner powder direct from the jet mill using dry air or nitrogen as the driving gas, but this did not seem attractive as a product, and alternative approaches were sought.

A literature survey of electrostatic printing technology suggested that liquid toners offered far more promise than dry toners for this application because they provide high resolution in very simple equipment and have much more latitude in composition than dry toners. Additional experience showed that the original expectation that a true colloidal dispersion of PARMOD™ would be required for a useable liquid toner was not true, and that the latitude was even greater than expected.

A trip to Specialty Toner, Inc. in Fairfield, NJ served as an introduction to the liquid technology, and a mass of useful information was obtained on the toners themselves and on the hardware to use them. An even more important contact was made with Electrox Corp in Newark, NJ. Partnerships has purchased an Electrox prototype printer to support this Phase II program, and all of the meaningful work in developing toners has been done with it.

In the second year of Phase II fifty-five liquid toners 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 toner has been developed with the desired printing, transfer, and curing properties.

Liquid Toner Technology

Liquid toner technology is described in reference (4). It 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. The technology was pioneered by Ricoh and Savin in the early 1970's. Improvements in the toner to permit depositing thicker images were developed by Benzion Landa, who has since founded an independent company, Indigo, to commercialize that technology. A sizeable joint venture between DuPont and Xerox called DX Imaging was founded to pursue high quality commercial printing applications. The venture went out of business in 1990, but some activity remains in the parent companies. Versatec and CalComp have produced electrostatic plotters, and AM Graphics has an electronic printing system.

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 requirement to evaporate the residual dispersant from the finished product makes liquid toner technology unattractive relative to dry toners for office copying applications. It is not a serious barrier to industrial use.

The charge control agents (charge directors) are typically ionic surfactants and metal soaps added to the resin particles. N-vinyl pyrrolidone is used for negative toners. Divalent and trivalent metal carboxylates are excellent charge control agents for positive toners, and are of course acceptable constituents of PARMOD™ mixtures.

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. Acids such as phosphoric acid incorporated in the particle and leached into the inverse micelles enhance the charging effect. Non-leachable acids such as copolymers of styrene-sulfonic acid with basic inverse micelles of divalent metallic soaps give negatively charged toner particles and positively charged inverse micelles. Aminoalcohols are very effective inverse micelle formers for negative toners.

Electrostatic printing

An electrostatic printer shown schematically in Figure 3.1 was obtained from Electrox Corporation of Newark, New Jersey. The printing process works by applying an electrostatic charge to a photoimaged layer on a grounded substrate. 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. This image can be cured directly by heating the substrate to convert the PARMOD™ to pure metal traces, which are well-bonded to the polymer cladding.

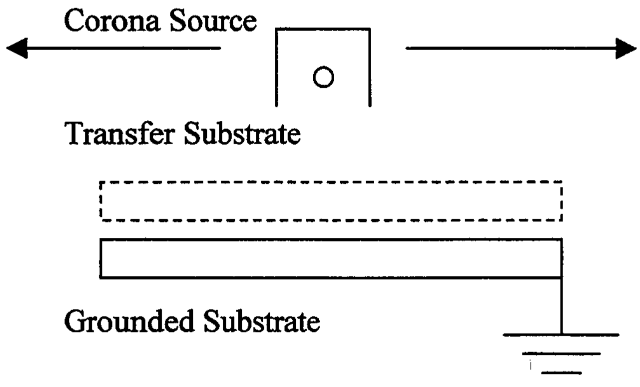


Figure 3.1 Electrostatic printer

Alternatively, the image can be transferred to a transfer 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 charge. Under the influence of the transfer charge, the toner is transferred through the dispersant 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.

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 sufficiently charge the particles 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.

Charge Directors: Metal Carboxylate Salts

The search for a charge director began with long chain metal carboxylate salts. The long organic chain of the carboxylate allows for dispersion in the non-polar alkane dispersant through the formation of inverse micelles, and the ionic interaction of COO^- group with the silver particles produces a charge on the particles. The metal carboxylate needs to be adsorbed on the surface of the silver particles in order to impart a charge to the particles. With adsorption on the surface, the long organic chain of the metal carboxylate then protrudes into the alkane solvent to form inverse micelles. This should allow dispersion of the silver particles.

Initially silver flake was used as the silver particle. The silver flake was coated with a silver carboxylate salt dispersed in an alkane solvent. These toners did print, but had major problems. When the printing was good (a complete image without a halo) there was almost no adhesion of the particles, meaning the image broke up very quickly after forming. The conductivity of the suspension (which is related to the amount of charge on the particles) could not be varied, since the charge director was an intimate part of the particle. In order to get better adhesion, the conductivity of the suspension had to be raised to increase the amount of charge per particle.

As a way of varying the charge, the silver flake (uncoated) was dispersed in the alkane solvent and then the silver carboxylate salt was dissolved in the dispersion. By varying the concentration of the carboxylate salt, the conductivity of the suspension (and therefore the particles) could be changed without changing the silver particle concentration. Tests on these toners resulted in very poor printed images. Although the conductivity of the suspension could be raised, the amount of charge per particle was not increased; thus the highly conductive suspension simply washed away the printed image.

Charge Directors: Carboxylic Acids

The next approach was to use a carboxylic acid as CD. The conductivity of the suspension could be controlled relatively well with the addition of more acid, and the acid had a stronger affinity for the surface of the silver particles, thereby imparting more charge per particle than the carboxylate salt. Several carboxylic acids were tested for variations due to changes in the properties of the acid. Mono- versus di-acids, short chain versus long chain, saturated versus unsaturated, and weaker versus stronger acid value were all studied. In the end, there was no corresponding pattern between printing properties and the various acid properties.

As toners, the carboxylic acid charge director with a silver flake particle did not work particularly well. The printed images tended to have a halo indicating the presence of oppositely charged particles or did not print the centers of the features in the image. The adhesion of the particles was however fairly good. The conclusions from these results were that the carboxylic acid does not provide enough charge per particle. This results in only partial charging of the toner and thus poor electrostatic prints.

Charge Directors: Carboxylic Acids with Surfactants

It was determined that in order for the carboxylic acids to work, they had to be able to ionize better in the non-polar dispersant. This was accomplished by adding a second component, which would more readily form inverse micelles in the solvent, but have a weaker affinity for the surface of the silver than the carboxylic acids. These inverse micelles then allowed for better solubilization (ionization) of the carboxylic acid coated particles, which in turn provided more charge per particle. Several types of surfactants were tested for this role of the second charge director (CD2), including fatty amines, polymeric esters, phosphated diglyerides, sulfonates, and functionalized diblock copolymers. Each of these types of surfactants was paired with several different carboxylic acids to determine the best combination in terms of printing properties.

This double CD system worked much better overall than the single CD formulations. Once again, as seen with the various acids, there were no consistent patterns seen in the various combinations studied. Some of the combinations gave very poor printed images while others gave very good printed images, but no correlation could be made to the properties of the CD components.

The polymeric ester surfactant did not work well in conjunction with the carboxylic acids because, while the acid gave the particles a negative charge, the polymer ester provided a positive charge. These conflicting charges made both the positive and negative printed image. In the two component formulations, the two components must both provide the same type of charge to the particles, in this case a negative charge.

The phosphated diglyceride also did not work. With time, the formation of agglomerates could be seen in the dispersion. The printed images were not very good. The print was very thin and the centers of the features did not print. Due to the poor printing performance and the lack of stability, these were not considered further.

The sulfonate surfactant in combination with a carboxylic acid was found to have the capability of providing a tremendous amount of conductivity to the suspension. This was good and bad. It made providing enough charge on the particles easy, but also made it difficult to keep the suspension conductivity under control. The problems seen with these toner formulations were all related to controlling the conductivity of the suspension. If the suspension was too conductive (>6 pmho/cm) then the particles lost adhesion very quickly. It was found that a suspension conductivity of about 2-3 pmho/cm worked the best. Toner E-46 (comprised of silver flake, carboxylic acid, sulfonate, and alkane solvent) worked the best giving a good printed image (the edges of the features were, however, rough) with good adhesion of the particles. This formulation is a printable liquid toner, but not for high-resolution images.

The silver flake used had a 10 micron average particle size. This was believed, in part, to be the cause of the resolution problem with the edges of the image. By decreasing this particle size, the edges of the image should become smoother. A smaller silver particle (50 nm) was obtained for this purpose. It was synthesized so that the particles were coated with a carboxylic acid as they formed. The use of this coated silver nanopowder meant that a carboxylic acid did not have to be added to the dispersion.

The sulfonate toner E-50 was formulated using the coated silver nanopowder. This toner worked very well, giving a very sharp, high resolution printed image with good particle adhesion. This formulation worked very well as a toner; however, the suspension conductivity was not stable. Since the suspension conductivity is vital to the printing properties of the toner, this instability was a major problem.

The fatty amine surfactant with a carboxylic acid could not give as high a conductivity as the sulfonate, but provided a stable suspension conductivity. The formulations with the silver flake printed very well, but as seen before, the edges of the image were rough. The highest suspension conductivity that worked was only 0.7 pmho/cm. If the suspension conductivity was raised any higher, the particles lost adhesion.

Toner E-40 was formulated using the coated silver nanopowder with the fatty amine surfactant. This toner gave very good resolution and good adhesion; however, it printed well only up to a conductivity of about 1.0 pmho/cm. This is still very low compared to common liquid toners which have suspension conductivities of 20-100 pmho/cm. The ability to print only at such low conductivities indicates that the particles do not have a very strong charge and thus can be easily washed away by a low conductivity suspension. The charge on the particles needs to be as strong as possible not only to give a stable image but also to give a complete, clean transfer of the image in transfer processing.

A functionalized diblock co-polymer (FDCP) charge director was formulated with the silver flake plus a carboxylic acid and also with the coated silver. The silver flake toners printed very nice images, but as with the previous silver flake formulations, the edges of the image were very rough. These two toners did print well at higher suspension conductivities of 7.0 and 6.6 pmho/cm respectively and were stable with time. The coated silver nanopowder formulated with the FDCP and carboxylic acid 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 3.2. The properties of the best such samples are reported in Table 3.1. The thickness of these traces was measured by cross-sectional optical microscopy and also with profilometry. When the 10 micron 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 micron thick. It was shown that over a 125 cm long trace that was 0.396 mm wide, (3156 squares) resistance values of as low as 90 Ω could be obtained with resistivity values as low as 5.7 microohm-cm. These values are adequate to produce useful circuitry on the original photoimaged substrate without having to transfer the image to another substrate.

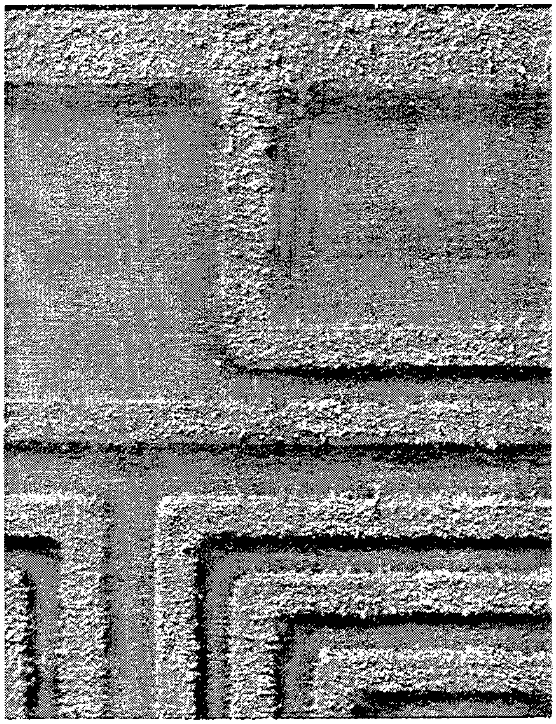


Figure 3.2 Electrostatically printed and thermally cured silver PARMOD™ image. Magnification 50x, 140 micron lines and 60 micron spaces.

Transferring the Image

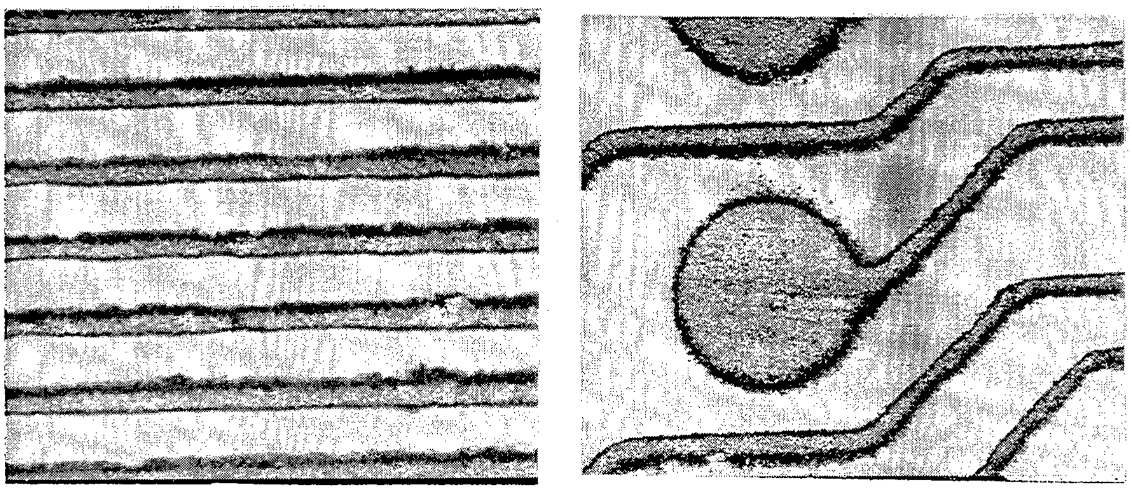
While printing directly on the original substrate may be adequate in some cases, a process in which the image is transferred to another substrate allows for a wider variety of substrates and for much faster production, since a single printing plate can be used to make numerous transferred images.

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, Kapton® or coated Kapton® 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.

Toner E-40 transferred sharp images, but they were always very thin. The toner would not completely transfer from the printed image to the substrate. Thus most of the toner was always left on the printed image. This poor efficiency of transfer was probably related to the charges produced by the fatty amine CD2. The fatty amine was not able to provide a large enough charge on the particles to allow complete transfer. The CD2 which was found to provide the best charge was the FDCP, and this was used in toner E-43.

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 Kapton®, polyester, Tedlar, silicone rubber, and G10/FR4 epoxy glass, all fell apart with time. 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. This instability of the transferred toner on polymer substrates has yet to be understood.

The high resolution transferred images made using toner E-43 were then cured to give a conductive silver trace shown in Figures 3.3 a and b. The cured metal properties of these samples are shown in Table 3.1. The samples on glass were cured at 400°C in air to give good silver adhesion to the glass surface (as tested using the Scotch tape test). The resistivity values obtained were as good as 1.7 $\mu\Omega$-cm. Although the resolution on Kapton® 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.



Figures 3.3, a, b. Electrostatically printed silver PARMOD™ images transferred to glass and cured. Magnification 50x. The lines in Figure 3.2 a are 60 microns wide with 120 micron spaces. The lines connecting to the pads in Figure 3.2 b. are 40 microns wide.

Table 3.1. Cured Properties of PARMOD™ Liquid Toners.

Toner/ Conduct. (pmho/cm)	**Substrate**	**Temp/time (^{o}C/sec)**	**Ohms per 125 cm**	**Cross sect. area (cm^2)**	**Resistivity (microohm-cm)**
Prints					
E40/ 0.48	Polymer	220/180	115	7.92*10^{-6}	7.3
0.68	"	"	90	"	5.7
1.06	"	"	150	"	9.5
E43/ 3.90	"	"	97	"	6.1
7.5	"	"	235	"	15
2.9	"	"	350	"	22
Transfers					
E43/ 2.70	glass	400/300	115	3.17*10^{-6}	2.9
2.70	"	"	67	"	1.7

Conclusions

The goal of this task to develop a PARMOD™ based liquid toner that could be electrostatically printed, transferred, and cured to give a high resolution, conductive trace was achieved. Further work still needs to be done to fine tune the properties for specific applications and to enable the high-resolution transfer to polymer substrates. Toner E-43 performs very well as a liquid toner, and owing to its PARMOD™ properties cures very well to give highly conductive silver images. At this point, E-43 can be used to print fine lined, high resolution images that can be transferred to glass and cured to give a highly conductive printed circuit trace.

Task 4. Adhesion of PARMOD™ to Various Flexible and Rigid Substrates

Early in Phase II most of the activity in Task 4 related to creating multilayer circuits. It was found that silver PARMOD™, which had been found to stick well to FR-4 epoxy-glass, would not stick to inner layer material, which is nominally the same composition. It has since been found that, except with a few types of epoxy-glass, an adhesive is necessary to get good adhesion on rigid boards, as it is on polyimide flexible substrates. The remainder of Task 4 has been devoted to investigating the suitability of various adhesives and measuring their performance.

Adhesion to Metals

In addition to adhesion to the polymer substrate, bonding of the PARMOD™ traces to metal pads and components is important. Preliminary work had been done on adhesion of silver and copper PARMOD™ to copper traces and component leads. The newer silver PARMOD™ compositions such as B-86 will bond to clean copper surfaces without special treatments. Copper PARMOD™ adheres even more readily because of its higher processing temperature and the acid constituent of the preferred compositions.

Copper Circuit Traces on Kapton® FN

The primary substrate utilized in all of these studies has been DuPont Kapton® FN, consisting of a Kapton® H core with FEP Teflon® coated on both sides. Other Kapton®-related substrates evaluated include Kapton® H, Kapton® EKJ, and Kapton® KJ. Table 4.1 shows a comparison of properties for the flexible Kapton® substrates evaluated.

Table 4.1. Summary of PARMOD™ Performance on Kapton® Films.

Film	Temperature	Resistivity	Appearance	Tape Test
Kapton® FN	250	7.6	Dull	clean
Kapton® H	320	4.8	Bright	did not adhere
Kapton® EKJ	250	7.0	Bright	did not adhere
	265	5.1	Bright	spotty
	300	4.8	Bright	clean
Kapton® KJ	300	4.8	Bright	clean
Al_2O_3	250	6.0	Bright	Did not adhere

With the introduction of a new series of inks based on cleaner, spherical powder, it has become possible to cure copper PARMOD™ circuit traces at temperatures as low as 250°C to achieve good consolidation and fairly good electrical conductivity. The adhesion of the traces to the Teflon® FEP coating of Kapton® FN has also been found to be adequate at 250° C as shown in Table 4.1. However, temperatures greater than 250°C are required for the copper circuit to become consistently bright and shiny and to get good adhesion to other substrates, and these are the limiting factors in determining the cure temperature.

PARMOD™ copper circuit traces of limited thickness (up to 3 mils) deposited and cured on 3 mil Kapton® FN can withstand a tight 180° bend with the metal on the outside, which is equivalent to an extension of 17% , without losing electrical continuity, though with some increase in resistance. This ductility is due primarily to the physical interaction between the copper trace and the FEP coating, which has apparently infiltrated the void structure of the circuit trace and stabilized it. Stand alone PARMOD™ copper traces do not exhibit this much ductility.

The mechanism for the adhesion of copper to Kapton® FN appears to involve softening of the FEP film, essentially embedding the circuit in the film. This mechanism is suggested by the near identity in the glass transition temperature of the FEP coating and the lowest temperature at which good adhesion can be achieved. It is also evident visually in that the PARMOD™ traces appear to be sunk into the FEP coating.

A problem that has been observed is movement of the film relative to the copper circuit leading to tensile stresses in the circuit traces. Cracks have been observed at cure temperatures greater than 320°C and for times longer than approximately 3 minutes. The cracks appear to be due to consolidation and shrinkage of the copper trace, as well as thermal expansion of the Kapton® FN substrate and the rigidity of the curing PARMOD™ mentioned above under Task 2. The mobility of the FEP coating is demonstrated by the fact that XPS studies of copper traces showed fluorine on the surface of the copper as well as at the interface between the copper and the Kapton® FN substrate.

Copper Circuit Traces on Kapton® H

It is possible to screen print patterns onto uncoated Kapton® H, and the screened patterns are dimensionally stable during heat treatment. Unfortunately, there is inadequate adhesion between the copper and the Kapton®. This supports the contention that the bond between the Kapton® FN and copper discussed previously involves the FEP coating. The circuits heat-treated on Kapton® H are very bright and shiny, likely due to the fact that there is no FEP to contaminate the system. Further, the transverse cracks that have been observed on Kapton® FN have not been observed on Kapton® H, further supporting the contention that differential motion between the well-bonded rigid copper and FEP-coated Kapton® plays a role in creating the cracks.

Copper Circuit Traces on Kapton® EKJ

An alternative to Kapton® FN is Kapton® EKJ, a substrate with a Kapton® E core and KJ coating. The KJ coating is a polyimide with a glass transition temperature of 220°C, which is lower than the FEP coating on Kapton® FN at 255°C , and much lower than that of the Kapton® E core. Circuits printed on Kapton® EKJ and Kapton® KJ alone have excellent electrical properties, and the circuits are bright and clean. At cure temperatures below 290°C the circuits do not adhere well to the substrate, though the electrical properties are excellent (Table 4.1). At higher temperatures, the copper adheres to the substrate and the electrical properties are still excellent. The mechanism of adhesion appears to be the same as with Kapton® FN, namely physical wetting of the copper traces by the fluid adhesive.

Another consideration related to the use of EKJ and KJ substrates is the tendency for these films to curl at temperatures where adhesion is improved. This phenomena may be due in part to the copper circuit being embedded in the KJ film and in part due to differences in the coefficient of thermal expansion between the copper and the composite substrate.

Copper Circuit Traces on Uncoated Epoxy-Glass

The development of copper inks which could be heat treated at temperatures in the 250°C to 280°C range made it possible to extend the application of copper PARMOD™ inks to epoxy-glass laminate substrates. These low cost rigid boards can withstand only moderate temperatures up to 270°C. Copper circuit traces heat treated on this substrate are generally not as clean and bright as when they are deposited and heat treated on Kapton®. Further, the traces do not stick well to the epoxy-glass, and the conductivity is not as good as circuits produced on Kapton® FN. The properties of copper PARMOD™ circuits on coated and uncoated rigid substrates is summarized in Table 4.2

Table 4.2. Summary of Copper PARMOD™ Performance on Rigid Substrates.

Film*	Coating	Temperature	Resistivity	Appearance	Tape Test
G-10	No	250	355	Dull	powdery
FR-406	No	265	6	Dull	did not adhere
FR-406	LARC-SI	265	5.5	Bright	clean
G-11	No	265	6.4	Dull	did not adhere
G-11	LARC-SI	264	4.3	Bright	clean
P-95	No	280	7.2	Bright	did not adhere
P-95	LARC-SI	263	5.0	Bright	clean

* G-10, G-11, and FR-406 are epoxy-glass substrates.
P-95 is a polyimide-glass substrate.
LARC-SI is a soluble polyimide

The reason for the failure of the uncoated epoxy-glass circuits may be that the epoxy from the substrate matrix is a source of carbonaceous contamination, which could interfere with the overall consolidation process of the PARMOD™ ink. This contamination means that a barrier coating of some type is necessary on the epoxy-glass to prevent interaction with the copper circuit. The barrier coating must also act as an adhesive between the epoxy-glass and the copper.

Copper Circuit Traces on Uncoated Polyimide-Glass

Polyimide-glass laminate is an attractive, albeit expensive, alternative to epoxy-glass in that it can withstand higher temperatures, and the polyimide does not outgas to as great an extent as the epoxy-glass. Copper circuits heat-treated at temperatures from 250°C up to 300°C on polyimide-glass substrates were bright and clean with electrical properties equivalent to those obtained on Kapton® FN as shown in Table 4.2. Unfortunately, the circuits did not adhere to the substrate.

Soluble Polyimide Adhesion Promoter for Rigid Boards

To overcome the lack of copper adhesion to the epoxy-glass substrate, a soluble polyimide was deposited on the substrate. This material is designated as LARC-SI. It was developed by NASA Langley and is being commercialized by Par Technologies of Newport News, VA. The polyimide coating acts as a barrier between the copper-containing ink and the contamination from the epoxy-glass substrate. The circuits produced were bright and shiny with excellent electrical properties as shown in Table 4.2. Further, the adhesion to the epoxy-glass substrate was improved.

The use of the soluble imide was extended to the polyimide-glass substrates as well. The circuits produced were bright and shiny, and the adhesion of the copper to the polyimide-glass substrate was improved in this case also.

Preparation of Demonstration Circuit Boards for Tobyhanna Army Depot

The utility of the coated epoxy-glass substrates has been demonstrated with the printing and heat treatment of copper circuit traces on G-11 epoxy-glass. An initial board was prepared on uncoated G-11, and the circuit, though bright copper in the center of the board did not adhere well to the substrate. Coating the G-11 with LARC-SI soluble imide resulted in a bright circuit that adhered very well to the substrate.

The double-sided circuits shown in Figure 4.1 have been selected by Tobyhanna Army Depot personnel and Partnerships as a test vehicle to demonstrate PARMOD™ technology for CAD/CAM integration in producing spare parts for military electronics. An initial series of boards with silver PARMOD™ traces were produced by screen-printing and by dispensing under computer control. The latter approach demonstrated the ease of duplicating an existing circuit board by "teaching" an Asymtek dispensing machine the coordinates of all the traces and having it produce one or several duplicates automatically. The teaching process took approximately 1-½ hours per side and dispensing to create the traces took approximately 10 minutes per side.

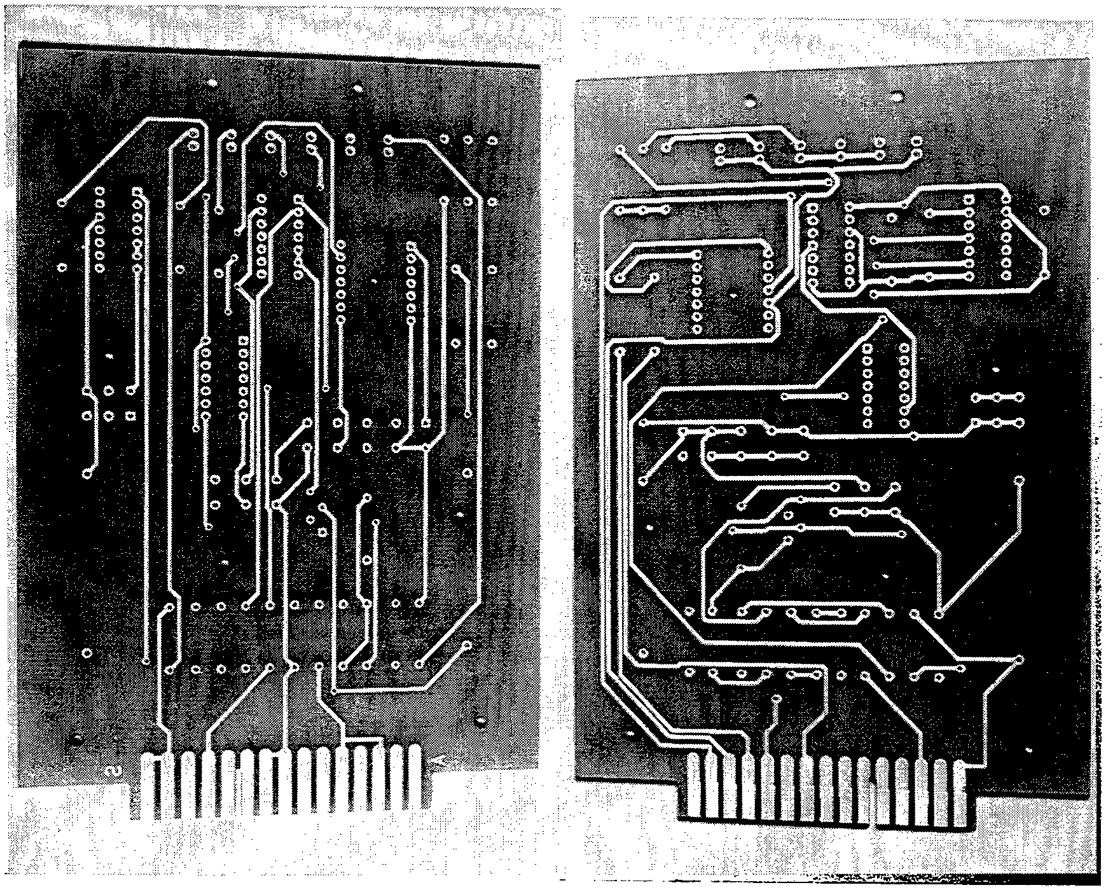


Figure 4.1 Circuit board chosen as a test vehicle for Parmod™ technology in prototyping and spare parts for military electronics.

Regrettably, the silver PARMOD™ boards were found to be unsatisfactory due to solder leaching of the traces in the wave-soldering machine. Coating the traces with solder mask cured the leaching problem but the solder mask penetrated the porous surface of the PARMOD™ and could not be removed in development. A solution to this problem is to screen the solder mask to avoid coating the pads in the first place. A dry film solder mask which does not penetrate the porous silver is another possibility. However, the bulk of the attention has shifted to copper PARMOD™ that does not suffer from solder leaching.

Copper circuits deposited and heat treated on LARC-SI-sealed G-11, were sent to Tobyhanna for evaluation. Initial tests showed that solder mask penetrates the porous copper surface and cannot be removed making soldering impossible. Hot Air Solder

Leveling (HASL) pretreating of the boards before applying the solder mask is a solution that has shown promise. Samples on soluble imide-coated polyimide-glass boards are being prepared in a continuing effort to establish this Dual Use Technology. A major program has been proposed to evaluate and qualify the boards so produced, as described in Active Business Developments below.

Alumina Substrates and Circuit Transfer Technology

An alternative to the preparation of a final product circuit on the substrate on which it will be used is a process by which the circuit is heat treated on a substrate from which it can be readily removed by adhesion onto the final substrate. In this way, low-cost, low-temperature substrates can be used.

Boron nitride-coated alumina substrates have been used to heat treat circuits at high temperature. The circuits release very well from the substrate, however, there are problems with the ductility of the copper and with achieving the right level of adhesion to the initial substrate to maintain the proper patterns while allowing the circuit to be removed. Kapton® H can also be used as an initial substrate in circuit transfer.

RFI Tags by Transfer Technology

The circuit transfer technology has been utilized to prepare LC circuits that comprise radio frequency identification (RFI) tag for various identification and tracking applications. Thick (~125 micron) coils were deposited and heat treated on BN-coated alumina substrate. It was very difficult to remove the coils from the alumina and secure them to the final polyester substrate without introducing transverse cracks. In one case, the coil was encased onto the alumina substrate with an adhesive coated polyester film. The backside of the tag (the capacitor) was mated to the coil using an adhesive. This tag resonated. PARMOD™ silver RFI tags are under active development as discussed below.

Metallizing Photodefined Dielectrics and High Density Interconnects

Metallization of both laser drilled and photodefinied microvias has been demonstrated. The compatibility of PARMOD™ materials with permanent, photoimageable dielectrics permits the application of PARMOD™ metallization to sequential build circuits in a very straight-forward way, offering the potential for time and cost savings. The cure conditions of the metallization and of the dielectrics are compatible, so that the metallization is almost "free" in terms of processing time and complexity. PARMOD™ metallization is also virtually free of adverse environmental impacts, simplifying the processing sequence further. A case study of the application of this technology to high density circuit metallization of a disk drive controller has provided s a quantitative example of the cost advantages of the PARMOD™ approach which is included below in Comparison of High Density Circuit Fabrication Costs.

Simultaneous Photodielectric Cure and Metallization

Probelec® from Ciba Specialty Chemicals is a widely used epoxy-based photoimageable dielectric intended for high-density sequential build circuitry. We have used it to demonstrate metallization with silver PARMOD™. Probelec® 7081 is a liquid coating which is dried at 90 C for 30 minutes to remove solvents. It is then photoimaged and developed with a solvent to remove unexposed material. Probelec® is normally cured at 150 C for 60 minutes, typical cure conditions for epoxy-based materials. Silver PARMOD™ metallization requires much less time but a higher temperature, up to 260 C, to bond both to the dielectric and to the existing copper conductors. The well-known tradeoff between temperature and time may be used to increase the cure temperature to accommodate the metallization, while using the fast conversion time of the PARMOD™ material (and the epoxy at these temperatures) to shrink the time at temperature to avoid damaging the epoxy and the FR-4 substrate. Additional research will be required to demonstrate that indeed the properties of the epoxy are unaffected or to develop materials which can withstand these conditions.

Pyralin® from DuPont, has been used for copper metallization on polyimide laminates and copper foils. This material works by photopolymerizing a precursor polymer, allowing the unexposed film to be removed by a solvent. The developed image is then imidized in a final cure at temperatures up to 400°C in an inert atmosphere for 30 minutes or more. During the cure, part of the precursor is eliminated as vapor, requiring a well-vented oven with applicable emissions control equipment. The Pyralin® cure conditions are more than adequate for copper PARMOD™ metallization, namely 250 - 340°C for a few minutes in an inert atmosphere during which the organic portion of the PARMOD™ compound decomposes and also leaves as vapor.

This congruity in the curing requirements of the metallization and the dielectric make it possible to combine the two processes to save time and processing complexity. This can be done by applying the PARMOD™ material after the photodielectric image has been developed, but before it has been cured. The PARMOD™ paste is squeegeed across the surface of the circuit to fill the conductive paths and vias with paste. Excess paste on the surface is removed by scrubbing, and the circuit is oven treated to simultaneously cure the dielectric, decompose the PARMOD™ compound and bond the resulting metallization to the dielectric. Remaining traces of metallization on the surface can be removed by microetching or abrasion, and another layer can be added in the same way as many times as desired to make sequential build up structures of any desired complexity.

High Density Interconnects

Sequential layers have been constructed on FR-4 laminate using Ciba's Probelec® photoimageable epoxy to image two layer patterns. The first layer contained rectangular pads 0.5 mm by 6 mm representing connections to underlying low-density circuitry. These were brought up to 100-micron traces on 150-micron pitch on the surface, representing connections to a semiconductor device. The samples were metallized by squeegeeing on silver paste, as described above, and curing at 260 C for 60 seconds. The resulting pattern is shown in Figure 4.2. The traces showed good electrical conductivity and resisted removal with tape.

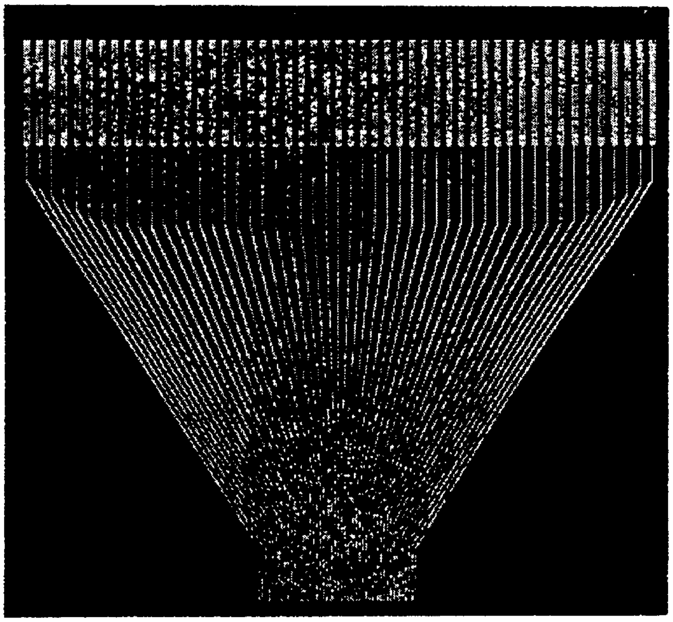


Figure 4.2 Fanout pattern on FR-4 with Probelec® photoimageable epoxy dielectric metallized with silver PARMOD™. 100 micron traces on 150-micron pitch.

Similar results have been achieved with photoimageable polyimides and copper metallization. The same pattern has been imaged with DuPont Pyralin® on a 10 mil thick copper substrate. In this case, the under layer contained no vias and the top layer contained the fanout pattern. This was metallized as above with a copper PARMOD™ composition followed by final cure for 60 minutes at 350 C in nitrogen.

These results, while still fragmentary, suggest that it will be possible to integrate the metallization of photodefined high-density circuitry with the thermal cure cycle of the dielectrics themselves, thereby eliminating costly and complex metallization by conventional electroless and electrolytic techniques. The additive nature of the PARMOD™ metallization eliminates the photolithographic and etching steps required to circuitize sequential build layers with a consequent saving of time and money. The environmental impact of decomposing the PARMOD™ compounds is the same as for curing photoimageable polyimides, and takes place under the same conditions, eliminating separate compliance issues relating to the metallization.

Microvias

It is possible to metallize microvias that are exposed on at least one surface with PARMOD™ materials. Early experiments were done with laser drilled holes through double-sided polyimide laminate. It was found to be possible to connect the opposite sides of a 100-micron diameter via in a 75-micron thick laminate by screening silver PARMOD™ material on one side. The result was a sliver rivet bonding the two sides.

More recent results are shown in Figure 4.3 in which 100-micron diameter laser drilled holes through one side of a 150-micron thick self-bonded polyimide laminate have been metallized with copper.

Figure 4.3. Laser drilled 100-micron microvias supplied by Teledyne Electronic Technologies metallized with copper.

These results were quite gratifying in the completeness of filling the microvias that could be achieved with relatively simple and quick processing. The apparent soundness of the bond to the copper laminate on each side is also encouraging. A cost model for the application of PARMOD™ to metallizing high-density circuits is given below.

Adhesion of Silver PARMOD™ to Various Substrates

As with the copper system, silver inks have variable adhesive properties depending on the substrate. The curing temperature of the silver inks has been reduced to 200°C, but depending upon the substrate, the temperature required for adhesion is usually higher. Good adhesion occurs directly on some substrates, while others require an adhesive coating in order to get good silver adhesion.

High temperature substrates such as glass, alumina, or Indium-tin oxide (ITO) all provide suitable adhesive properties without any additional adhesive coating. Corning 7059 alkali-free glass and standard soda-lime glass both give good adhesive and electrical properties when cured at temperatures of 300°C or higher (as determined by the tape test). Glass coated with ITO shows good adhesion with cure temperatures of 400°C and alumina substrates work at temperatures of 420°C. All of these substrates require temperatures of 100-220°C in excess of the cure temperature to get good adhesion. Since these are high temperature materials, the high temperatures are not a problem.

Polyimide substrates, such as Kapton®, require an adhesive coating on the surface for good adhesion of the silver. Kapton® FN, as mentioned previously, has an FEP coating with a T_G of 255°C. When curing the silver ink above this glass transition temperature, good adhesion is obtained. Kapton® EKJ has a polyimide coating with a T_G of 220°C. Good adhesion of silver can be obtained with temperatures of 220°C, but temperatures of 255°C are required for good adhesion after creasing the sample. As mentioned for copper, these adhesives work by softening and infiltrating the pores on the bottom surface of the silver trace giving a mechanical bond to the substrate.

Epoxy-glass rigid substrates are commonly used for printed circuit boards. The silver PARMOD™ could be cured on some types of these substrates with good adhesion, but not others. The G10/FR4 type of substrate, which is a low temperature epoxy, worked very well giving good adhesion with cure temperatures as low as 200°C. The G11/FR4 type which is a high temperature epoxy, did not give good adhesion at temperatures up to 260°C, where the epoxy started to brown.

In an attempt to find lower cost flexible substrates, samples have been obtained from a number of manufacturers to determine if any of them offer promise. Despite the reduction in cure temperature of the silver PARMOD™ to 200°C, adhesion to most of the low cost flexible polymer substrates is poor. Good adhesion is obtained by heating the sample to a temperature just above its glass transition temperature. When this was done with the low temperature polymer substrates, good adhesion could be obtained in some cases, but the polymer had lost its integrity by either melting or dramatically shrinking. The polymers that could withstand the heat treatment, did not give good adhesion. The most promising result was with Kaladex 2030 [polyethylene naphthenate (PEN)]. The silver did not adhere to the surface, but the substrate maintained its integrity. The silver trace could then be transferred to another substrate and adhered using common adhesives, such as acrylic. The substrates tested and the results achieved are shown in Appendix B in Tables B-1; Kapton® FN and FR-4, B-2; Glass substrates and B-3; Low temperature substrates.

Conclusions

1) Both silver and copper PARMOD™ form a good bond to copper pads.
2) An adhesive is needed to bond PARMOD™ to polyimide substrates.
3) Silver PARMOD™ will adhere to some low temperature epoxies.
4) Copper PARMOD™ requires a barrier layer on epoxies.
5) Both silver and copper PARMOD™ can be used with photodefined dielectrics.
6) PARMOD™ can be used to metallize microvias
7) Silver PARMOD™ will adhere to glass
8) None of the low temperature polymer substrates tested to date have shown real promise.

Comparison of High Density Circuit Fabrication Costs

This section examines the cost impact of implementing microvia technology by showing the before and after costs for a board that has been redesigned for microvia technology. The microvia technologies compared in this analysis are two variations on the photoimageable dielectric technology: one with screen printable PARMOD™ conductive inks over the photoimaged dielectric layer, and the other with more conventional plating and patterning over the photoimaged layer.

The method used for cost modeling is Technical Cost Modeling, as pioneered by IBIS Associates. A description of this method can be found elsewhere (5). The design used for this comparison is from a disk drive controller. Table 5.1 shows how the "conventional" disk drive controller board design compares to its microvia-based successor.

Table 5.1 Comparison of Conventional Versus Microvia Board Design

Disk Drive Controller	*Conventional*	*Microvia*	*Units*
Number of "conventional" metal layers	8	4	
Number of microvia metal layers	-	2	
Board width	4.3	4.3	in
Board length	7.84	5.25	in
Number of boards per 18x24 panel	10	16	
Number of PTH vias (diameter 1)	1,460	583	16 mil
Number of PTH vias (diameter 2)	12	12	22 mil
Number of PTH vias (diameter 3)	60	60	23 mil
Number of PTH vias (diameter 4)	196	196	40 mil
Number of microvias (diameter)	-	2,100	5 mil

Figure 5.1 shows how the two microvia technologies are implemented for this study. Liquid photodielectric technology is used to create microvias, then conductive ink is screen printed to fill the vias and create the circuit traces simultaneously. Alternatively, microvias created with the photovia technology can be plated and patterned, which metallizes the vias and creates circuit traces.

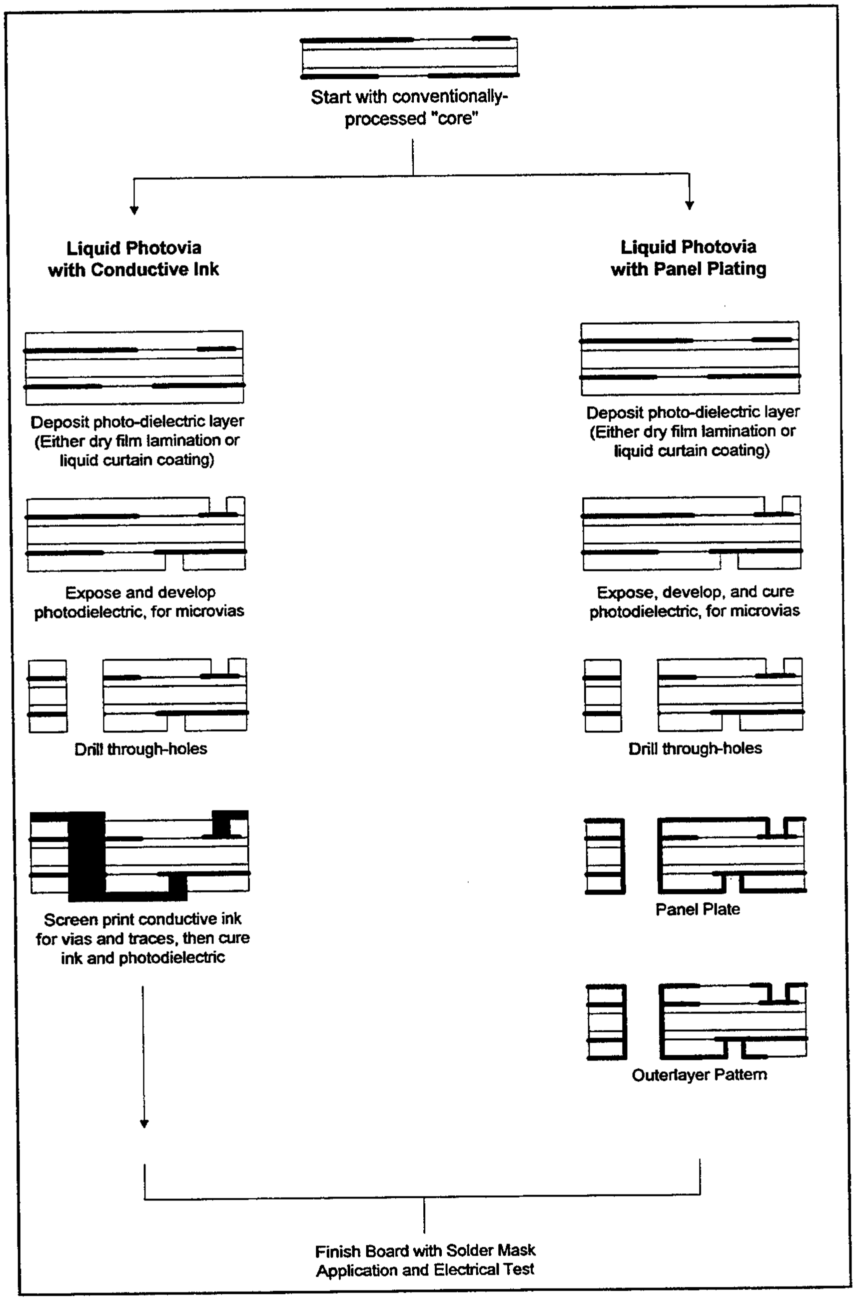
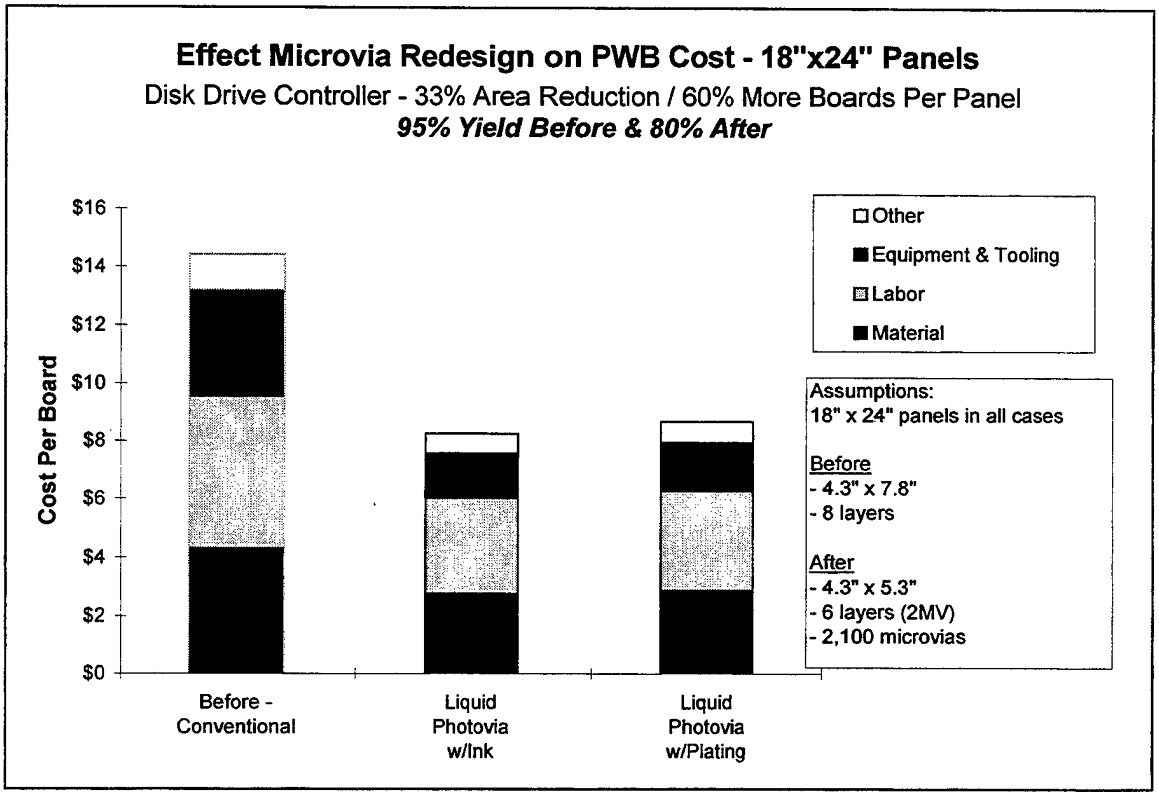


Figure 5.1 Process Flow for Two Microvia Technologies

Cost Modeling Results

Figure 5.2 shows the cost comparison for the disk drive controller application. Many of the critical modeling assumptions are listed on this graph. Given these assumptions, both microvia technologies cost less than the conventional board. This result stems mainly from the board area reduction possible through the use of microvias, which allows more boards to be processed per panel, which allows a lower cost.

The model assumes that 1.20 cc/sqft of conductive ink is consumed per layer that is deposited (including ink for filling microvias and circuit traces). At the baseline assumption of five grams/cc ink density and a price of $0.40 per gram of ink, about $2.45/sqft worth of ink is consumed per build-up layer. With these assumptions, it appears that it costs 4.6% less to use conductive ink technology than to plate up the surface of the photovia layer. Since the metallization is only a small fraction of the total cost, the percentage saving in metallization cost is greater still. It is important to note, however, that while plating has been proven, screen printing conductive inks in vias and traces simultaneously has not been proven yet. This graph serves to answer the question, "what if conductive inks could be used in such a way?"



5.2. Comparison of Conventional vs. Microvia Boards - 18"x24" Panels

Another way of comparing the cost of producing microvia boards using conductive ink and by plating under the assumptions of this analysis - including similar yields between photovia-ink and photovia-plate - is to calculate the crossover with panel plating, which occurs at 72 cents per gram. Below an ink price of 72 cents per gram, the conductive ink technology costs less than plating

Most fabricators cannot currently use 18" x 24" panels for microvia-style boards. For this reason, cost analysis has been conducted at smaller panel sizes. For the two technologies studied in this comparison, the panel size should not be smaller than 15" x 20" or else the microvia costs will be higher than those for the conventional case.

Another confounding effect on the cost impact of microvia technologies is manufacturing yield (no rework assumed). Figure 5.3 shows how cost changes with yield. This graph illustrates the wide variation in cost due to yield. More importantly, this graph can be used to compare these two technologies, if there is development data that suggests that one technology would have a different yield than another. With the assumptions used here, the crossover yield difference appears to be about 4%. However, this yield difference does vary over the range shown. At lower yields the tolerable difference would be less than 4%, while at higher yields the tolerable difference would be higher.

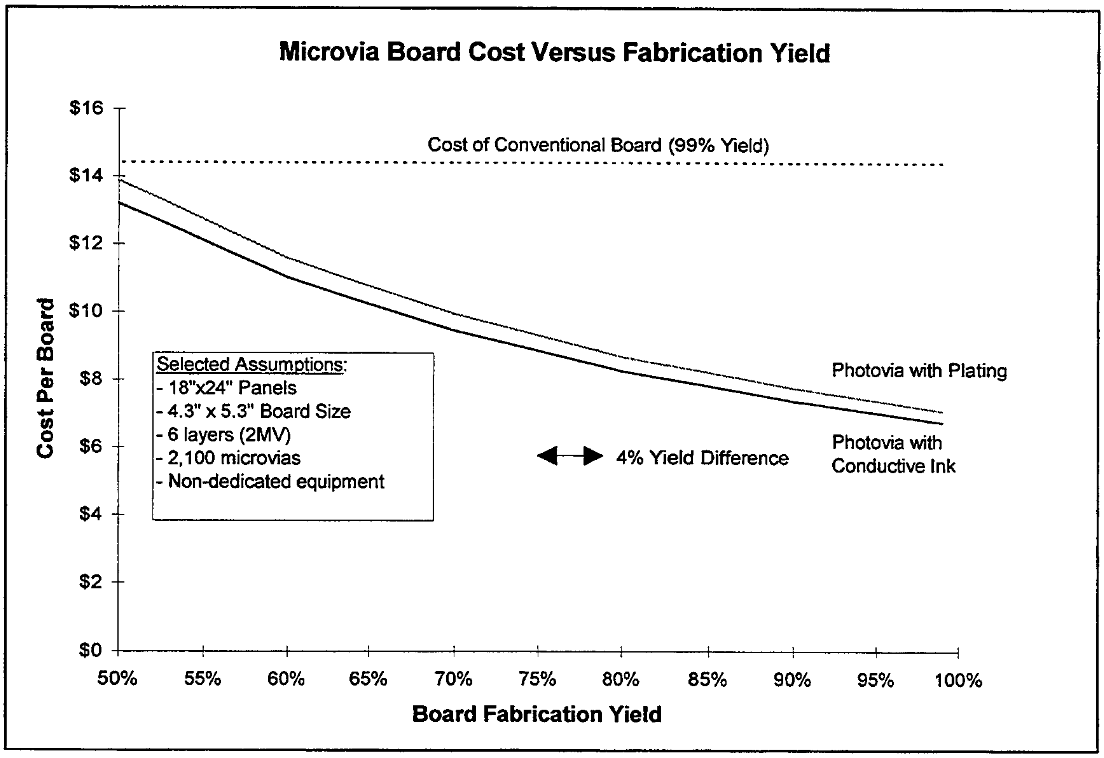


Figure 5.3. Cost Impact of Manufacturing Yield

Conclusions

Although this particular implementation of conductive ink technology has yet to be proven, the cost analysis shows that the photovia technology with conductive inks can provide a lower cost solution as compared to photovia with panel plating. However, the difference in cost is small enough that slight changes in either technology - yield, material costs, or other factors not shown here - alters the standings of which technology costs less. The meaning of this analysis is that these technologies can be comparable. Most importantly, both versions can cost less than a board fabricated with conventional technology, provided that microvia technology allows board area reduction.

This section is based on material prepared by Adam Singer of IBIS Associates, 55 William St., Suite 220, Wellesley, MA 02181-4003, for a feature article in the August issue of Circuitree Magazine.

Commercialization Technical Activities

Technology Management & Funding, LP, (TMF)

A new company, Parelec, LLC, was formed on February 22, 1996, jointly owned by Partnerships Limited and TMF to commercialize the PARMOD™ technology. TMF are actively seeking corporate partners to serve the electronics market with PARMOD™-based products and processes via an innovative Technology Equity Consortium. The objective is to secure up to five industrial participants who will own equity in the consortium and have nonexclusive licenses to practice the technology. The hope is that these participants will be major companies in electronic material supply with a worldwide geographical distribution to provide maximum impetus to support the adoption of the technology quickly in as wide a field as possible. Partnerships Limited Inc. anticipates continuing to provide research and development services to the consortium under a long term agreement.

Sales & Marketing Process Management (SAMPM)

In June, 1997, Parelec, LLC, contracted with SAMPM to provide sales and marketing support to develop customers for PARMOD™ products and technology. The principals in SAMPM have been very active in developing prospects for commercial sales, as described below. They have also developed a joint venture opportunity to apply PARMOD™ for Radio Frequency Identification Tags, which may be our first major application.

Institute for Interconnecting and Packaging Electronic Circuits (IPC)

The IPC is the industry trade association for the printed wiring board producers. Their role is primarily the creation of industry standards and technology dissemination. Partnerships personnel have attended a number of IPC meetings and presented papers on PARMOD™ technology as described below.

High Density Interconnect Structures Subcommittee

A new subcommittee devoted to the emerging technology of microvias and high density interconnect has been established by the IPC. One of the authors (PHK) is a charter member of this subcommittee and is playing a role in writing the standards for materials and processes in this market area. Data on silver and copper PARMOD™ are included in IPC document 4104 "Qualification and Conformance of Materials for High Density Interconnection Structures and Microvias".

Related Research

NIST/Advanced Technology Program

The National Institutes for Science and Technology (NIST) solicited responses for focused Competition 98-6 known as the Microelectronics Manufacturing Infrastructure Initiative. The National Center for Manufacturing Sciences (NCMS), the Interconnect Technology Research Institute (ITRI) and the National Electronics Manufacturing Initiative have joined forces with industry participants to prepare a response. Partnerships Limited is one of thirteen participants responding with a proposal. Partnerships is part of the metallization team and will extend the electrostatic printing technology demonstrated in Task 3 of Phase II to still finer lines and spaces.

NSF/STTR

Partnerships Limited, Inc. and the Electrical Engineering Department of Princeton University were awarded a Phase I Small Business Technology Transfer (STTR) grant by the National Science Foundation to investigate Materials Technology for Printing AMLCDs in September, 1997. This grant supports the extension of PARMOD™ to printing high conductivity conductors on glass and amorphous silicon to lower the cost and increase the achievable size of thin film transistor arrays.

Meetings and Papers

Partnerships personnel have attended the following meetings. Papers based on the work in this contract were presented at the meetings marked with an asterisk.

NEPCON, February, 1997, Anaheim, CA
IPC Expo, March, 1997, San Jose, CA**
IPC Flex, May 19-20, 1997, Phoenix, AZ**
IPC Works, October 5-9, 1997, Washington, DC
ISHM '97, October 12-16, 1997, Philadelphia, PA
IPC/IMAPS, Organic High Density Interconnect, November 20-21, 1997, Santa Clara, CA**
IPC Interim Meeting, February 26-27, 1998, Tempe, AZ

Invited Paper

A feature article entitled "PARMOD™ Metallization of Circuit Traces and Microvias" is scheduled to appear in the August issue of Circuitree magazine.

Patents

The following Patent Applications have been filed

Phase I

U.S. Patent Application "Electrical Conductors Formed from Mixtures of Metal Powders and Metallo-Organic Decomposition Compounds" Serial No. 08/501,393. Filed July 12, 1995, Paul H. Kydd, Inventor. Notice of allowance, June 12, 1997.

Divisional Application, (Same title), Serial No. 09/034,069. Filed March 3, 1998.

Phase II

PCT Application "Low Temperature Method and Compositions for Producing Electrical Conductors", Serial No, PCT/US97/16,226. Filed September 12, 1997. Paul H. Kydd, Gregory A. Jablonski and David L. Richard, Inventors.

Provisional Patent Applications:

Fifteen U.S. Provisional patent applications have been filed to protect various aspects of the technology developed in Phase II

Active Business Developments

Tobyhanna Army Depot/CECOM

An active search for Dual Use applications of PARMOD™ technology in the Department of Defense has met with success in a specialized military requirement. Military electronic systems are different from civilian equipment in that they are much more expensive and much longer lived. As a result, there is a demand for spare parts, and specifically circuit boards, to maintain systems which would be prohibitively expensive to replace, but which are no longer supported by the original manufacturer. Compounding this problem is a desire, and in some cases a requirement, to upgrade the systems with design changes. There is, therefore, a need for technology which can be used to replicate vintage PWBs from drawings or CAD files, if they exist, or directly from the original parts if they don't. In addition there is a need to be able to modify the boards and test the results.

PARMOD™ is ideally suited to this need because it can be used to metallize holes and draw circuit traces directly from CAD files or by teaching a dispensing machine or a printer from the original parts. Changes and design upgrades can be incorporated and tested in prototype boards and then implemented in a few tens or hundreds of parts to keep systems up and running.

This problem is common to all the services, but the primary interest has been found at the Tobyhanna Army Depot that is now part of CECOM at Ft. Monmouth. A joint program has been initiated to evaluate the possibility of producing spare parts based on PARMOD™. A specific circuit, MP-41905, has been chosen as a test vehicle, and parts are being made both by screen-printing and by computer-controlled dispensing as described above. A significant program to validate this technology is being planned for FY 1999.

Via Metallization

A technically related relationship is being developed with Direct Imaging Inc. who have a prototyping system for ink jet printing a resist on copper laminate direct from CAD files. The printer contains an etcher so that the machine can turn out circuit laminates from drawings directly with no intermediate tooling. The system includes a computer-controlled drilling machine and a laminator for producing multilayer prototypes for through-hole components. Heretofore, the layers have been electrically connected by driving hollow pins through them to make mechanical contact with all the circuit traces penetrated by the hole. This system is reliable, but expensive and unconventional relative to plated-through holes. PARMOD™ injected into the holes can be cured to a metallization equivalent to that usually applied by electroless plating followed by electroplating, but much faster and without the investment, complexity and environmental problems of the conventional processes.

Silver PARMOD™ has been supplied to Direct Imaging for resale to their customers following successful trials at a major customer.

A still larger market is hole metallization for conventional circuit boards. Every board manufacturer faces the need to metallize holes to allow solder to flow through them to make connections and to secure through hole components. Conventional plating technology is reliable and proven, but slow, costly and environmentally undesirable. So-called direct metallization processes to replace electroless pre plating are becoming widely accepted as an alternative. PARMOD™ provides yet another route which can be integrated with the drilling operation to provide faster, less costly metallization. This market will be pursued in conjunction with hardware suppliers such ass Direct Imaging, Asymtek and vendors of drilling equipment.

This application is relevant to the Tobyhanna program because hole metallization is required for the prototype and spare parts boards to be made there as well.

Low Cost, High Volume Printed Circuits

An opportunity exists to supply very low cost circuits in enormous volume for use as Radio Frequency Identification (RFID) tags. These take the form of tuned resonant circuits that interact with a remote interrogation device to identify themselves with a binary code. The essential requirement is a circuit with very low resistance and correspondingly high "Q" which can be produced in large volume at low cost. PARMOD ™ is ideally suited to this application. Extensive testing and development over the past year has resulted in silver PARMOD™ tags with the required performance and attractive cost. Process scaleup is underway with the objective of providing tens of thousands of tags per month at competitive prices in CY 1998. The application is airport security. Another major market which has been identified by one of our collaborators is the U.S. Post Office. A joint venture with a major U.S.-based material supplier is being organized to exploit this opportunity

Implementation of this technology will provide production experience relevant to quantity production of flexible circuits, which are more technically demanding, but far more valuable than RFID tags.

Conclusions

The work done in Phase II has successfully demonstrated solutions to the problems of creating and applying copper PARMOD™ mixtures. The principles underlying the composition of the ink and the conditions under which they should be processed have been elucidated. An initial Dual Use application is being actively pursued with the U.S. Army CECOM to demonstrate and qualify technology to produce spare part circuit boards by printing copper PARMOD™ under digital control. Other Dual Use applications in the FAA and the U.S. Post office are being worked on actively.

An entirely new electrostatic printing technology based on PARMOD™ liquid toners has been demonstrated in the laboratory and is showing great promise as a way to metallize high-density circuits and microvias at very low cost. A major program to establish this technology as part of a consortium on High Density Interconnect Fabrication has been proposed to the National Institutes of Science and Technology.

Initial shipments of PARMOD™ have gone to customers and three early applications have been identified. A major effort is underway to organize corporate partners to provide and support the technology worldwide.

Recommendations

Continued technical development is needed to transition the discoveries of this Phase II program into useable technologies. Preliminary product specifications have been created and the products have been characterized in a preliminary way, along with the processing conditions necessary to develop the best properties.

The Parmod™ materials themselves are relatively satisfactory in a number of potential applications which have been evaluated. The interaction of the PARMOD™ with the substrate is less satisfactory. Task 4 has shown that the PARMOD™ ink and the substrate are an interactive system in which both constituents contribute important characteristics to the finished circuit. This complex interaction will require more study by Partnerships and substrate suppliers to achieve optimum system solutions.

A massive effort is needed to characterize and qualify the circuits made with PARMOD™ technology. This is a revolutionary approach to interconnect creation. It offers significant advantages in cost, speed and environmental acceptability. It is competing with photolithographic technology that has been under development for forty years. The initial applications will be in prototyping, research and RFID where the technical requirements are not extreme, and the reliability requirements are much less stringent than most applications. Penetration of the more critical applications will require building an experience base which can support projections of adequate life and reliability. This will be time consuming and expensive.

Simultaneously, a major program can be justified to pursue the opportunities for further advance presented by this revolutionary technology. Extensive work is proposed to exploit the unique electrostatic printing technology developed in Phase II. Adaptation of this technology to metallizing high density interconnect structures presents an unlimited opportunity in the fastest growing field of circuit creation. Further work on additional conductors, particularly nickel and palladium is planned. The adaptation of PARMOD™ to other thick film technology such as the creation of passive components, resistors, capacitors and inductors is very promising.

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Appendix A

DRIFTS Experiments on Copper PARMOD™ Inks

Methods

The samples were prepared by screening a 1-cm x 1-cm square pad of the copper ink C136-7 onto Kapton® FN. The screen parameters were 280 mesh, 1.2 mil wires, and 1.5 mil emulsion, which give a wet print thickness of 2.8 mils. The sample was then placed in the sample cup of a variable temperature cell on a seagull apparatus in the FTIR instrument.

FTIR of Copper Ink Samples

Experiments were run on the c-136 ink (Cu powder + Cu flake + NDA), and on a mixture of Cu powder + NDA, the Cu flake + NDA, and Cu2O + NDA. The peaks used for identification of compounds in the compositions were as follows: C=O stretch for NDA @ 1700 cm^{-1}; C=O stretch for Cu Neod. @ 1600 and 1400 cm^{-1}; CH3 and CH2 stretches for NDA and Cu Neod. @ 2975, 2940, and 2880 cm^{-1}; CO stretches for carbon dioxide @ 2370 and 2335 cm^{-1}; and vibrations seen in Cu2O representing Cu_XO @ 1538, 1457, 1397, and 650 cm^{-1}.

The experiments were run to emulate the conditions of the tube furnace. Three sets of conditions were used: 1) the sample was heated to 360 C in a N2 flow, 2) the sample was heated to 120 C in a N2 flow, then to 360 C in a N2/H2O flow, and 3) the sample was heated to 300 C in a N2 flow, then to 360 C in a N2/H2O flow.

A. Copper powder + Copper flake + NDA (C-136 ink)

Experiment 1) on the C-136 ink composition showed Cu Neod. is formed as the sample is heated. The loss of NDA is seen at about 260 C, which correlates with NDA's boiling point of 255 C. The Cu Neod. that is formed during heating remains throughout, even after sitting at 360 C for 3 minutes.

Experiment 2) showed the same results as 1) above. The addition of the water vapor at 120 C did not change the results.

Experiment 3) showed the formation of Cu Neod. and the loss of the NDA as seen in 1) above. But when the water vapor was added at 300 C, the Cu Neod. was lost and CO2 was formed along with Cu_XO. The Cu_XO remains at the end.

It was found that the ink C-136:

a) produces Cu Neod. when heated
b) loses NDA at its boiling point (255 C)
c) removes Cu Neod. only when water vapor is added at 300 C
d) produces CO2 and Cu_XO when the Cu Neod. is removed

B. Copper powder + NDA

Mixing Cu powder with NDA at room temperature produces Cu Neod.; therefore, the starting composition is really Cu powder + NDA + Cu Neod.

Experiment 1) on this composition showed Cu Neod. was lost as the sample was heated, but reformed at about 250 C and then remained throughout even after sitting at 360 C for 3 minutes. There was no loss of NDA seen. Also seen was the formation of Cu_XO at 120 C that remained until 360 C where it was removed. CO2 was also seen starting at about 300 C.

Experiment 2) showed the same results as 1) above. The addition of the water vapor at 120 C did not change the results.

Experiment 3) showed that when the water vapor is added at 300 C, the Cu Neod. is removed and Cu_XO and CO2 are formed. The Cu_XO remains at the end. Also seen, but not yet confirmed, was the production of aldehyde and anhydride immediately following the addition of the water. Both the aldehyde and anhydride were formed and removed within the collection time of 2 spectra (about 11 sec).

It was found that the Cu powder:

a) produces Cu Neod. at room temperature with NDA
b) loses some of this Cu Neod. upon heating
c) produces more Cu Neod. at about 250 C (b.p. of NDA)
d) shows no loss of NDA
e) final Cu Neod. can only be removed with the addition of water vapor at 300 C
f) CO2 and Cu_XO are formed with the removal of Cu Neod.

C. Copper flake + NDA

Mixing Cu flake with NDA at room temperature produces Cu Neod.; therefore, the starting composition is really Cu flake + NDA + Cu Neod.

Experiment 1), 2) and 3) give the same results with only one major difference. NDA is lost as the sample is heated and Cu Neod. is formed. At 360 C, Cu_XO is formed. The difference is when Cu Neod. is lost. In 1) it is lost at 360 C, in 2) it is lost immediately after adding the water (120 C), and in 3) it is lost after adding the water (300 C).

It was found that the Cu flake:

a) produces Cu Neod. at room temperature with NDA
b) removes Cu Neod. at 360 C in N2
c) removes Cu Neod. at 120 C with the addition of water
d) removes Cu Neod. at 300 C with the addition of water
e) production of Cu_XO at 360 C

D. Cu_2O + NDA

This ink was made as a control of sorts to try to sort out some of the chemistry seen in the other compositions. The spectra of the powder by itself proved useful in identifying the presence of Cu_XO peaks in the other compositions. The spectrum of the powder mixed with NDA showed NDA and Cu Neod. were present at room temperature. Only experiment 3) was completed on this composition.

Experiment 3) showed the formation and loss oxide as the sample was initially heated, indicating an interaction of the NDA with the surface of the powder. NDA was removed at about 260 C as would be expected. At the same time, Cu Neod. was produced. Upon adding the water vapor at 300 C, the Cu Neod was removed, but oxide was produced at the same time. Also seen with the removal of the Cu Neod. was a removal of the CH3 antisymmetric environment without any change to the CH3 symmetric or CH2 antisymmetric environments. Exactly what is happening is not clear at this time, but such a change in the carbon chain environment generally would indicate an ordering or disordering of the molecule on the surface of the metal/metal oxide. It does clearly indicate that with the loss of Cu Neod. (C=O), there is not a loss of the organic chain.

It was found that the Cu_2O:

a) produces Cu Neod. at room temperature
b) the oxide surface constantly interacts with NDA as it is heated
c) with the removal of NDA, Cu Neod. is formed
d) Cu Neod. is removed with the addition of water at 300 C
e) Cu_xO is formed with the removal of Cu Neod.

Appendix B

Substrates Tested with Silver PARMOD™

Table B-1: Silver ink B-86 resistivity and adhesion data on Kapton® FN and G-10 FR-4

Substrate	Temperature (° C)	Resistivity (μΩ-cm)	Tape/Crease Test	Comments
Kapton® FN	300	3.9	Good/Good	7 week old ink
		3.8	Good/Good	"
	280	3.8	Good/Good	"
		3.7	Good/Good	"
	260	4.2	Good/Good	"
		4.2	Good/Good	"
	300	3.4	Good/Good	7 week old ink re-roll milled
	260	3.7	Good/Good	"
	270	3.8	Good/Good	12 week old ink re-roll milled
	270	3.6	Good/Good	new ink
Kapton® EKJ	255	3.3	Good/Good	
	230	3.5	Good/(Good to /Poor)	crease test good on one side
	220	3.5	Good/Poor	
	200	3.5	Poor/Poor	
G10/FR-4 epoxy glass, low temp McMaster Carr	220	4.4*	Good/Good	*assume 26 mg of Ag present
		5.5*	Good/Good	
	200	5.7*	Good/Good	
		5.7*	Good/Good	
	190	5.7*	Poor/Poor	
	170	30*	Poor/Poor	
Cu clad FR-4, McMaster Carr	260	NA	Good	Have to cure at 260 C for Cu substrate
	250	NA	Poor	
	200	NA	Poor	

Table B-2: B-86 ink on glass

Substrate	Temp. (° C)	Resistivity (μΩ-cm)*	Tape test	Comments
Corning 7059 low alkali glass	300	3.7	Good	
		4.8	Good	
		4.2	Good	
	280	3.1	OK	Tape test problem is believed to be with "dirty sample"
	260	3.3	OK	
		3.3	OK	
	220	4.4	Poor	
ITO glass	400	2.2*	Good	*Since ITO conducts the resistivity values are "enhanced"
		---	Good	
	300	---	Poor	
	220	---	Poor	
Glass slide (soda lime)	400	3.7	Good	
		Shorted		
	300	3.3	Good	
	280	4.0	ok	
	220	4.4	Poor	
Alumina	420	5.7	Good	yellow ring around the silver trace
	365	4.2	OK	
	315	---	Poor	

*Resistivity values are based on an assumed 26 mg silver on a standard 598 square serpentine.

Table B-3: B-86 ink on low temperature substrates

Company	Substrate	Temp. (° C)	Resistivity (μΩ-cm)*	Tape test	Comments
GE	GETEK	200	5.7	Poor	dark brown where Ag was
	ULTEM	200	3.5	Poor	softened and warped
		220	4.2	Good	melted and warped
	NORYL	200	173	Good	softened and shrunk

ICI	Kaladex 2030	200 220	4.4 Shorted	Poor Poor	substrate ok melted and warped
Hoechst	Aresin uniax film	200 220	4.2 Shorted	Poor Poor	substrate ok melt and warp
	Aresin balanced	200 220	4.4 Shorted	Poor Poor	substrate ok melt and warp
Precision	Inner layer	220	3.0Ω/23.7 cm	Poor	substrate ok
Laminate	Mylar???	200	NA	Poor	shrunk very small
Allied Signal	Inner layer	220	2.9Ω/23.7 cm	Poor	substrate ok
	FR-4 epoxy glass assume high Temp	230	4.3Ω/23.7 cm	Poor	substrate ok
McMaster Carr	FR-4 epoxy glass, high temp G-11	250 200	4.5 4.7	Poor Poor	had bubbles in it substrate ok
	G-7 glass/silicone	200	7.1	Poor	yellowed where Ag
	Phenolic paper grade xx	220 200		Poor Poor	bubbled and warped bubbled and warped
	melamine	220		Poor	crackled, peeling apart
	FEP Teflon	260		Poor	very warped
	polyester	200		Poor	melt and warp
DuPont	Tedlar	220		Poor	50% shrinkage
	Dartek F101, (Nylon 6,6)	250		Good	melt and warp
		220		Poor	substrate ok

* Resistivity values are based on an assumed 26 mg silver on a standard 598 square serpentine.

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