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The Replacement of Precious Metal Thick Film Inks
Using Conductive Polymer Technology

by

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Project Summary

Thick film hybrid electronics using precious metals such as gold, silver, and the platinum group are an integral part of the processing of most electronic components. The high intrinsic cost and strategic nature of these materials present natural motivation for investigation into alternative technologies that could reduce or eliminate them. The purpose of this work was to evaluate the feasibility of incorporating current and future synthetic metals into thick film technology for electronic and aerospace applications. The work carried out in this study included a literature review to identify available potential synthetic metal candidates. This included discussions with researchers active in this program. Herein is a brief discussion of thick film technology and the potential utilization of synthetic metals. Also included are preliminary test results on several prototype synthetic metal thick film materials. Evaluations were carried out based on conductivity, short-term stability, adhesion, and tractability. Initial observations indicate many technical obstacles to practicality. However, the overall results were considered encouraging, and sufficient feasibility was demonstrated to warrant further study.

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Introduction

The evolution of electronic design requirements and the natural effect of cost and productivity requirements has led to the inevitable growth of what is called "Thick Film Hybrid Micro Electronics".

The development and growth of microcircuit technologies were precipitated when the aerospace industry presented a need during the early '60s for electronic circuitry with increased functional capability per unit volume, reduced weight, and improved reliability and environmental stability. The requirements could not be achieved with conventional, exclusively discrete electronic components and printed-circuit boards or circuit card assemblies. Attempts to miniaturize discrete versions of circuit functions generally failed or resulted in assemblies which were not only costly and difficult to assemble, but fell short of reliability requirements. As a result, new avenues within the field of microminiaturization were sought to meet the desired objectives. Three major technologies evolved:

1. Thick Film Technology - The use of precious metal inks screen printed on various substrates to provide conductive, resistor, and dielectric patterns.
2. Thin Film - The use of vapor deposition or sputtering to place thin films of conductor, resistor, or dielectric material on a wide range of substrates.
3. Monolithic Integrated Circuit Technology - This is the classic semiconductor application to integrated circuitry. This product is usually referred to as the silicon "chip".

All three technologies have found a place in microelectronics with "thick film" technology finding a place in resistor networks, low volume circuits, complex arrays, and applications requiring medium to high power, high voltage or stable, tight-toleranced passive components. Thick film has the added advantage of low product cost, low design cost, low capital investment, and fast turnaround time. These factors have led to the wide variety of applications. A Table of typical applications is listed below.

Table I: Typical Applications for Thick Film Circuits

<u>Consumer</u>	<u>Commercial</u>	<u>Military</u>
T.V.	All computers	Proximity fuses
Radio	Computer peripherals	Fire control
Phono	Telecommunication	Missiles
Electronic toys	Desk calculators	Helmet radios
Garage door openers	Safety equipment	Sonar/Radar
Power tools	Emergency lighting	Guidance systems
Automotive	Medical instruments	IR detectors
Digital time pieces	CAD control systems	Enemy detection
Household appliances	Test equipment	Communications

The principal materials for this technology can be broken down into three groups.

1. Conductive Inks - Composed of platinum, gold, palladium,

silver or a combination of these metals. These materials are traditionally applied by screen printing.

2. Dielectric Inks - These are screen printed coatings that have an extremely highly dielectric constant and are used as insulating barriers.
3. Resistor Inks - These are screen printed inks that are normally made with oxides of ruthenium, molybdenum, titanium with ruthenium offering the most desirable properties.

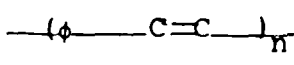
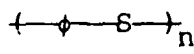
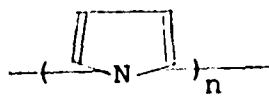
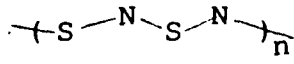
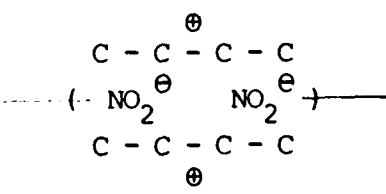
The market for these three products currently exceeds \$480,000,000 per year with projections for a doubling of that amount by 1987. It has been reported in a paper recently presented to the 1984 IEEE Electronic Components Conference that "by 1989 hybrid micro-electronics technology will be recognized by all engineers, scientists, and business leaders as a 'glamour' industry on a comparable or even more attractive level with the semiconductor industry".

Synthetic Metals - Review

As stated, the initial phase of this study was used to conduct a literature review of synthetic metal/conductive polymer technology. Examples of typical SMs include: polyacetylene, polypyrrole, polyphenylene, polythiazyl and intercalated graphite.

A summary of some of the properties of conductive polymers

receiving the most current interest:

<u>Name</u>	<u>Formula</u>	<u>Representation</u>
Polyacetylene	$(CH)_x$	 doped form
Polyphenylene Vinylene	$(C_6H_5-C_2H_2)_x$	
Polyphenylene Sulphide	$(C_6H_5-S)_x$	
Polypyrrole	$(C_4H_4N)_x$	
Polythiazyl	$(SN)_x$	
Intercalated Graphite	$(c)_x$	 doped form

Conduction is achieved in virtually all these materials through doping or intercalation of the polymer with substances that can contribute to, or remove electrons from the extended, delocalized electron system of the polymer chain. The term "doping", or more correctly intercalation, is encountered in all discussion of conductive polymers. Typical dopant concentrations range from one up to forty mole percent of the polymer. Examples of such dopants include Lewis Acids such as FeCl_3 , AsF_5 ; Lewis Bases such as sodium naphthalide, and proton acids such as nitric acid. Most SMs are either semiconductors or insulators without doping. The conductivity can vary anywhere from three to six orders of magnitude over a narrow range of dopant concentration (1-6). Potential use of this on/off relationship can be made in thick film methodologies. Electrical and thermal conductivities of a number of SMs have been reported near that of the classical metals such as copper and nickel (1-6). All SMs to some extent are air sensitive and therefore unstable over time, if unprotected. This combined with the overall intractability have limited practical application. The number of potential conductive polymers and copolymers is virtually unlimited. Current emphasis is on development of more stable and processable materials.

Experimental

Primary criteria for the properties of potential synthetic

metal candidates for PTF applications as described earlier include conductivity, stability, tractability and ease of synthesis. This last item was important for this study due to the limited time available. It was necessary to use easily obtainable samples. Many of the synthetic metals currently under study require somewhat tedious and lengthy synthesis. Therefore, this study concentrated on materials meeting the aforementioned criteria and be obtainable in a short time. Four different types of SMS were chosen for consideration. All materials were manufactured by outside laboratories. The four materials investigated:

<u>Material</u>	<u>Source Lab</u>	<u>Form</u>
Intercalated Graphite	Intercal Corporation	Powder
Pyrolyzed Polyacrylonitrile (PPAN)	University of Florida	Powder
Polyphenylene Vinylene (PPV)	University of Massachusetts	Thin Film
Polythiazyl (SN) _x	West Chester University	Film

All of the above materials are reported to have good conductivity and reasonably good stability (7-9). Initially, it was attempted to produce conventional thick film inks by rendering the particular polymer into an active dispersed phase. This approach was successful for the Intercalated Graphite. This material sample was intercalated with copper chloride. As a powdered material form, the Intercalated Graphite and PPAN were dispersed into standard thick

film vehicles (e.g. ethyl cellulose/terpineol), screen printed per standard practice, and cured. A summary of the application methods is given in Table II. The PPV made according to a previously described procedure (7) has as an advantage a stable, water soluble precursor polymer. This was dispersed with commercially available water-based vehicles such as Klucel* and Carbowax**. The polythiazyl was prepared and deposited as a film onto Mylar according to a method previously described (8). All sample ink formulations were screen printed or stenciled through a mask. Standard thick film conductor/dielectric/resistor test patterns were used and cured.

Performance testing consisted of measuring the DC resistance and the adhesion evaluated both by standard thick film test methods. In those formulations tested as PTF resistors, the temperature coefficient of resistance was also tested.

Results and Discussion

The PPAN and IG yielded quite usable inks in traditional PTF vehicle systems. The print quality and general ink properties were acceptable. The PPAN although interesting, provided no real improvement over conventional carbon based PTF conductors/resistors.

* Trademark of Hercules Corporation

** Trademark of Union Carbide Corporation

<u>Material</u>	<u>Processed Form</u>	<u>Cure</u>	<u>Estimated Thickness</u>	<u>Conductivity</u>
IG (CuCl ₂)	PTF Ink* - Screen Printed	150°/30 min.	1.0 mil*	0.1 - 1 MΩ
PPAN	PTF Ink** - Screen Printed	150°/1 hour	1.1 mil	1 - 2 MΩ
PPV	Stencil/Thin Film Deposit/ Dope AsF ₆	300°/1 hour	0.2 mil	0.5 - 1 kΩ
(SN) _x Br _{0.4}	Vapor Deposit on Mylar thru stencil/ Dope Bromine	100°/30 minutes	0.3 mil	0.3 - 0.5 kΩ

* .001" = 1 mil

** Standard PTF vehicle systems such as ethylcellulose were used.

The copper intercalated graphite, however, did have certain unique properties not previously observed. The higher bulk density and surface properties versus conventional carbon based inks, allowed for a higher weight loading and therefore broader conductivity ranges. The properties as a PTF resistor included a TCR (thermal coefficient of resistance) both lower and more positive than any PTF resistor seen to date. This observation agrees with theoretical predictions, since these materials are in fact pseudo-metallic, and a positive TCR is characteristic of metals.

The PPV precursor proved difficult to work with as a PTF raw material. The water-based ink formulations generally had poor print qualities. The charged prepolymer appears incompatible with many commonly used vehicles. However, it is felt that with continued investigation a suitable water-based ink could be developed. Due to these difficulties, the PPV was examined as a stenciled thin film. Layer depth was built by applying successive coats of the prepolymer, then cured. The PPV conductor pattern had relatively low conductivity due to the thin coating. This could be improved upon by building thicker layers, but was impractical here. The cured, doped PPV layer had a gold/green color and had acceptable adhesion onto glass. The possibility of using various additive/subtractive techniques as currently used in electronics to produce PPV based circuits exists. The films of bromine doped polythiazyl on Mylar appeared blue/black

in color. The adhesion was quite good on Mylar. As with the PPV system, a polythiazyl/PTF system using an additive/subtractive approach may be worthwhile to pursue.

The conductivity of all the prototypes tested was one to two orders of magnitude less than a typical PTF conductor made of silver. Despite the fact that the reported conductivities of various SMS approach the metals' in bulk form, in a dispersed ink the point contact path of conductivity greatly reduces this. Therefore, it is believed that synthetic metals as the dispersed active phase in PTF inks have definite limitations. Not investigated here but worthy of investigation is the use of SMS as the vehicle phase of PTF inks. The possibility exists that rather than replacing the precious metals altogether, the SMS could reduce the quantities required to achieve the needed conductivity. The PPV and polythiazyl applied not as dispersed media exhibited considerably higher (per unit volume) conductivity than the dispersed SMS. The ambient stability of all the samples was considered reasonably good -- higher in fact than expected. All samples were coated with a conformal epoxy overcoat to protect them from environmental attack. The net loss of conductivity over a three week period was less than 10 percent. Time did not permit any accelerated life testing. This better than expected stability could likely be attributed to the environmental protection from the ink vehicles and/or the epoxy overcoat. This

observation is encouraging for future work.

Conclusion

This work was undertaken as a feasibility study with limited actual testing. However, the four synthetic metal/conductive polymer systems studied in polymer thick film applications gave generally favorable results. There are many obstacles to be overcome in order to go from feasibility to practical applications. Prime among these is the need to develop alternative procedures to the conventional screen printed hybrid circuit. Application of these materials as a dispersed phase is not thought to be the best method of utilizing them. A method whereby the application could be as a bulk continuous form would greatly increase the sheet conductivity and possibly eliminate the need to dissolve or disperse. One of several possible approaches would be to utilize existing polymer processing methods, e.g. extrusion molding. The question of ambient stability which has been a fundamental shortcoming of all SM/CP technology to date remains to be determined. The limited observations suggest that incorporation of these materials into organic resin systems combined with protective overcoats greatly increase the probability of long-term stability.

In conclusion, the feasibility of utilizing synthetic metals/conductive polymer materials in polymer thick film hybrid electronic applications has been demonstrated. Despite apparent technical difficulties, it is believed that more extensive research in this area is warranted.

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