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# INVESTIGATION OF MULTILAYER PRINTED CIRCUIT BOARD MATERIALS

## FINAL REPORT



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**Autonetics Division of North American Rockwell Corporation**

**Marshall Space Flight Center  
National Aeronautics and Space Administration**

# **INVESTIGATION OF MULTILAYER PRINTED CIRCUIT BOARD MATERIALS**

## **FINAL REPORT**

By  
J. E. Meinhard

October 1969

Prepared under Contract No. NAS 8-21477 by

**Autonetics Division of North American Rockwell Corporation**

3370 Miraloma Avenue, Anaheim, California 92803

**Marshall Space Flight Center  
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# INVESTIGATION OF MULTILAYER PRINTED CIRCUIT BOARD MATERIALS MATERIALS REPORT

By J. E. Meinhard

Autonetics Division of  
North American Rockwell Corporation  
Anaheim, California

## SUMMARY

Inherent in conventional multilayer board manufacturing methods are a number of latent factors critical to product reliability. By far the most important of these are associated with the through-hole circuit interconnections scheme. This scheme, according to present practice, requires the close cooperation of two highly mismatched materials, namely, copper and z-direction glass-epoxy lamination layers. Under repeated exposure to environmental stress, such as that experienced by an orbiting satellite, the mismatch in properties results in distortion and ultimate rupture of physical continuity. Such an event is likely to be accompanied by a more or less permanent lapse in circuit electrical performance, and impairment or loss of the mission.

The purpose of this program is to reduce the present process liabilities by developing a three-dimensional circuit technology which employs materials of greater compatibility.

This report describes the development of a process concept to achieve this end. It consists of substituting organic conductors for copper conductors, at least in the z-direction, and unfilled organic polyimide for the glass-epoxy dielectric. Feasibility of the essential process steps was demonstrated, and significant progress was made in providing an appropriate organic conductor. The polyimide dielectric, in addition to achieving a higher thermal expansion compatibility, even with metallic conductors, showed unusual tractability in process techniques and a superior stability toward physical degradations of all types. Full advantage of these properties was taken to eliminate a variety of additional reliability problems, such as board drilling, delamination, corrosive residues and pattern misregistration. The materials and techniques required to obtain these results are described in detail.

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## INTRODUCTION

Present day multilayer board technology is afflicted by certain materials compatibility and fabrication problems that may impair the continuity of product performance, particularly when under the influence of environmental stresses. Some of the more important problems are mechanical failure of z-direction conductors\* due to thermal expansion mismatch with the surrounding insulating medium, long-term effects associated with interlayer misalignment, corrosion induced circuit failure due to ineffective removal of chemical residues, plating failures due to polymer residues mechanically distributed on metal surfaces, delamination and/or warping resulting from anisotropic thermal and water absorption properties, electrical leakage under low pressure (high altitude) conditions, and exclusion of intermetallics that may cause embrittlement and failure of electrical connections. Such problems are materials-and-process inherent; clearly, they cannot be resolved except by a totally new process approach where materials properties and fabrication steps are more in accord with themselves and with an enduring reliability of electrical function.

The objectives of this program are to examine the indicated problems, to assess their importance, particularly with respect to long-term reliability in both terrestrial and space environments, to seek alternatives in materials and processes by which these problems might be solved, and to test experimentally the feasibility of the most promising of the alternatives considered.

The approaches to these objectives fall naturally into various phases. The first was a comprehensive survey of the current multilayer board manufacturing arts in order to bring under scrutiny all known process-inherent problems, such as those arising from materials non-uniformity, contamination, corrosion, lamination control, plating, etching, etc. A simultaneous effort was directed toward an investigation of new materials and techniques with emphasis on materials compatibility, availability, electrical and physical properties, sterilizability, and manufacturing techniques. In this early phase of work a broad range of approaches was considered so that no potentially valuable advance in the art would be overlooked. These included polyimides as dielectric media, organic conductors, screened and fired ceramics, and vacuum deposited thin film layers employing inorganic dielectrics and metal conductors. In all cases, analyses were to be made, both by conferring with materials suppliers and by laboratory tests, to establish the process steps required and the intrinsic advantages and limitations, particularly as they affected design parameters and accommodation to environmental stresses. The results of these investigations were expected to provide a foundation for selecting the final approach in which attention would be concentrated on one or two of the several approaches considered earlier. Feasibility of the selected approach was to be proved in laboratory embodiments which would be evaluated with respect to warpage, delamination, appearance, electrical properties, mechanical properties and the degree to which the selected system met and resolved presently prevailing reliability problems. A detailed account of these investigations appears in succeeding sections.

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\*Z-direction denotes lines perpendicular to the plane of the board; i. e., the short dimension; x, y-planes lie within the board and are normal to the z-direction.

A basic philosophy that has served this program throughout can be summarized in a word: compatibility. This term defies definition in a mathematically precise sense primarily because its level of abstraction permits coverage of all aspects of congruity for a given system, even those not suspected. In addition, an observed compatibility of one sort is no guarantee of the presence of others, and solving one compatibility problem may introduce others. Although compatibility can be quantified with respect to a single, measurable property applicable to two materials, the restricted nature of such evidence must not be overlooked. In a sense the multilayer board is a basically incompatible system which might be loosely defined as an appropriate distribution of electrical conductors within an insulator. It might (and probably should) consist of only two isotropic materials. But one property, electrical conductivity, apparently must differ in these two materials by a factor of at least  $10^{20}$ . Near-perfect consonance in all other respects would be ideal, but surely impossible of achievement. Generally speaking, the conductor should possess overlapping energy bands and electron degeneracy, whereas the insulator should have a distinct band-gap, preferably of 3 eV or higher. These basic structural differences give rise to a multitude of differences in properties, many of them irreconcilable. Fortunately, it is essential to operate only on those differences that mean something to long-term reliability and to seek ways of manipulating such differences to within tolerable proximity. In achieving such a degree of materials compatibility it may be necessary to yield a point, or two, in the conductivity difference between "conductor" and "insulator." If so, the difference between, say,  $10^{15}$  and  $10^{20}$  ohm cm may become academic.



# INITIAL SURVEY

## Dichotomy of Manufacturer and User

Initial objectives required the examination and definition of dominant problems associated with modern multilayer technology so improved three-dimensional circuit concepts could be invented. In this analysis, attention was given mainly to the widely used epoxy-glass prepreg structures with emphasis on materials nonuniformity, contamination, lamination methods, plating, etch-back, and other manufacturing aspects considered important to subsequent board performance and reliability. To accumulate timely information, four manufacturers were visited who had agreed to talk over the important process problems. Emerging from the data collected were the following general items:

1. A prevalent lack of knowledge regarding the basic chemistry and physics of process steps
2. Heavy reliance on the product integrity of raw materials suppliers
3. Wide differences of opinion on proper raw materials handling and storage
4. Variations in prepreg properties affecting gel time, resin flow, etc
5. Occurrence of blistering, measing, delamination, internal spots
6. Anticipation of increasing problems with through-hole drilling
7. Divergence of opinion regarding the value of etch-back
8. A reactionary posture toward more stringent testing

It soon became apparent that the problems identified by the manufacturers were related mainly to appearance and initial functionality of the product, reflecting a pre-occupation with meeting production schedules rather than the reliability requirements, particularly those of the long-term variety, of users. It was further evident that the search for solutions to these problems might, at best, effect new process economies which would succeed only in perpetuating the existing technology and whatever reliability hazards it engendered. A shift in focus at this time to the major concerns of the user confirmed the relative triviality of these problems by simultaneously calling attention to a dominant structural problem; namely, the plated through-hole.

The plated through-hole, essential for providing interlayer electrical communication, is subject to several problems, often simultaneously. To begin with, the thermal expansion coefficient of the epoxy-glass layer in the z-direction is a factor of five, or more, greater than that of the copper plate. This fact, coupled with the relative incompressibility of the epoxy-glass layer, results in the mechanical working of, and build up of fatigue in, the copper with each thermal excursion to which the board is subjected. Mechanical failure eventually follows, which may or may not destroy electrical integrity. Perhaps most insidious is the type of circuit open that appears only

under certain environmental stresses. No stop-gap measures are known that guarantee against the work-hardening accruing from repeated flexing or stretching, and a new concept clearly is required.

A further problem to the user is possible interlayer misregistration which may result in the incomplete contact of one or more internal metallizations with the through-hole geometry. This problem becomes ever more critical as circuit geometries increase in complexity. In such instances, the degree of residual contact and its effect on reliability are not disclosed by ordinary electrical test or by any other nondestructive technique. The user, therefore, has no means of resolving these doubts and is forced to seek alternatives if he wishes to guarantee the success of a mission.

Yet another problem goes by the name of "epoxy smear," which generally refers to the dispersal of thin films of epoxy over internal metal conductor surfaces exposed during through-hole drilling. Fouling of metal surfaces by this means prevents reliable electrical contact with electroless and electrolytically deposited copper. The problem is "solved" by dissolving the epoxy in sulfuric acid (etch-back), which introduces a new problem — residual acid. An alkaline rinse therefore is used as insurance against the latter possibility. The overall problem, however, is that the user has no assurance that any one of these steps has been complete; that is, it would be technically possible to discover evidence of poor electrical contact due to epoxy smear, evidence of beginning corrosion due to interlaminar residual acid, and other evidence of initial corrosion resulting from traces of alkali, all in the same board, or at least, in the same shipment of boards. In space missions, where malfunctions can be costly, these deterioration effects can be treacherous.

The problems here defined are inherent in the materials and processes used in the manufacture of modern multilayer boards. That is to say, solutions to these difficulties will not be found in a manipulation of present technology but must be sought in totally new concepts. Subsequent work on the program, therefore, was addressed to this objective.

### Ceramic Systems

The consideration of potentially useful new multilayer concepts included a detailed examination of ceramic systems in the hope of discovering process innovations through which solutions to the reliability problems outlined in the previous section might be remedied or circumvented. It soon was learned that although the concept of ceramic multilayer structures was not new (Ref 1) the degree of development and sophistication lagged far behind that of the prepreg structures. It further was learned that ceramists generally are unconcerned by z-direction conductor reliability (perhaps with vindication, because x, y-compatibility is an essential prerequisite), but are preoccupied with miniaturization. This is quite natural since ceramic substrates are limited in size because of the fragility of green (unfired) tapes. Though miniaturization often is proclaimed (and occasionally justified) as a route to greater reliability, equating the two is highly suspect in the absence of hard physical evidence. The overall case for ceramic systems, therefore, seemed a little tenuous.

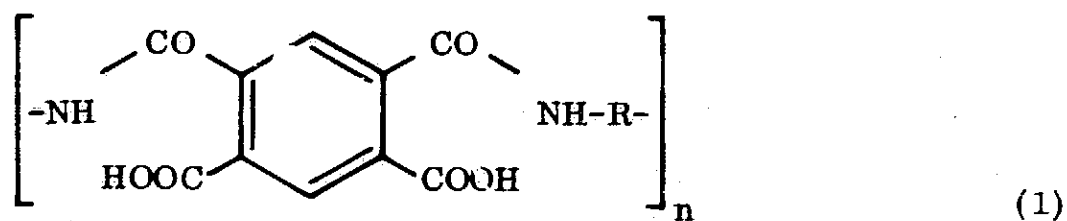
Nevertheless, two process innovations were available for consideration. One was the formation of through-holes by the thermal decomposition of appropriately located nodules of photoresist buried under a vapor deposited insulating layer of silicon dioxide (see Appendix A). Control of hole contours and avoidance of lifting adjacent dielectric layers loomed as difficult problems requiring an extended developmental effort. The second was based on the recent availability of a new dielectric, crystallizable glass-ceramic, which fires to a rigid structure that prevents "swimming" of screened patterns on subsequent firings. Other properties, such as mechanical strength, inertness, heat transfer ability, lack of a requirement for harsh reagents, lack of porosity, favorable dielectric properties and freedom from the necessity of a "substantial fixed cost of tools and machines" (Ref 1) remained as favorable arguments.

Convincing as these advantages are, they still must be assessed in terms of their ability to solve the problems previously identified. Ideally, this should be achieved without substantial sacrifice of pre-existing advantages, such as size. Ceramic boards presently are limited to areas of 4 x 4 in., or less, which would tend to make them attractive mainly for Level I packaging applications. Although some Level II applications are in use, the size limitation of ceramic boards places them at a distinct disadvantage. Also, at the present time, ceramic systems appear to be limited to four layers, two on each side of a central substrate (Ref 1). For various reasons, this may represent an upper limit, or a close approach to such a limit, with presently available materials. A further limitation is the lack of an obvious approach to the introduction of through-holes in dielectric layers by a photo/etch process. The screening techniques presently employed do not appear sufficiently developed to offer a clear solution to the misregistration problem defined earlier. Finally, the advantages cited above are not necessarily unique if they can be realistically anticipated for organic systems, or, as in the case of tool and machine costs, are irrelevant to the present program. For these reasons, the further investigation of ceramic systems was abandoned. Information and laboratory data accumulated in this area are summarized in Appendix A.

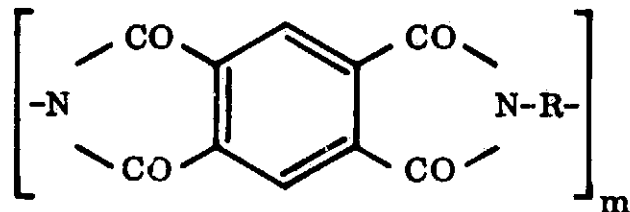
#### Organic Polymer Systems

Technical Considerations. — From the beginning, polyimide structures were considered as favorable, both for substrates and for dielectric isolation of conductor layers deposited on such substrates. It was further expected that a dielectric comprised of incompletely cured ML varnish would provide a chemical route for the etching of through-holes because of the availability of free carboxyl groups, thereby making possible the greater accuracy of circuit definition and registration associated with photolithographic procedure. Subsequent curing of the ML varnish at a higher temperature would then render it insensitive to further etching by the same means. The relevant chemical structures may be represented as follows:

Partly cured:



Completely cured



(2)

where generally  $m > n$ . The composition initially is dispersed in solvent, which facilitates application and escapes during the first cure cycle. The resulting composite of layers should at least approach a monolithic three-dimensional dielectric medium in which the various conductors, or their terminations, would be embedded.

Success of the preceding idea depended on interlayer bonding following final varnish cure. This expectation did not soon materialize because of the inertness of the imide structures, both in the substrate (Vespel) and the cured varnish. However, the problem was a chemical one and was regarded as resolvable. In the interim, incompletely cured ML varnish was considered as an alternative because the presence of residual unbonded polar groups provided an apparently successful adhesive bond to Vespel as well as to itself in a multilayer mode. After some further tests and theoretical considerations, this idea was abandoned because the residual free carboxyl groups could provide protons for charge transport between adjacent, oppositely polarized conductors. Other problems might arise from the affinity for water and the sensitivity to alkaline solutions. The latter would interfere with the confinement of through-hole etching to the last formed layer.

A further feature was the intended application of organic conductors in the multilayer circuitry with the expectation that this would circumvent the thermal mismatch problem stated above and the composite structure would be able to undergo a thermal stress without suffering serious internal mechanical stresses. Because of the generally recognized poor electrical conductivity of organic solids, this particular idea seemed the most unrealistic of the entire concept, except possibly in the z-direction where path length (and therefore potential drop) would be small. But this is precisely where the pre-existing thermal mismatch problem lies, and the possibility of resolving it by filling the through holes with thermally matching organic conductors was considered worth pursuing. A refinement of the original concept therefore lay in using metallic conductors in the x, y-circuitry and the organic conductors for interlayer circuit connection.

In addition to offering better thermal matching, the concept seemed to deal effectively with the other problems identified above. Thus, registration between layers would depend only on photolithography (which is subject to accurate control) rather than on physical alignment of a stack of layers. Furthermore, pattern etching would be done one layer at a time, thereby providing opportunity for step-by-step inspection. In addition, the opportunity for smearing organic resinous materials over metallic contact areas would be absent. The technique nevertheless would require the use of a caustic solution for through-hole etching which, in a mishandled operation, implied the possibility of interlayer retention of ionic contaminants. This possibility is comparatively small, however, in a one-layer-at-a-time process where

the chance of internal entrapment of reagents is small and the effectiveness of rinsing operations is great. Therefore, it seemed that the total concept, if physically demonstrable, would be almost completely responsive to the state-of-the-art problems enumerated earlier.

A further modification of concept substituted aluminum for the original Vespel substrate. A first ML varnish layer then is required to isolate the first layer of circuitry from the aluminum. The aluminum substrate, if thin, could be later stripped off (if desired) by an etchant, or, if thick, could be retained as a heat sink. Tests of the concept were eventually made and are described in a later section of this report.

Initial Experiments. — Initial laboratory effort on insulating media was invested in determining the optimum methods of working with available polyimide materials. It was necessary to develop a polishing technique for machined Vespel substrates (4 x 4 x 0.062 in.) to produce surfaces on which fine-line etching could be achieved. Construction of a device to ensure reasonable coating uniformity of ML varnish on Vespel also was required.

An additional problem was the appearance of fine bubbles in cured ML varnish layers. Two possible sources of the gas were low temperature storage (40 F) of bulk varnish (to inhibit premature cure) and steam evolution during the cure cycle. Dissolved gases were eliminated from the varnish by vacuum outgassing at elevated temperature (140 F). Rate of steam evolution was controlled by a gradual temperature advance to the 400 F cure level. These steps proved effective in eliminating the occurrence of bubbles.

Another problem was the dewetting, or delamination, of varnish layers during cure. The gradually increasing cure temperature regime proved helpful in reducing this effect. Further control was obtained by wetting the Vespel with dimethylformamide (DMF) prior to varnish application. However, complete prevention of delamination by these means, even at the lower cure temperature of 400 F, was not immediately successful. Thus, at the cure temperature of 600 F required for complete condensation to the polyimide structure, delamination was expected to be even more serious, and it appeared that it would be necessary to work out an alternative chemical bonding route.

In addition to the above dielectric materials, the synthesis of polymeric materials for later use in the formation of organic conductors was also initiated in this phase of effort. The objective was to incorporate these materials in charge transfer complexes. Thus it was required that the polymers be either electron donors or electron acceptors. In all, four such polymers were prepared. Their structures, methods of synthesis, and general properties are given in Appendix B. The most important member of this group, as revealed in later work, was poly (2-vinylpyridine) which formed the backbone of one of the best organic conductors ultimately developed on the program.

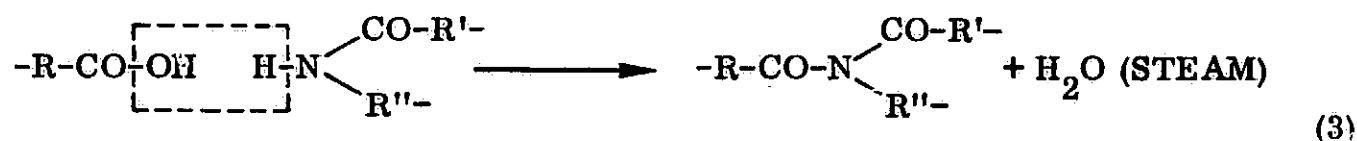
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## DIELECTRIC SYSTEM

### Technical Discussion

The decision to concentrate attention on polyimides as dielectrics was based on an impressive catalog of favorable properties (Ref 2) and on the availability of an incompletely condensed version of the material, PYRE-ML (duPont), hereinafter referred to as "ML varnish," which seemed advantageous in terms of adaptability to process techniques. In particular, it was expected that the presence of free carbonyl groups in incompletely cured polymer would afford a means of through-hole fabrication by strong base attack through selective masking. A subsequent cure cycle could then be used to toughen the layer against through-hole etching in the succeeding layer. With a volume resistivity of  $10^{17}$  ohm cm (Ref 2, p. 115) the successful function of ML varnish as a dielectric was assured from the beginning.

A difficulty lay in steam evolution during the cure cycle and it was quickly appreciated from initial experiments. This evolution was an intrinsic aspect of the condensation process, which may be formulated as follows:

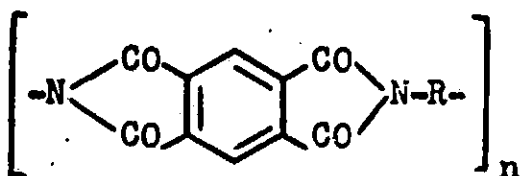


The net effect was to produce an underside lifting of the film being cured. A companion problem was the contractile behavior of freshly applied varnish films, even on polyimide substrates, in what appeared to be a process of coacervation accompanying the evaporation of solvent. This type of behavior is not uncommon among the lyophilic colloids, and ML varnish would seem, from its viscosity and other properties, to be a sol belonging to this category. It was not clear initially whether the predominant cause of the observed delamination, or "dewetting," lay in the generation of steam or in the coacervation. It was abundantly clear, that these effects had to be brought under control before process feasibility could be claimed.

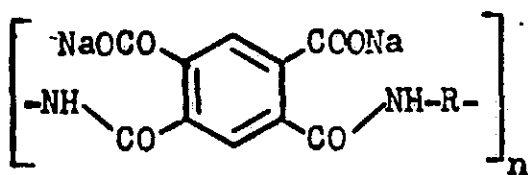
An obvious approach to the steam generation problem was to prolong the cure cycle so that the permeability of the condensing varnish film was at no time exceeded by local water concentrations. Such a process modification already had been worked out for preventing the occurrence of bubbles, as described in the previous section, and was believed adequate as far as it went. The coacervation problem, however, was still present and required an approach wherein the surface character of the last applied (and cured) varnish layer would be altered so as to firmly anchor the succeeding varnish application. Inasmuch as early experiments offered little in the way of confidence that this problem could be solved purely by solvent alterations, it was thought that a chemical bonding system, based on the known chemistry of the polyimides, would be necessary to interlock one layer with another. The process decided upon involved treatment of the outer surface of completely cured polyimide with strong base to open up the imide groups. A following treatment with dilute acid could then be

used to remove residual base and provide open groups necessary for co-condensation with the succeeding varnish layer. The complete process can be formulated as follows:

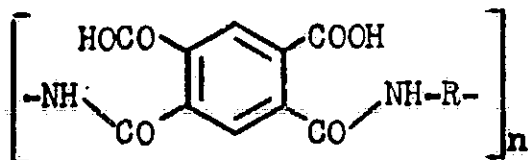
1. Completely cured polyimide before treatment:



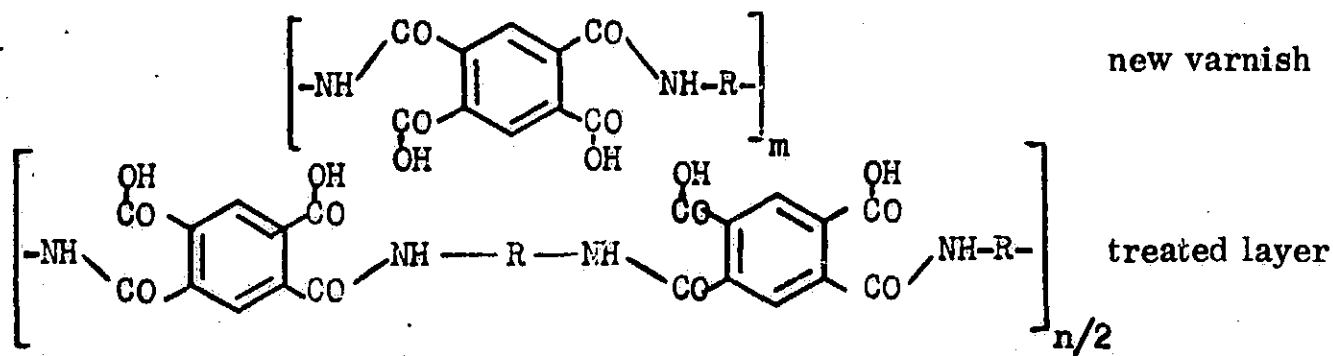
2. Surface after treatment with NaOH:



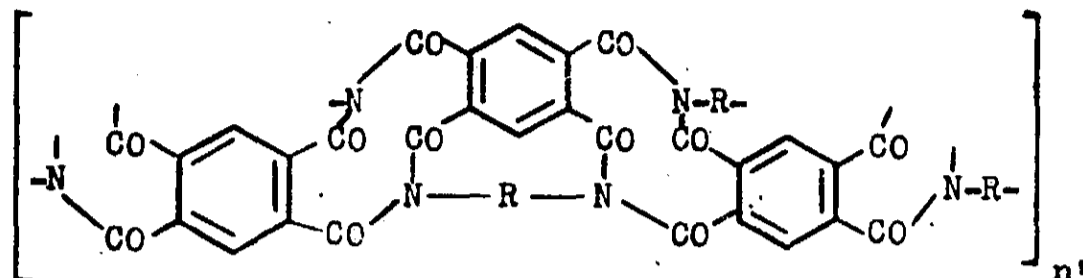
3. Surface after acid rinse and water rinse:



4. Application of new ML varnish layer:



5. Final Cure:



It will be noted from the structure given in Step 5, Final Cure, that build up of a totally monolithic dielectric structure is possible from this sequence. In effect, this not only would confine through-hole etching (to be inserted between Steps 4 and 5) to the last applied (undercured) layer but also would prevent the possibility of delamination since the molecular bonding would be of the same type in the z-direction as in the x, y-planes. Furthermore, the procedure appeared to sacrifice no advantages in process flexibility. This, therefore, became a priority object of experimentation.

Other questions concerning the behavior and physical properties of the polyimide, such as the interaction with water, metallization adherence, thermal expansion compatibility with conductors, and process details of through-hole etching, also became objects of investigation but do not require separate treatment here.

### Experimental Investigations

Interlayer z-Direction Bonding. — The interlayer bonding concept described in the preceding section was tested on a polished Vespel (duPont's completely cured polyimide board) substrate using the following sequence of steps:

1. Apply saturated sodium hydroxide solution three minutes at room temperature.
2. Rinse in water, then 10 percent hydrochloric acid, then water.

The treated area exhibited a matte appearance and a lowered contact angle with surface water, indicating that polar groups had been formed. The surface then was coated with ML varnish and cured at a temperature gradually increasing to 400 F over a period of two hours. For "complete" cure this was followed by an increase to 600 F maintained for 1 to 1-1/2 hours. Specimens cured to both temperatures were investigated but it was found impossible to separate bonds so made, using all mechanical means available, without destruction of the bulk material on both sides of the original interface. It was concluded tentatively that the curing process established a monolithic polymer through the released surface carboxyl and amide groups and the newly applied polyimide layer. The process was designated as "z-direction polymerization."

A second means of z-direction bonding was found based on initial solvent swelling of the substrate surface. This was achieved by a brief treatment of the surface with



dimethylformamide (DMF) and by incorporating a small proportion (10 percent by weight) of DMF in the varnish. Assuming a flexible linear characteristic as the dominant molecular geometry, one can visualize the process somewhat as follows:

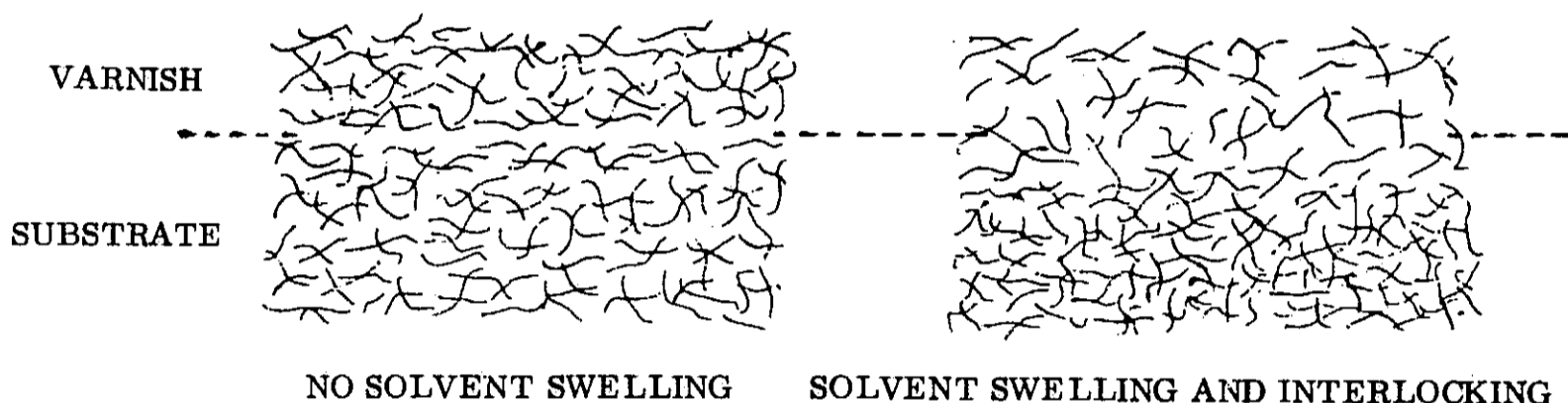


Figure 1. Postulated Preferential Solvent Effect on Molecular Chains

The interlocking of polymer chains, as represented in the diagram at right of Figure 1 should provide an anchor for the newly applied layer. Furthermore, the chemical structures are such that full development of a purely imide composition is never achieved, and some amide groups are always present in the substrate. This means that the opportunity for additional crosslinking, especially with a fresh varnish layer, is present to a certain degree, thereby forming to some extent the same kind of chemical bonding as that provided in z-direction polymerization. The function of the DMF is visualized as simply to open up the molecular chains necessary to expose unused amide and carboxyl groups and to allow the intermingling with them of analogous structures from the varnish layer in sufficient proximity that heat-cure produces imide crosslinking in the interfacial region. This second process was termed "z-direction interlocking."

The degree of interfacial chemical bonding in z-direction polymerization undoubtedly is considerably greater than that in z-direction interlocking and the "adhesive" bond, therefore, should be somewhat greater. As a matter of experimental fact, however, the bond strengths developed in the two processes were indistinguishable and resisted all attempts at rupture or delamination by all mechanical means we were able to find or invent. Tests to destruction always encompassed the bulk materials present. It nevertheless was considered likely that differences would be found as more intimate knowledge of the material was gained. To date, however, advantage still lies in the convenience and simplicity of the z-direction interlocking process, where the only required additive is the volatile DMF, and no evidence of anisotropic behavior therefrom has been found.

Interaction With Water. — Comparison of the water absorption of Vespel (unfilled polyimide) with G10 epoxy fiberglass in terms of weight gain as a function of days exposure at 85 C and 82 percent relative humidity was determined and is plotted in Figure 2. The data reveal no substantial difference between the two types

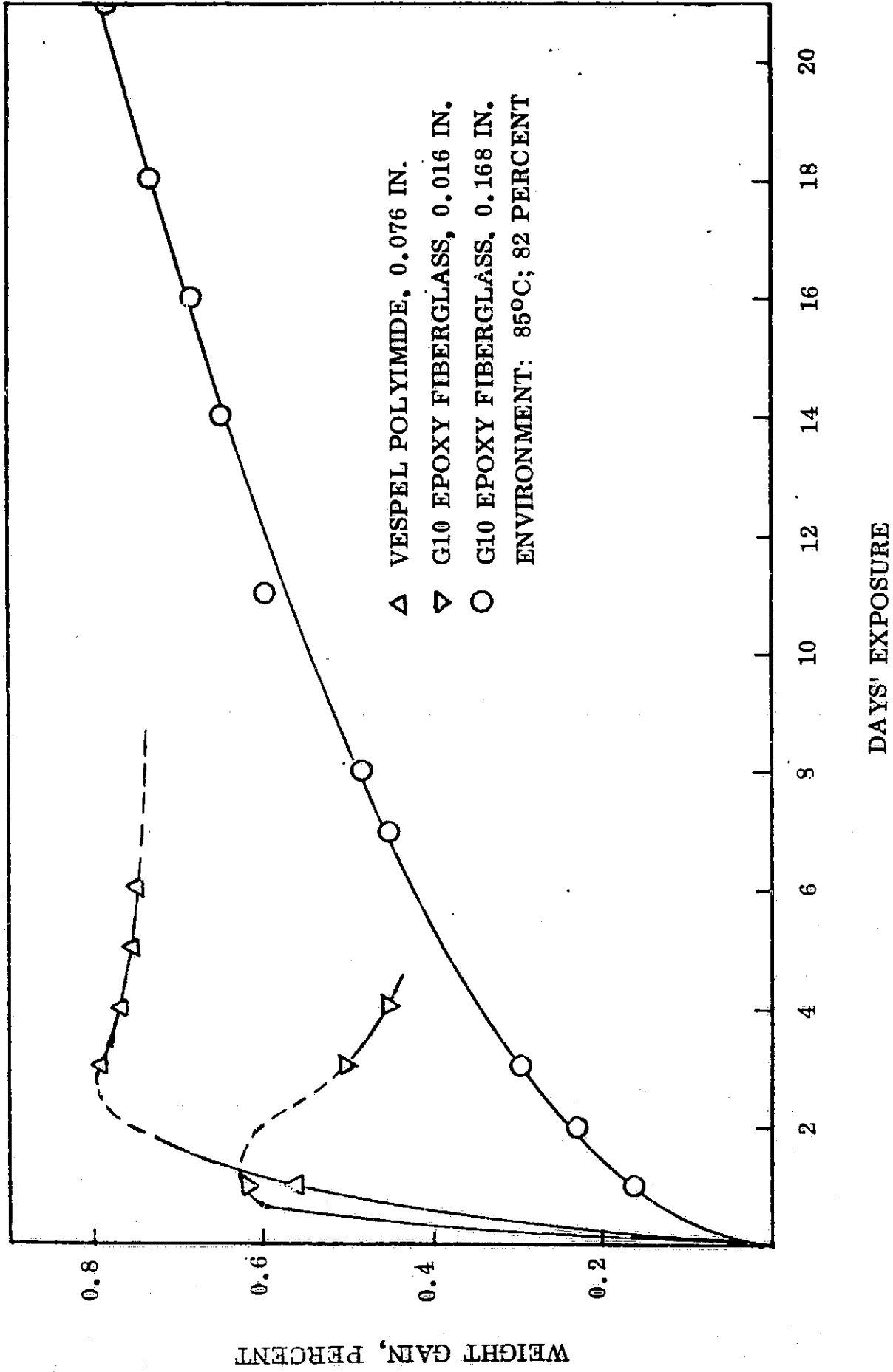


Figure 2. Weight Gain of Epoxy Fiberglass and Vespel Polyimide in a Humid Environment

of material with respect to ultimate water up-take. Possible effects on the electrical or mechanical properties introduced thereby were not disclosed, of course, by these results.

The effects of moisture absorption on the adhesion of a layer of ML varnish on Vespel were examined. The varnish layer was applied uniformly according to techniques previously developed and cured three hours at 600 F (preceded by gradual advance in temperature to accommodate steam dissipation). The humidity test was conducted according to MIL STD 202C, Method 106B, for ten days. This test applies a cyclic environment ranging from room temperature to 150 F and 80 to 98 percent relative humidity. Following this treatment the varnish layer resisted all attempts at mechanical rupture of the interlayer bond, nor did it show any other evidence of change, either visual or mechanical, from properties existing prior to test.

Investigation of the electrical properties of an approximately 0.001 in. thick polyimide layer applied to a polished metallic aluminum substrate and cured at 600 F was made under various conditions of ambient humidity. All electrical tests were made immediately following exposure to prevent loss of information through subsequent equilibration. The data are presented in Table I as resistances measured in ohms. The results indicate a negligible change in current leakage properties in going from room ambient conditions (estimated at 35 to 40 percent R. H.) to a relative humidity of 98 percent. However, in very dry environments a substantial increase in resistance (decrease in leakage) will be noted. It is suspected that a continuum of adsorbed polar molecules is interrupted at some point in the process of desiccation. In the moist ambients more pertinent to the objectives of this program, it is seen that resistances generally lie in the range of  $10^9$  to  $10^{10}$  ohms, which is only about a factor of ten lower than those obtained on epoxy-fiberglass layers sixteen times as thick using the same metallization pattern. It is estimated from this that bulk and surface current leakage associated with the use of polyimide as a dielectric may be equivalent to, or less than, that of conventional laminates.

Metallization Adherence. — Polyimide substrates have been obtained consisting of 0.032 in. thick Vespel (duPont) sheets. Gold was vapor deposited in a vacuum chamber (CHA Industries) at  $5 \times 10^{-5}$  torr with the substrate at ambient temperature. The gold was deposited to a thickness of about 30,000 Å. It adhered well to the substrate, and, even though the substrate was flexible, no gold flaked off. The circuitry passed the "tape test." The initial test pattern artwork was prepared by reducing a complex 5 x 9 in. multilayer pattern down to a pattern 2 x 3 in. This resulted in 2.5 mil lines and 1 mil spacing. Photoresist (Shipley AZ-1350H) was applied by spraying and the pattern was spray etched with an iodine etchant.

An insulating layer was applied over the gold circuit pattern by spraying the surface with ten coats of ML varnish. This was diluted with DMF to the proper viscosity. The layer was cured for two hours at 400 F to yield a coating with adequate flatness for further deposition of gold. Problems were experienced with this particular Vespel product because the surface structure consisted of extruded, longitudinal fibers and was rough. Therefore, it was necessary to develop a method of surface polishing in order to facilitate fine line etching. In spite of this additional surface treatment, channels from the dislodgement of fibers remained and became filled with gold during the deposition process, causing interconductor line shorts.

TABLE I  
ELECTRICAL BEHAVIOR OF 1-MIL POLYIMIDE  
LAYERS AS A FUNCTION OF HUMIDITY

Conditions	Panel	Measured Resistance (ohms)		
		M-1 to M-2 (a) ("surface") (b)	M-1 to Substrate ("bulk") (b)	M-2 to Substrate ("bulk") (b)
Initial room conditions	1	$3.7 \times 10^9$	$1.9 \times 10^{10}$	$1.8 \times 10^{10}$
	2	$1.2 \times 10^{10}$	$<1 \times 10^3$	$9.0 \times 10^9$
6 hr at 150 C, then 1/2 hr in desiccator	1	$>1 \times 10^{15}$		
	2	$5.5 \times 10^{10}$		
24 hr additional in desiccator	1	$1.7 \times 10^{11}$	$5.1 \times 10^{11}$	$1.7 \times 10^{11}$
	2	$4.2 \times 10^{10}$	$<1 \times 10^3$	$3.8 \times 10^{11}$
After 24 hr more in desiccator	1	$1.5 \times 10^{12}$	$3.4 \times 10^{11}$	$3.6 \times 10^{11}$
	2	$4.7 \times 10^{11}$	$<1 \times 10^3$	$3.5 \times 10^{11}$
After 5 days 98% R.H., room temperature	1	$1.5 \times 10^9$	$4.0 \times 10^9$	$1.5 \times 10^9$
	2	$7.1 \times 10^8$	$<1 \times 10^3$	$1.3 \times 10^9$
After 24 hr in room ambient	1	$2.7 \times 10^{10}$	$6.8 \times 10^{10}$	$1.3 \times 10^{10}$
	2	$3.6 \times 10^9$	$<1 \times 10^3$	$5.1 \times 10^9$
After 24 hr more, room ambient	1	$1.4 \times 10^9$	$1.9 \times 10^{10}$	$1.7 \times 10^{10}$
	2	$4.0 \times 10^9$	$<1 \times 10^3$	$3.7 \times 10^9$
(a) M-1, M-2 denote adjacent parallel metallization patterns on the polyimide surface.				
(b) Inexact terminology because the bulk contributions to surface, and the surface contributions to bulk, current measurements are not known.				

As a result of these tests a nonfibrous version of Vespel board was procured, sawed into 4 x 4 in. squares and mechanically polished. Adhesion of vacuum deposited gold to variously cured ML varnish layers and to these polished Vespel substrates did not meet expectations based on earlier observations of its adhesion to fibrous polyimide substrates. It was not known whether this failure was related to deposition process parameters or to the more specular quality of the surfaces being studied. The availability of gold-polyimide tape conductors (product of Minnesota, Mining and Manufacturing Co.) tends to discount the latter possibility. A full-fledged investigation into the deposition process to determine conditions necessary for strong gold adhesion, however, was not undertaken since a predeposit of chromium had been found to anchor the metallization firmly to the polyimide surface. Etching of the gold-chrome composite layer presented no problems, and line-width and spacing tolerances down to

0.0025 in. were readily achieved. It was further observed that a cured ML varnish layer is easily peeled from a specular gold surface but cannot be separated from a chromium layer without destruction of the polymer.

In the interest of developing a monometallic system, efforts also were made to deposit chromium alone on cured ML varnish layers because of its demonstrated adhesion. In depositing a layer of about 5000 Å, considerable thermal energy was translated to the substrate (because of the higher required source temperature) which became warped as a result. Cooling and partial recovery of substrate to its former shape was accompanied by crazing of the metallized surface. The approach was abandoned.

Copper was deposited alone in another experiment. The choice was based on the potential coordination bonding of the copper atoms to adjacent imide nitrogen atoms, and also on the closer match (than gold) in thermal expansion coefficient with that of the polyimide layer. The adherence of the copper was found to be minimal. It is further felt, however, that in any practical process the use of thin films of copper, or most other oxidizable metals, would be troublesome from the standpoint of corrosion. A fingerprint, or other chance inoculation of salts, could drastically damage a thin susceptible conductor. The continued use of gold as the x,y conductor therefore was favored. The departure of its expansion coefficient from that of polyimide is not large and is at least partially offset by the temperature differential between the depositing atoms and the substrate.

Use of a very thin bonding layer of chromium was continued. The function of the chromium probably is that of an oxygen getter, the necessity of which might later be eliminated by more thorough outgassing or prebaking of the substrates. The attainment of adhesion and line etching without detrimental effects on the insulating media were considered to meet initial feasibility objectives.

Thermal Expansion. — Selection of metals for conductors in x,y planes, and for possible substrates as well, requires a consideration of their thermal expansion coefficients to obtain as close a match as possible with that of cured ML varnish. Values of a representative list of metals taken from the literature (Ref 3) are compared in Table II with those reported for polyimide varnish (Ref 2, p 225). The range given for polyimide varnish is derived from the manufacturer's literature (duPont) and does not represent an independent evaluation. The reference does not offer a reason for the range given; however, SP Polymer, which is a completely cured polyimide, is listed at 28 in./in./deg F, suggesting that a lower coefficient, such as those reported for ML varnish, is associated with incomplete condensation of the polyimide. Other questions, such as the effect of imbibed moisture on the thermal expansion of polyimide, also remain unanswered. In view of these uncertainties, coefficients lying within the entire range given for the varnish were classified tentatively as appropriate candidates. This would include the following metals: aluminum and magnesium alloys, lead, silver, tin, and potentially copper.

TABLE II  
THERMAL EXPANSION COEFFICIENTS OF METALS AND  
POLYIMIDE VARNISH

Substance	Expansion Coefficient (in. /in. /deg F x 10 <sup>-6</sup> ) (a)
Aluminum Alloys (Wrought)	12.2 to 14.0
Cobalt	6.8
Niobium	3.8
Tantalum	3.6
Tungsten	2.5
Copper	9.8
Lead	16.3
Magnesium Alloys	16.0
Nickel	7.2 to 7.8
Gold	7.9
Silver	10.9
Platinum	4.9
Palladium	6.5
Tin	13.0
ML (polyimide) Varnish	11.0 to 22.0
SP Polymer	28.4
Epoxy G10 laminate, z-direction	28.0 to 260 (b)

(a) Compiled from Ref 3  
 (b) Measured on a 0.43 in. diameter x 2.00 in. long cylindrical specimen consisting of 384 layers. The mechanical stress relief mechanism here would not necessarily be equivalent to that of a conventional board. The higher coefficient is applicable above the glass transition temperature, 210 to 220 F.

An additional possibility exists in the use of metal plates, rather than Vespel, as substrates which might introduce certain advantages, such as lower cost and heat-sink and electrical ground capabilities. According to Table II, aluminum and magnesium stand out as being the most compatible with cured ML varnish in thermal expansion and consequently should be favorable materials for substrates. Varnish layers, therefore, were applied to substrates of both metals and cured both at 400 and 600 F. In all cases, very strong adhesion to the metal was found. No special chemical treatments were used on the metals, which in the case of magnesium was a milled surface, whereas the aluminum (in 4 x 4 in. squares) was polished to a mirror finish. The films were of the order of 0.0005 to 0.0010 in. thick. Chromium/gold metallizations were deposited on the aluminum-supported films and patterns etched. Subsequent electrical tests of the aluminum supported circuits, previously recorded in Table I, revealed that only one of the four metallizations had excessive current leakage due to a probable discontinuity in the ML varnish film.

Assuming the existence of a good adhesive bond, this result was not entirely unexpected because of the presence of at least a small degree of resilience in both the

organic and metal layers, a situation which contrasts sharply with silicon microcircuit passivation. In the latter case both the silicon and its glassy oxide are highly rigid bodies with a factor of ten mismatch in thermal coefficients of linear expansion. We were able to show experimentally in a previous program (Ref 4) that the minute pinholes in the oxide layer, which still are plaguing the semiconductor industry, are formed in the process of cooling from the oxide growth temperature (1000 C or more) to room temperature. Accompanying the cooling process was an introduction of compressive stress measured at 40,000 psi. In the present case the thermal expansion mismatch between aluminum and polyimide cannot be greater than a factor of 2 and, with additional investigation, probably could be matched almost exactly in the temperature range of normal use. Furthermore, any stress arising from an expansion mismatch would be that accruing from a 530 deg drop in temperature (i. e., the polyimide cure temperature to room temperature) rather than a drop of 1800 F. The use of a thin polyimide film as an isolation dielectric on an aluminum substrate therefore appears highly feasible.

Evidence of delamination of the varnish film from the aluminum substrate as a result of the humid environment treatments also was sought but not found. A contributing factor undoubtedly lay in the anchoring, or bonding, properties associated with the thin oxide layers unavoidably present on the metal surfaces. Enhancement of such bonding by prior anodization of the aluminum surface could be employed if demanded by future requirements.

Through-Hole Etching. — Initial attempts to etch through-holes with ammonium hydroxide (using a chromium mask) in an ML varnish layer cured at 400 F did not succeed. Available literature evidence (Ref 2) indicates that incompletely cured ML varnish is soluble in this base and that this varnish layer probably was over-cured. Definition of proper cure cycles and investigation of stronger bases were required before an effective procedure could be established. The through-hole etching procedure was arrived at empirically and consists of the following sequence of steps:

1. Apply varnish in a dilution of ten parts with two parts by weight dimethylformamide (DMF).
2. Bake ten minutes at 200 F.
3. Apply "Riston" photopolymer (duPont T. M.).
4. Let stand 30 minutes to develop maximum adhesion of photopolymer.
5. Expose to uv through desired mask.
6. Develop "Riston" (the developer, also supplied by duPont, is reported to be 1,1,1-trichloroethane).
7. Bake 15 minutes at 200 F (to further harden the remaining photopolymer against attack by the following caustic treatment).
8. Immerse three minutes in 33 percent NaOH solution.

9. Rinse sequentially with water, HCl, water (deionized).
10. Treat with DMF and gentle rubbing (the varnish does not dissolve in the ordinary sense but is swollen by the NaOH treatment. Combined solvent and mechanical action are used to expedite its removal. The "fixed" photopolymer apparently endures all of this).
11. Repeat Step 8 for one minute (to assure complete removal of residual varnish where exposed).
12. Rinse as in Step 9.
13. Repeat Step 10.
14. Remove resist with SR stripper (duPont: a methylene chloride based photoresist remover).
15. Rinse in water; air dry.
16. Bake 30 minutes at 200 F, then 60 minutes at 400 F.

Undoubtedly, the procedure is susceptible to further optimization, such as the possible introduction of ultrasonic agitation in Step 10, or even in Step 8. Nevertheless, it does establish production feasibility and serves to complete the basic dielectric requirements needed for a self-contained three-dimensional circuit fabrication process based on polyimide as the insulating medium.



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## CONDUCTOR SYSTEM

### Technical Discussion

General Considerations. — The foregoing dielectric system adopted vacuum deposited metallizations, subsequently photo-etched to delineate circuit patterns in the x,y-planes (for tests of feasibility), but did not define the z-direction conductor. In spite of a highly effective z-direction bonding characteristic, a layer-by-layer process may, in fact, suffer some unavoidable z-direction anisotropy in thermal expansion properties. Consequently, the choice of a z-direction conductor is likely to be more critical than those occupying x,y-planes, and the ultimate reliability of the board may hinge on this choice.

Several z-direction conductor possibilities appear to exist, including plated metal, gold-filled polymer and organic conductors.

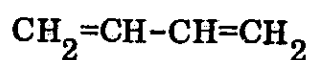
Plated metal conductors, although potentially feasible because of the closer match with the polyimide dielectric in expansion properties, are still limited in their approach to high compatibility with the organic material in other respects. A match in thermal expansion properties, even if exact, does not imply a match in mechanical properties under a high vibration environment, a match in heat transfer properties under asymmetric thermal stress, or a match in water imbibition and possible swelling in a highly humid environment. All of these effects, especially with repetition, are potentially inimical to the structural integrity of the multilayer board. Finding a metal meeting all of these implied compatibility requirements seemed less likely than finding an organic material with an electrical conductivity approaching that of a metal.

A metal-filled polymer, at first glance, would appear to offer the best of both worlds—simultaneous metallic and organic properties. However, each dilutes the other. The necessity for inter-particle metallic contact sets an upper limit on the proportion of admixed polymer and, therefore, on the degree of "organic character." Although some advantage exists over pure metal in the possibility of forming a strong interlocking bond with the surrounding dielectric, the long-term stability of such composites is also in question. Metal migration from silver-filled epoxy, particularly in the presence of oxide or ceramic surfaces, is well known. Although this may not occur with a gold-filled polymer, the problem of stability would still have to be considered in addition to accepting a less than satisfactory match with the properties of the dielectric.

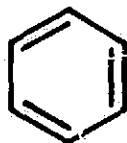
The decision to investigate organic materials for z-direction conductors, or, conceivably, for the entire three-dimensional conduction network, is reasonable, particularly when the molecular structure requirements are fully appreciated and the entire range of potentially useful synthetic routes thereby indicated. Before this could be done properly, however, it was necessary to establish a set of experimental criteria upon which molecular structure goals could be based and synthesis products evaluated. Foremost among these was conductivity, expressed hereinafter in terms of its reciprocal, resistivity (ohm cm). The upper limit of resistivity was selected somewhat arbitrarily on the assumptions that an optimum z-direction geometry through one layer would yield a resistance one one-hundredth the resistivity of the conductor

material, and that an interlayer resistance of one ohm over such a path could be tolerated. This line of reasoning automatically yielded 100 ohm cm as the resistivity limit against which the success of all synthetic efforts would be measured.

The structural requirements for electronic conductivity in organic solids have been defined fairly succinctly (Ref 5) and are provided either by extensive conjugation or by charge transfer (or donor-acceptor) complexing. In the latter case, conjugation generally is a prerequisite of the interacting molecules. In this investigation, the term conjugation is used in its canonical sense, i. e., in reference to alternating double and single bonds, such as



BUTADIENE

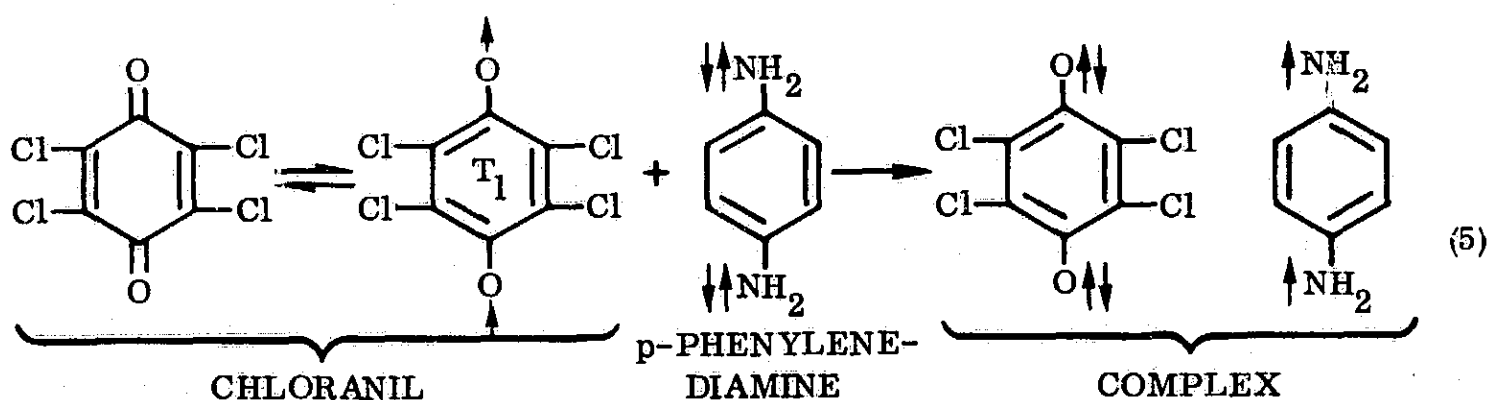


BENZENE

(4)

without specific reference to the delocalization of pi electrons. Calculation of electron delocalization by the LCAO-MO method was not considered a realistic approach because of the inexact nature of the requisite wavefunctions and the inability of the method to reveal partial localization on such a well-known example as the 9,10 carbon atoms of anthracene in the triplet state. It, nevertheless, will be understood that within its purview, conjugation is associated with a certain looseness or mobility of electrons which does not extend to saturated regions of the molecule or beyond the molecular boundaries.

In its simplest terms, charge transfer can be regarded as a means of extracting at least one electron from a conjugated molecular confinement of the type described above and cooperatively holding it in a shallow trap from which it can be expelled with a minimum expenditure of energy. Thus, whereas conjugation alone implies intramolecular electron mobility, charge transfer complexing implies intermolecular electron mobility as an added behavioral feature and as a contribution to the electrical conductivity. The concept can be visualized by a simple sample:

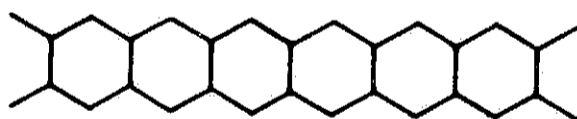


(5)

Here the electron acceptor (chloranil) is assumed to be promoted to the triplet state as indicated ( $T_1$ ), resulting in the unpairing of two electrons (arrows) and the localization of a partial positive charge on both oxygen atoms. Although the quinoid form

probably dominates the equilibrium, the formation of a limited number of  $T_1$  states is energetically feasible because of the introduction of Kekule' (or benzenoid) resonance stability. The net positive charge on the oxygen atoms immediately attracts electrons from a donor, such as the nonbonding electrons of the nitrogen atoms of p-phenylenediamine shown (arrows). The reaction proceeds to completion because the nitrogen atoms are able to carry a net positive charge much more gracefully than the oxygen atoms. Although the participating electrons undoubtedly are orbitally paired (as indicated by the formation of deep color in the complex), they are not completely spin paired, as proved by the EPR spectrometry of many such complexes. The foregoing somewhat sketchy discussion should serve as a foundation for the molecular categories considered herein. Of all the types of conductive organic solids known, the charge transfer complexes probably are superior for the purposes of this program.

A second criterion of importance was thermal stability because the final cure of each application of polyimide is conducted at 600 F. Thus, the organic conductor must be able to undergo repeated temperature cycles without outgassing or loss of conductive properties. Unfortunately, thermal stability of organic conductors cannot be assumed even if they are highly polymeric. A number of cases are known where thermal effects, either alone or in conjunction with water, are able to cause "unzipping" of polymer molecules with the release of original monomers or other low molecular weight fragments. There is, however, a molecular rationale for achieving high thermal stability in polymers (Ref 6). In the past, the main approach has been to provide for substantial cross-linking between polymer chains. Unfortunately, this introduces insolubility and infusibility which render the materials intractable in the kind of process techniques of importance here. A more modern approach is the development of "ladder" polymers (Ref 6, p 103) which may be represented as follows:



(6)

Such chains cannot be thermally broken except by simultaneous severance of chemical bonds on opposite sides of the same cell, which is a low probability event. Conversely, the severance of one bond has an improved probability of recombination because the remaining bonding system tends to hold the respective atoms in convenient juxtaposition. A further stability aspect of these materials is that they contain a high degree of aromaticity and behave toward environmental oxygen as though they had been already dehydrogenated (or oxidized). As long as the aromatic conjugation remains localized in the repeating molecular segments, the material retains good insulating properties. If molecular tailoring is performed so as to introduce communication between the conjugation of adjacent segments, a conductor is formed. Many examples of this are found in the pyrolyzed polymers.

Ladder polymers are not easy to make. But a near approach to ladder-like character goes a considerable way in achieving the ideal structure and stability. The polyimides (Vespel and ML varnish) used on this program as dielectrics are excellent examples. The polybenzimidazoles are similar in ladder character (Ref 6, p 104, 105)

and also can be dissolved in common polymer solvents. Furthermore, the conjugation is not segmented but extends throughout the molecular chain. Unfortunately, one of the two nitrogen heteroatoms of each imidazole unit is non-participating and the room temperature resistivities generally lie above  $10^{12}$  ohm cm (Ref 5, p 75). In polyquinoxaline (Ref 6) both nitrogen atoms participate in the conjugation, but the conductive properties of this material do not appear to have been investigated.

The focus of attention on ladder structures was not intended to be exclusive. Other conjugated, conductive structures of high thermal stability exist, such as the metal phthalocyanines. Furthermore, some difficulty was expected in getting a ladder polymer to form a charge transfer complex, if required, for meeting the conductivity specification. It was desirable, however, to be able to call upon specific structural concepts as a guide to synthetic efforts.

A third criterion consisted in the possession of molecular properties that could be exploited in an application technique capable of placing the organic conductor exactly where it belonged on the circuit board. Of particular interest here were solubility in specific media from which films could be deposited, for example, by a screening process, and vaporization properties compatible with a vacuum deposition method.

The solubility of polymers is a very broad subject. In general, chain type polymers are soluble while cross-linked are insoluble. Solubility of a given polymer does not necessarily imply good film or layer forming ability. A further and more serious complication arises from the fact that the structural requirements for high conductivity confers, in the majority of cases, the properties of insolubility and infusibility. Consequently, the probability of finding a film forming polymer of high electronic conductivity was felt to be rather low and tests were limited to simple "go, no-go" determination with relatively strong solvents, such as dimethylformamide. There were, of course, other potential alternatives, such as deposition (possibly by electrophoresis) of insoluble particulates followed by compaction or inoculation with a binder, or deposition in a soluble (nonconductive) form followed by chemical or thermal treatment to develop conductive (and insoluble) properties.

Vacuum deposition was aimed at achieving the same purpose. The extremely tractable behavior of copper phthalocyanine (Ref 7) under these conditions is well known. Other phthalocyanines of similar stability but increased conductivity could be examined. Even though they were not polymeric, their thermal stability qualified many of them for the system under development. Another possibility was to dissociate a charge transfer complex and reconstitute it on a substrate under conditions of vacuum deposition. In selected cases, therefore, thermal excitation under vacuum was explored.

On the basis of the foregoing considerations a decision was made to concentrate primarily on organic conductors, leaving plated metal, or metal-polymer, z-direction conductors as secondary alternatives. The decision was further refined to four classes of compounds:

1. Polymeric charge transfer complexes, particularly those of TCNQ with a donor polymer

2. Metal phthalocyanines
3. Polyaminoquinones
4. Pyrolyzed polyacrylonitrile

Each of these classes is unique with respect to structural rationale, synthesis routes, and handling techniques, thereby requiring individual treatment in the subsequent discussion of experimental activities. Following is a summary in which the available experimental evidence is used in comparing and rating these classes.

Test Methods. — For resistivity measurements the compressed powder method was generally employed unless the specimen originally was self-coherent and dense.

A pellet from the raw material was formed in a circular die of approximately 3/4 in. diameter by compression at 35,000 psi using a Carver Laboratory Press, Model B. This pressure substantially exceeded the required 80 Kg/cm<sup>2</sup> (1,140 psi) specified by Akamatu and Inokuchi (Ref 8) to reach the resistivity vs compaction plateau for many powdered organic samples. It was assumed that by maintaining an invariant compaction pressure, it would at least be possible to draw valid comparative conclusions among the various samples investigated. In some instances, small additions of Carbowax were required to improve particle cohesion.

Accurate pellet thicknesses were required and were derived directly from measurement of the relative positions of tool and die after compaction. Thicknesses usually fell in the range of 0.04 to 0.07 in. To both sides of the pellet were applied circular silver paint contacts of 0.562 in. diameter. This geometry provided a surface current path substantially longer than the bulk path, thereby reducing the possibility of spurious current leakage effects. Resistivities were measured by d-c technique using a General Radio resistance bridge or a Keithley electrometer. Usually six to ten readings were taken over a period of time under continuous bias to establish whether or not an ionic contribution to the current was present. In such an event resistance would increase with time as a result of electrode polarization by the discharge of ionic carriers. Resistivities were computed from the current path length-to-area ratios and the observed resistance or current-voltage readings.

Other test methods, such as those applicable to thermal stability, solubility, and vacuum deposition, were not brought into clear, quantitative definition within the period of the program mainly because of the provisional nature of process requirements. Therefore, these tests are described in the following experimental section at the points where they were applied.

#### Experimental Investigations

Donor Polymer — Acceptor Polymer Complex. — One type of completely polymeric charge transfer complex would be that formed from a donor polymer and an acceptor polymer (another type is discussed in a following section entitled "Polyaminoquinones"). There is no a priori reason why such a complex should be more conductive than charge transfer complexes made from simpler molecules. In fact, probably neither the donor nor the acceptor could be regarded as "strong" in

the same sense as is TCNQ. In addition, the very size of the polymer molecular entities might seriously hinder a 1:1 matching of donor and acceptor sites and an efficient utilization of such sites in "liberating" conduction electrons.

In a sense, therefore, such an experiment is largely academic — except for one potentially important reason: thermal stability. The usual charge transfer complexes often are heat-labile. If loss of simple complex-forming molecules, such as TCNQ, can occur at ML varnish cure temperatures, then less vulnerable materials must be found. This possibility was offered in a completely polymeric system, and it was expected that appropriate structural criteria for both thermal stability and high electrical conductivity could eventually be defined and wedded together in single molecular system.

To test the above concept a polymeric analog of a previously prepared bisphenol derivative of 5-nitroisophthalic acid (Appendix B, p 7) was allowed to interact with poly (phenyliminodiethanol-bisphenol A carbonate) (Appendix B, p 6). Generation of the complex was evidenced by the formation of a blue-black insoluble product. Unfortunately, the material was difficult to isolate because of its instability, and no further experiments were undertaken. The absence of a significant literature foundation on this type of composition further augmented the decision to abandon the approach.

TCNQ-Polymer Complex from JPL. — The strong electron acceptor character of tetracyanoquinodimethan (TCNQ) in the formation of charge transfer complexes with electron donors has been known for almost a decade (Ref 9, 10, 11). The electron donor, in turn, may be any element, simple compound or polymer possessing nonbonding electrons, such as those frequently associated with organic nitrogen atoms. At an early stage in this program Dr. A. Rembaum of the Jet Propulsion Laboratory forwarded samples of a complex of this type to us in which the donor was a nitrogenous polymer.

According to Dr. Rembaum, the substance was formed by quaternizing a polyurethane similar to one prepared by us (Appendix B, p 6) using ethylene dibromide, followed by reaction with the lithium salt of TCNQ. The polymer was black and flexible, and was reported to have a resistivity of  $10^6$  ohm cm. While this was well beyond the resistivity limit previously established, the sample was regarded as a first step in developing more conductive materials.

The polymer was prepared for test by coating opposite sides with uniform areas of silver paste and its resistivity determined with the aid of a megohm resistance bridge and an applied dc field of the order of  $10^4$  volts/cm. Resistivity was found to be in excess of  $10^8$  ohm cm, or two orders of magnitude higher than that originally observed. This kind of discrepancy, at this time, was believed to be caused by the gradual loss of TCNQ from the complex. This created some misgivings that TCNQ salts would be applicable at all, because it was recognized that excess TCNQ would be necessary for achieving the lower resistivities sought, which could be quickly lost at the 600 F cure temperatures required for the ML varnish. Thermal stability thus became an important aspect of continued investigation of conductive organic solids. Despite its favorable mechanical properties, the high resistivity of this material was considered sufficient reason to disqualify it from further consideration.

TCNQ-Poly (2-vinylpyridine) Complex. — Of all the nitrogenous donor polymers considered on this program for complexing with TCNQ, poly (2-vinylpyridine) (Appendix B, p 7) was by far the superior. Not only was the "donatable" electron density of this material (on a weight basis) better than four and a half times that of the polyurethane and polycarbonate (Appendix B, p 6) (as well as the donor polymer of the preceding section), but the participating nitrogen atoms were directly linked into the conjugation of the pyridine nuclei, thereby assuring a higher degree of electron delocalization (i. e., availability without creation of strong local polarization). The only material of clearly obvious superiority over this one would have been the analogous polymer derived from 2-vinylquinoline, but locating a source of this monomer defied our best efforts.

Two general synthesis routes were open for investigation: direct complexing of the polymer with TCNQ, and initial conversion of the polymer to the N-methylated derivative, followed by complexing. In view of recent patent literature (Ref 12) the latter course was adopted first. In general, the chemical procedure involved simple metathesis of an alkali metal salt of TCNQ, such as lithium-TCNQ ( $\text{Li}^+\text{TCNQ}^-$ ) or potassium-TCNQ ( $\text{K}^+\text{TCNQ}^-$ ), with an iodide salt of the nitrogen base. The resulting complex usually was insoluble in the reaction medium and precipitated as a deeply colored product while the lithium iodide remained in solution.

A second synthesis variable was the degree to which all of the polymer nitrogen atoms had been "TCNQ'ed." This turned out to be a far more important factor to the conductivity and the thermal stability than the presence of N-methylation, but it did not become evident until experimental evidence began to accumulate.

A portion of the poly(2-vinylpyridine), prepared by free radical initiated bulk polymerization of the monomer, was N-methylated with dimethyl sulfate, as taught by the Lupinski and Kopple patent (Ref 12). Initial complexing experiments were carried out on some of this material using  $\text{K}^+\text{TCNQ}^-$ , but met with limited success because of the low solubility of the potassium salt in the specified reaction solvent. During the course of these experiments some doubt arose as to the composition of the starting polymer.

The original N-methylated polymer therefore was analyzed for sulfate groups to estimate the extent of quaternization. The result indicated only about one in eight nitrogen atoms had been methylated. It also was suspected that the product contained initial  $\text{K}^+\text{TCNQ}^-$ . Extraction with acetonitrile left a bright blue insoluble residue somewhat similar in appearance to  $\text{K}^+\text{TCNQ}^-$ . Solubility of the polymer in acetonitrile and DMF (to form deep green solutions), however, was verified. Possible recovery of a product of reliable composition, was deemed unlikely, however.

Because of these uncertainties it became important to obtain at least comparative information on the expected effects, not only of N-alkylation but of alkyl substitution on the pyridine nucleus, as was the case in the original 2-vinylpyridine polymer. Information on the latter question was not located, although there seemed to be no reason why aliphatic substitution in the 2-position of pyridine should materially alter the electrical properties unless some TCNQ molecules were thereby crowded out. Data concerning the relative effects of N-alkylation, however, was found (Ref 13), the more relevant of which is given in Table III.

TABLE III  
PROPERTIES OF SOME TCNQ SALTS

Cation	Decomposition Temperature (Deg C)	Room T Resistivity (ohm cm)	Appearance
Pyridinium <sup>+</sup> TCNQ <sup>-</sup> (a)	158 - 195	10 <sup>6</sup>	Purple cryst
N-Methylpyridinium <sup>+</sup> TCNQ <sup>-</sup> (a)	~ 235	10 <sup>5</sup>	Purple cryst
N-Methylquinolinium <sup>+</sup> TCNQ <sup>-</sup> (a)	240 - 244	10 <sup>7</sup>	Purple cryst
Pyridinium <sup>+</sup> TCNQ <sup>-</sup> TCNQ <sup>0</sup> (b)	168 - 185	37	Blue-black
Quinolinium <sup>+</sup> TCNQ <sup>-</sup> TCNQ <sup>0</sup> (b)	~ 250	0.5	Blue-black
N-Methylquinolinium <sup>+</sup> TCNQ <sup>-</sup> TCNQ <sup>0</sup> (b)	245 - 250	3	Blue-black
N-Ethylquinolinium <sup>+</sup> TCNQ <sup>-</sup> TCNQ <sup>0</sup> (b)	237 - 239	8	Blue-black
N-n-Propylquinolinium <sup>+</sup> TCNQ <sup>-</sup> TCNQ <sup>0</sup> (b)	226 - 228	2	Black
2,2'-Bipyridinium <sup>+</sup> TCNQ <sup>-</sup> TCNQ <sup>0</sup> (b)	235 - 268	0.5	---

(a) Ref 13, Table VI, page 3385  
(b) Ref 13, Table VIII, Page 3386

It is clear from Table III that N-alkylation within a given series, (a) or (b), has a relatively minor effect on resistivity whereas doubling the TCNQ content, series (a) vs series (b), has an enormous effect. For example, the simple salt, pyridinium<sup>+</sup> TCNQ<sup>-</sup>, goes from 10<sup>6</sup> to 10<sup>5</sup> ohm cm via N-methylation, but to 37 ohm cm by simply adding TCNQ<sup>0</sup>. On this basis, it seemed to matter little whether our polymer was methylated or not, but that we could achieve a resistivity of 37 ohm cm if we could get our vinylpyridine polymer completely TCNQ'ed.

Three separate preparations of TCNQ complexes were carried through to the testing stage. The starting material for the first preparation was the poly(2-vinylpyridine) approximately 12 percent N-methylated with dimethyl sulfate. The material was converted to the iodide via potassium iodide treatment, and then to the TCNQ salt using the Lupinski and Kopple method (Ref 12). The TCNQ stoichiometry was chosen to provide a slight excess over two TCNQ's per methylated nitrogen, which amounted to about half a TCNQ per nitrogen on a total nitrogen basis. The deficiency of TCNQ in this preparation, which was designated TCNQ-PVP-1, was obvious from its relatively light purplish golden color.

Using the same partially methylated starting material, the second preparation was also conducted in accordance with Reference 12 but employing an optimum excess



of TCNQ. The uniformly violet colored product was isolated by filtration and was estimated to contain more than one, but less than two, TCNQ's per nitrogen atom. It was labeled TCNQ-PVP-2.

The third preparation began with original unmethylated polymer which was converted to the hydroiodide, with excess water removed by evaporation under reduced pressure. The resulting salt was treated immediately with TCNQ solution according to the improved method of Melby, *et al* (Ref 13). The deep blue product was separated by filtration, briefly washed, and dried *in vacuo*. The product was estimated to contain not quite two TCNQ's per nitrogen atom due to apparent loss sustained in washing. It was designated as TCNQ-PVP-3.

Compressed pellets of all three products were prepared and their electrical resistivities measured. Further samples were exposed to a half-hour thermal treatment to simulate a polyimide cure cycle. The relevant data are listed in Table IV along with those for polyaminoquinone, a synthetic product described in a following section but included here for comparison.

TABLE IV  
ELECTRICAL AND THERMAL PROPERTIES  
OF SYNTHETIC ORGANIC CONDUCTORS

Material	Room T. Resistivity (ohm cm) (a)	Appearance	Weight Loss at 650 F (%)	Appearance After Pyrolysis
PAQ-1 (b)	$3 \times 10^{12}$	Black Powder	80	Black Granules
TCNQ-PVP-1 (c)	$4 \times 10^6$	Gold and Violet, Mottled	91	Black Granules
TCNQ-PVP-2 (d)	$1.3 \times 10^4$ (Ref 12: $1.0 \times 10^4$ )	Violet	32	Black Globules
TCNQ-PVP-3 (e)	$5 \times 10^3$	Deep Blue	24	Black, Shiny

(a) Compressed pellet technique.

(b) A polyaminoquinone preparation described in a later section.

(c) TCNQ complex with poly(2-vinylpyridine) containing substantially less than one TCNQ per pyridine nitrogen.

(d) Complex estimated to have slightly more than one TCNQ per pyridine nitrogen.

(e) Complex having substantially more than one TCNQ, but probably less than two TCNQ's, per pyridine nitrogen.

It is evident from Table IV that the preparation, TCNQ-PVP-3, is only a factor of 50 higher than our previously established goal of 100 ohm cm. In view of the fact that this material probably is not completely TCNQ'ed, it appears there still is sufficient ground for expecting to meet and exceed the resistivity requirement, especially in view of the published resistivity of 37 ohm cm (Ref 13) for completely TCNQ'ed normal pyridine.

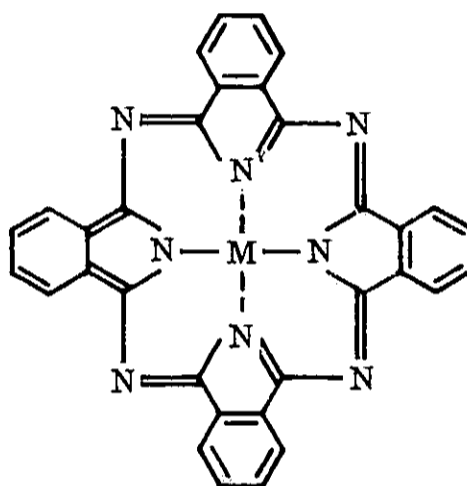
The somewhat higher resistivity of the partially methylated complex, TCNQ-PVP-2, may indicate a steric, or crowding, effect due to the presence of added methyl groups. This should not be a problem with free N-methylated pyridine, but the situation might be quite different where the pyridine moieties are linked together via ethylenic groups and their spatial domains thereby restricted. Thus, there appeared to be no advantage in using N-methylated raw material.

A further correlation evident from Table IV is the color sequence in the TCNQ preparations which conforms to an increasing TCNQ ratio. This is further supported by Melby, *et al*, (Ref 13) who report generally purple colors for "simple salts" (singly TCNQ'ed) and blue-black to black for "complex salts: (doubly TNCQ'ed).

Most important to the objectives of this program, however, is the decreasing pyrolytic weight loss with increasing TCNQ ratio and increasing conductivity. The thermal treatment used here was a half-hour exposure (in air) at 625 to 675 F, which is rather rough treatment. Although the percentage losses are quite high it should be remembered that almost all pyrolyses cause weight loss, if only due to dehydrogenation. In the present series, some burning must have occurred (the PAQ-1 sample was seen to glow at one point) although dissociation of complex may be a further factor. Repetition of the experiment in a nitrogen atmosphere would serve to differentiate between the two effects. It also should be noted in passing that 600 F curing of polyimide under nitrogen would be just as effective as it would in air. At any rate, the increasing thermal stability with increasing TCNQ ratio, which is not totally surprising (Ref 13), lies in a favorable direction for purposes of this program.

A further observation is the generally black character of the pyrolyzates. Deepening of color usually indicates increasing electrical conductivity. It should be recognized, however, that in the present case this does not amount to "graphitization," which requires far higher temperatures. The expected increase in conductivity is a result of the extension of conjugation and of the accompanying electron degeneracy introduced by the pyrolysis. It is precisely this electron degeneracy that we are after in organic conductors. In most respects, therefore, the high temperature treatments can be made to work in our favor. If the original molecular identity is lost in the heat treatment, the new identity should serve better. This could become a crucial advantage in the use of polyimide which does not lose its dielectric properties in the same treatment. In any event, the foregoing investigation tends to confirm the important electron acceptor properties of TCNQ in charge transfer complexes, and to support the expectation that materials sufficiently conductive for use in multilayer circuitry can be made thereby.

Metal Phthalocyanines. — The metal phthalocyanines have received considerable attention not only because of their conductive properties but also because of their remarkable chemical and thermal stability. They were of interest in this program because some of them (e. g., copper phthalocyanine) could be vacuum deposited in tenacious, pinhole-free films on room temperature substrates at pressures of the order of  $10^{-5}$  to  $10^{-6}$  Torr (Ref 7, p. 2). The copper derivative, however, is somewhat lacking in interplanar pi-orbital overlap and its resistivity is correspondingly high. "Interplanar" here refers to the plane of the molecule, represented as follows, with M denoting a divalent metal atom:



(7)

Attempts to improve the pi electron overlap by substituting other metals for copper have been made (Ref 7, p. 5), but in the case of silver, thermal stability was lost, probably because of its monovalency. The same authors recommended cobalt phthalocyanine as a further candidate.

Following the above lead, a small quantity of cobalt phthalocyanine was synthesized by four hours' refluxing of phthalonitrile with cobalt powder (Ref 14, p. 136). The recovered yield was small but sufficient for electrical tests. In a repetition of the synthesis, a portion of quinoline (in which cobalt phthalocyanine is somewhat soluble) was added, whereby the yield was substantially improved.

The product was obtained by filtration as fine microcrystals having a deep blue color with reddish-purple luster. It was purified by solvent washing and vacuum drying. A pellet specimen was prepared according to the previously described method. The measured resistivity was  $1.84 \pm 0.093 \times 10^8$  ohm cm in six readings taken over a period of ten minutes. This fairly constant result was taken as evidence that significant electrode polarization did not occur and ionic impurities were essentially absent.

The cobalt phthalocyanine satisfies the thermal stability requirements; i. e., it can be sublimed without decomposition (Ref 14, p. 136), but not the electrical conductivity requirement. Subsequent literature investigation disclosed that our result was reasonably accurate (Ref 15, p. 718) and that about the best that could be done would be to make the manganous derivative. The relevant data are given in Table V.

TABLE V  
ROOM TEMPERATURE RESISTIVITIES AND MAGNETIC  
MOMENTS OF METAL PHTHALOCYANINES

Metal	Resistivity (ohm cm) (a)	Magnetic Moment (d) (Bohr Magnetons)
Copper (b)	$10^{12}$	1.73
Cobalt (c)	$10^9$	2.16
Manganese (c)	$10^6$	4.55
(a) Ref 15, p. 718, 719 (b) Compressed powder (c) Single crystal (d) Ref 14, p. 45		

The sequence in Table V is confirmed by the corresponding paramagnetic properties (Ref 14, p. 45), that of the manganese derivative being 4.55 Bohr magnetons and significantly higher than other known compounds. The presence of paramagnetism implies the presence of unpaired electron spins and of possible electrical conductivity. The conductivity of the manganous derivative, however, still fell short of the goal of  $10^2$  ohm cm.

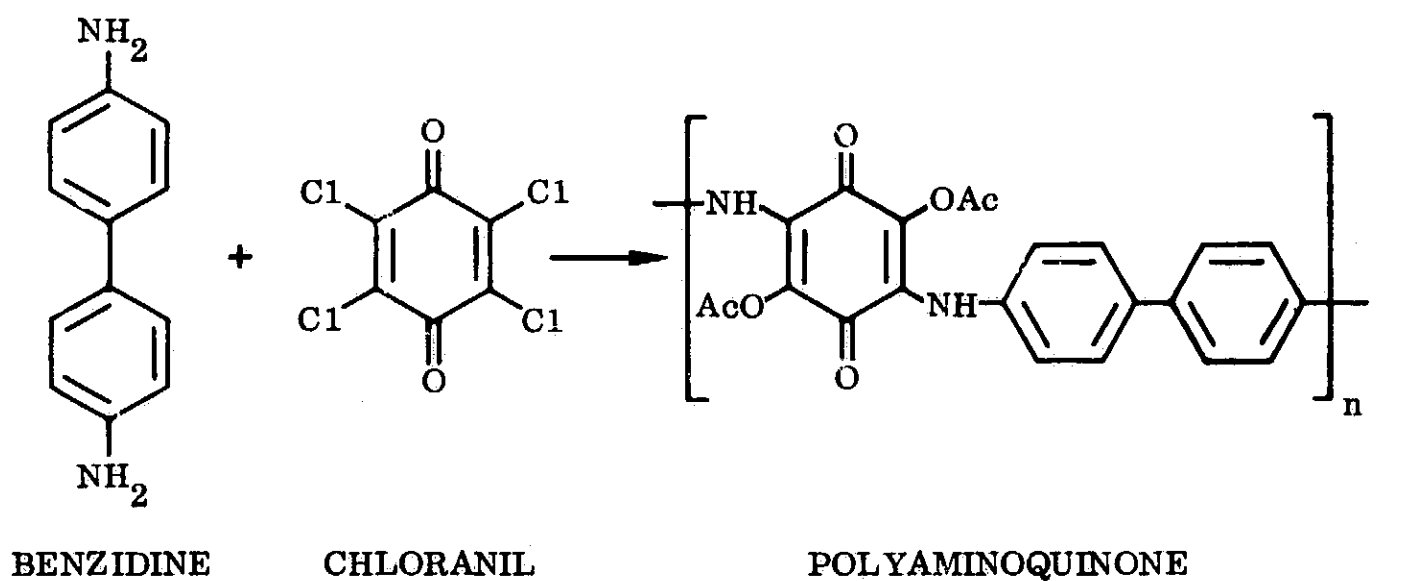
One further experiment was attempted: a combination of cobalt and manganous phthalocyanines in approximately 1:1 stoichiometry. The rationale for this was that a cooperative effect in molecular orbital overlap might be achieved in the combination that would be considerably exaggerated over that of either compound separately and would facilitate intermolecular tunneling. Cooperative effects with respect to magnetic dipoles already are known (e.g., the ferrites). Cobalt and manganous phthalocyanines are among those of highest magnetic moment known in this class (Table V). Paramagnetism correlates directly with unpaired electron spins, and EPR spectrometry of conductive organic solids yields a similar correlation between the unpaired spin population and conductivity. Working against this possibility is the generally observed effect of impurity scattering of charge carriers which results in an increase in the electrical resistivity (i.e., each compound would appear as an "impurity" to the other since no more than one divalent metal atom could occupy the central coordination position of the phthalocyanine molecule at one time).

Unfortunately the latter effect dominated. A product, prepared by interaction of phthalonitrile with a 1:1 (atomic basis) mixture of cobalt and manganese powders was isolated from the reaction mixture as a jet black powder, compressed into a pellet and its resistivity measured in the usual manner. The result was  $1.5 \times 10^{10}$  ohm cm, 100 times greater than that found for cobalt phthalocyanine and  $10^4$  times greater than that reported for the manganous derivative. In consequence, this line of investigation was reluctantly terminated.

**Polyaminoquinones.** — Investigations of the polymer formed from the interaction of benzidine with chloranil, and the corresponding nickel and copper complexes, have been previously made (Ref 16). Room temperature resistivities on compressed pellets

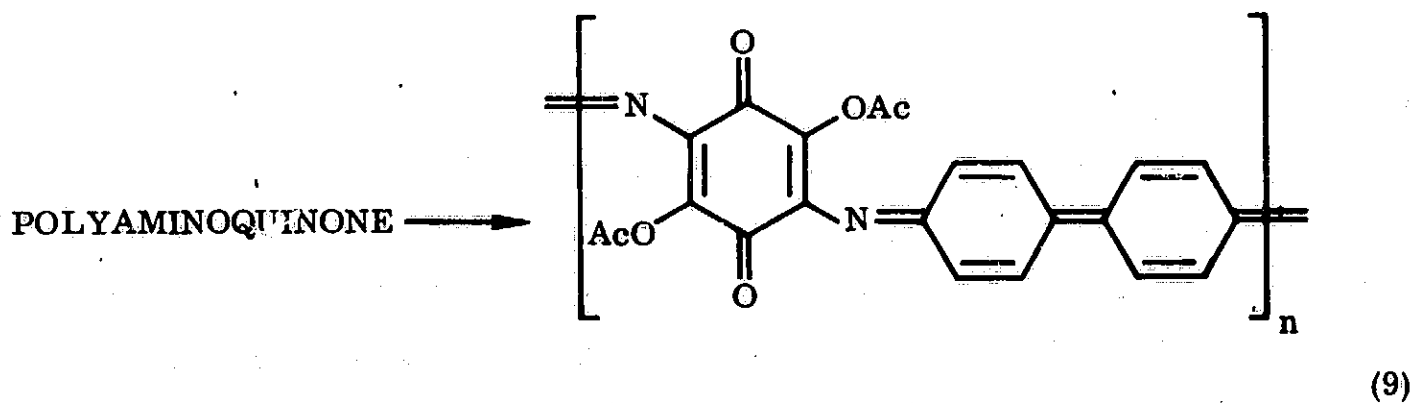
(100,000 psi) were of the order of  $10^{12}$  ohm cm and impractically high. However, opportunity for improvement on this very preliminary work appeared to exist because the synthetic route, which is comparatively simple, seemed susceptible to a variety of modifications in the direction of optimizing both conductivity and thermal stability.

The method of synthesis described by L. M. Woerner (Ref 16, Appendix I, p. 5) yields a dark brown insoluble polymer of the reported structure shown below:



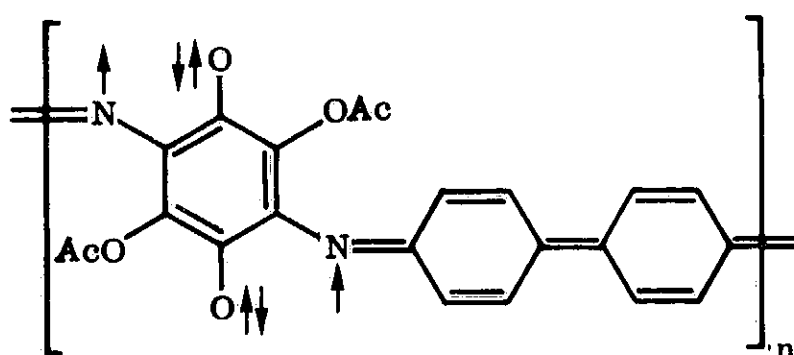
(8)

A possible modification was to carry out the synthesis with excess chloranil to oxidize the benzidine to the quinoid form:



(9)

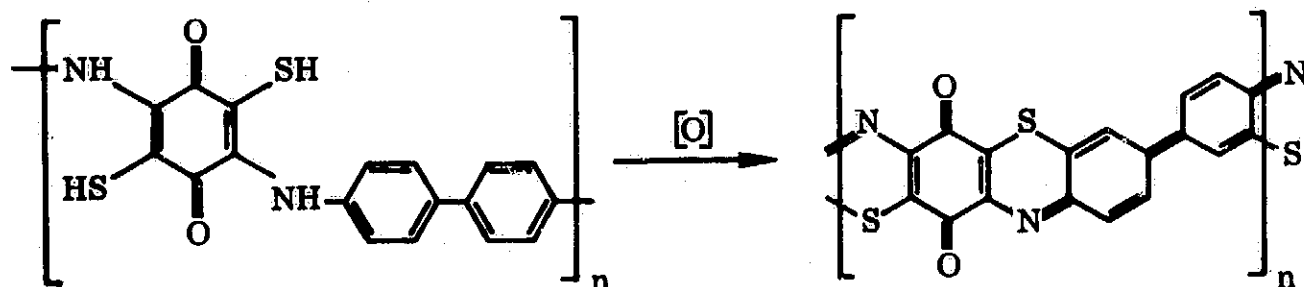
Under these circumstances the nitrogen atoms would be converted to a form in which they could transmit conjugation. In addition, the quinoid grouping would be still capable of promotion to a benzenoid triplet state which could act as an electron acceptor to the neighboring nitrogen atom donor:



(10)

We would thereby achieve built-in, or homomolecular, charge transfer with a correspondingly reduced possibility of dissociation under thermal stress.

In addition to the oxidative approach one could substitute sodium sulfide for the acetate in the synthesis which should yield a ring closure on subsequent oxidation:



(11)

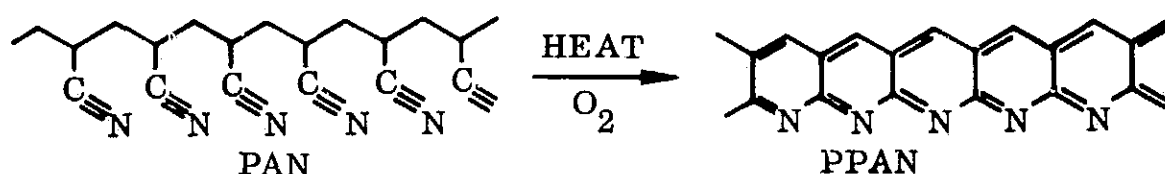
The resulting poly(thiazinoquinone) now would have a high degree of "ladder" character, which would bring it well into the range of the polyimide thermal stability, in addition to providing a structural foundation for significant electron degeneracy.

An initial synthesis aimed at the oxidized modification represented in formula (9) above was carried out with an excess quantity of chloranil. The product which was designated PAQ-1, was obtained as a jet black insoluble powder. The resistivity, determined by the usual technique, was disappointingly high:  $2.83 \pm 0.085 \times 10^{12}$  ohm cm in six readings taken over a period of 10 minutes. This result suggested that the

excess chloranil, although forming a more deeply colored complex, did not perform the expected oxidation because the resistivity was essentially unchanged from that previously reported (Ref 16). A thermal stability test, previously listed in Table IV resulted in an 80 percent weight loss and was equally discouraging.

Although a strong feeling remained that the synthesis routes indicated above for this class of materials could be pursued to a fruitful conclusion, it appeared advisable to drop further work on it, mainly because of a general lack of detailed information.

Pyrolyzed Polyacrylonitrile (PPAN). — Heating "Orlon" (polyacrylonitrile fibers) in air produces black, infusible, insoluble, nearly incombustible, electrically conductive filaments. Both the thermal stability and the conductivity are believed due to the formation of a highly conjugated ladder polymer (Ref 5, p. 49):



(12)

The thermal activation energy of conduction ranges from 0.06 ev to 0.33 ev (Ref 15, p. 483), and the room temperature resistivity, from 12 to  $10^{10}$  ohm cm. The large range in properties is associated primarily with pyrolysis conditions which cover at least a span of 400 to 700 C. Unfortunately, the higher conductivities probably are produced at the higher temperatures which may exceed the endurance of the polyimide dielectric. However, pyrolysis in the absence of air also is possible (Ref 17, p. 169-171) under which conditions polyimide is capable of sustaining temperatures up to 1000 F, or more, for limited periods (Ref 2, p. 255, 259). It was considered feasible, therefore, to evolve a regime that would fully develop the PPAN conductivity without compromising the integrity of the dielectric. Another attractive feature was that the material could be applied to the board in soluble form prior to pyrolysis.

It soon was discovered that commercial "Orlon" contains a certain proportion of polyester which was considered to be disadvantageous for the intended application. Attempts to locate an external source of polyacrylonitrile were unsuccessful; therefore, a quantity of polyacrylonitrile (PAN) was prepared in-house according to an established procedure (Ref 18) by emulsion polymerization of the monomer. The molecular weight achieved by this method is said to be extremely high (Ref 18). A portion of the white product was damp-dried on a clay plate, then dissolved in DMF. The DMF solution, painted on glazed ceramic substrates, formed adherent colorless films on solvent evaporation. The specimens then were placed in the same muffle furnace simultaneously with the pyrolysis samples listed in Table IV. As expected, black shiny films were produced indicating that a normal polyimide cure cycle might be sufficient to develop adequate conductive properties. The films appeared to be of good density,

showing no evidence of ablation. Adherence generally was good although some localized delamination and curling from the ceramic surface was present. The experiment tended to confirm process feasibility if sufficient conductivity could be developed in the pyrolysis.

Two additional samples of the original PAN were "bulk" pyrolyzed in air for six hours at 650 F. Designated PPAN-1 and PPAN-2, the second differed from the first by having contained an initial admixture of five percent sulfur (flowers). The intended purpose of the sulfur was to assist in the dehydrogenation and aromatization of the polymer, thereby creating a higher degree of electron degeneracy and, hence, greater conductivity.

The products were obtained as jet black, fluffy powders having poor interparticle cohesion. Preparation of pellets required the admixture of up to 15 percent Carbowax to obtain intact specimens for electrical measurement. The observed resistivities were surprisingly high:  $3 \times 10^9$  ohm cm for PPAN-1;  $2 \times 10^{11}$  ohm cm for PPAN-2. Even more surprising was the higher resistivity (by a factor of 100) of PPAN-2, which was supposed to be the more highly conjugated as a result of the sulfur treatment.

An explanation of these results obviously must await further investigation. Several experimental variables should be examined for their effects on final electrical properties. For example, what effect does the state of molecular aggregation in the initial PAN have on the molecular organization in the pyrolyzate? The above experiments suggest that a film derived from evaporation of a DMF solution produces a denser pyrolyzate than that from the original untreated PAN. The "contrary" result from the sulfur treatment is inexplicable (at this writing), but intriguing and demanding of further study.

The above results should be regarded as highly preliminary and not prejudicial to the real promise of PPAN as a potential z-direction conductor. In our estimation it is second in this respect only to the TCNQ complexes which, themselves, may create many fabrication problems not associated with PPAN.

Summary of Conductor Properties. — The outstanding properties of the candidates for z-direction conduction material examined on this program are assembled and compared in Table VI.

The information presented in Table VI shows that the metal phthalocyanines, although of impressive thermal stability, are much too high in resistivity to meet the electrical requirements of z-direction conductors. Accordingly they were deleted from further consideration. The polyaminoquinone, PAQ-1, is unsatisfactory in both aspects and was deleted also.

Perhaps the strongest remaining contender is the TCNQ-polyvinylpyridine complex (TCNQ-PVP-3) having the highest proportion of TCNQ (the compositions 1, 2, 3 being arranged in order of increasing TCNQ). This will be particularly true if, as expected, its pyrolysis product formed at the polyimide cure temperature is less resistive than the starting material. A further requirement, however, is that the pyrolyzate not yield gaseous reaction products on subsequent polyimide cure cycles which would tend to blister or rupture overlying varnish layers.



TABLE VI  
ELECTRICAL AND THERMAL PROPERTIES OF  
SYNTHETIC ORGANIC CONDUCTORS

Material	Initial Room T Resistivity (ohm cm)	Appearance	Attrition Due to Pyrolysis*	Resistivity After Pyrolysis (ohm cm)	Appearance After Pyrolysis
Cobalt Phthalocyanine	$2 \times 10^8$	Purple-blue	Minimal		Unchanged
Co-Mn Phthalocyanine	$1.5 \times 10^{10}$	Black	Minimal		Unchanged
PAQ-1	$3 \times 10^{12}$	Black	Excessive		Black granules
TCNQ-PVP-1	$4 \times 10^6$	Gold-violet	Excessive		Black granules
TCNQ-PVP-2	$1.3 \times 10^4$	Violet	Tolerable**	***	Black granules
TCNQ-PVP-3	$5 \times 10^3$	Deep blue	Tolerable**	***	Black, shiny
PPAN-1		Colorless	Tolerable**	$3 \times 10^9$	Black
PPAN-2		Colorless	Tolerable**	$2 \times 10^{11}$	Black

\*Carried out at the polyimide cure temperature, 650 F.  
 \*\*Assuming negligible evolution of gaseous byproducts on subsequent thermal treatments.  
 \*\*\*Should be measured; good probability of falling below the  $10^2$  ohm cm resistivity limit.

The pyrolyzed polyacrylonitrile (PPAN-1 and -2) falls far short of the realizable conductivity of about  $10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$  (Ref 15) although its thermal stability and lack of residual gas-forming tendency on further heating undoubtedly are superior to the TCNQ-PVP preparations. The high resistivities undoubtedly reflect to some (small) extent the intermixed Carbowax that was required as a binder in the formation of the required test pellets. Real progress will be made, however, only by optimizing the pyrolysis technique employed.

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## **CONCLUSIONS**

A new concept in the fabrication of three-dimensional circuitry based on a layer-by-layer process has been evolved and tested.

The isolation dielectric is a highly cured polyimide, applied in layers but molecularly interlocked in the z-direction to form a monolithic insulating medium. Circuits in the x, y-planes are produced individually by photolithography of vacuum deposited metallizations. Interplanar electrical communication is obtained by photo-etching through-holes in the last-applied dielectric layer and filling them with conductor. The multilayer structure is supported on a slab of Vespel (du Pont), a polyimide compatible with the polyimide varnish layers individually applied, or on an aluminum plate. In the latter case, a first layer of polyimide varnish must be applied to obtain electrical isolation of the first metallization from the aluminum substrate. Exposed circuit terminations are copper plated where required for component, cable, or mother-daughter interconnection soldering. A minimum sequence of operations embodying this approach has been defined which, following certain critical process steps, allows electrical tests to verify the absence of pinholes in the underlying polyimide layer and visual tests to verify registration with the previous circuit pattern. Such tests could become the basis of reliability guarantees not possible with more conventional procedures. The technical feasibility of most of the steps has been established as well as their sequential compatibility.

An important consequence of the substitution of polyimide for glass-epoxy laminates is the achievement of a closer thermal expansion match with most metals useful in board fabrication. In particular the z-direction expansion coefficient of epoxy-glass in conventional laminates is roughly a factor of five greater than that of the polyimide. Therefore, the change to polyimide alone should be sufficient to greatly reduce z-direction circuit failures due to unequal expansion. It is anticipated that this point can be demonstrated by thermal cycling tests in subsequent work.

A second consequence of the process is the potential elimination of misregistration. This results from the opportunity for visual inspection at each step and from the transparency of the polyimide layers, which contain no fiberglass. Positive control of alignment of artwork with previous patterns is therefore inherent.

A further advantage lies in the elimination of strong sulfuric acid treatments and the associated probability of interlaminar entrapment of corrosive chemical residues. Although chemical treatments are required for photoetching of metallizations and varnish layers, they are applied to one layer at a time which, by eliminating edgewise exposure of multiple laminae to corrosive chemicals, reduces the opportunity of internal entrapment and improves the effectiveness of rinsing operations.

Through-hole plating failures due to "epoxy smear" also are eliminated because drilling operations, which tend to drag polymer films along hole walls, are not required for circuit interconnection.

An additional consequence is the virtual elimination of the possibility of delamination. This is a result of the highly effective polymer layer interlocking procedures developed herein which appear to confer almost isotropic character on the dielectric medium. Such composites have resisted all efforts at mechanical

parting, even after exposure to a humid environment, and have displayed no visual evidence of degradation. Nor has any evidence of warping been found to date, although this possibility cannot be ruled out, particularly in the case of an asymmetric structure or of an asymmetric application of stress.

The proposed process excludes the possibility of intermetallic formation while offering a wide range of choices for the metal conductors in the x, y-planes. A noble metal, such as gold, offers certain fabrication and reliability advantages because of its inertness to oxidation, but its exposed terminations must then be copper plated to permit solder connections without risking the formation of intermetallics.

Efforts to develop organic z-direction conductors have been rewarded with organic products of steadily increasing electrical conductivity. In all cases it has been possible to confirm, and sometimes improve upon, existing literature results. Expressing these results in terms of room temperature resistivity, our polyaminoquinone was  $3 \times 10^{12}$  ohm-cm (literature: approximately  $10^{12}$  ohm-cm); cobalt phthalocyanine,  $2 \times 10^8$  ohm-cm (Literature:  $10^9$  ohm-cm); tetracyanoquinodimethan (TCNQ) complex with poly(2-vinylpyridine) made per the Lupinski and Kopple patent (Ref 12),  $1.3 \times 10^4$  ohm-cm (Literature, best value:  $1.0 \times 10^4$  ohm-cm); same complex, but improved preparation via the chemistry of Melby, et al, (Ref 13),  $5 \times 10^3$  ohm-cm (Literature, as above:  $1.0 \times 10^4$  ohm-cm). Based on the calculated assumption that the upper resistivity limit of a useful z-direction conductor should be  $10^2$  ohm-cm, our latest preparation still is a factor of 50 wide of the mark. This is a small factor considering that electronic resistivity in organic solids spans the range,  $10^{-2}$  to  $10^{18}$  ohm-cm, and we have every confidence that this resistivity specification can be exceeded.

Although a number of questions relating to process techniques and circuit board accomodation to environmental stress remain to be answered, it would appear from the present findings that soundness of technical approach has been verified and process feasibility established. In particular, no physical basis has emerged at any time during the program capable of casting doubt on the basic three-dimensional circuit concept developed herein. It also appears that embodiments of this concept should achieve a greater level of circuit board materials compatibility than has been possible heretofore while simultaneously eliminating many of the reliability hazards engendered by conventional processing. Therefore, further development and reduction to practice seem clearly worthwhile.

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## ACKNOWLEDGEMENTS

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## APPENDIX A CERAMIC MULTILAYER SYSTEMS

### Introduction

Ultra-high density packaging concepts being proposed for second generation microelectronics has focused attention on the use of ceramic substrates. These concepts of packaging are generally aimed at the use of uncased devices, such as flip chips or beam leaded devices, which can be bonded directly to the substrates by alloying or reflow processes. As the complexity of the devices increases from simple transistors to I. C. 's or LSI arrays, the need for multilayering of conductors to accommodate the increased number of output leads becomes apparent. Therefore, an assessment of ceramic multilayer technology is a timely and needed effort.

### Classification of Substrates

Ceramic substrates for use in electronic assemblies can be grouped in two general classifications according to their construction; i. e., singular and composite materials. Substrates constructed of singular materials include high purity alumina, beryllia, glass, single crystals, and high dielectric constant materials such as the titanates. Of these, the high purity aluminas have found widest usage for thick and thin film circuits. Pertinent properties of alumina and beryllia are summarized in Table I.

TABLE I  
PROPERTIES OF ALUMINA AND BERYLLIA

	Alumina	Beryllia
Density gm/cm <sup>3</sup>	3.7	2.9
Tensile Strength (psi)	25,000	15,000
Thermal Conductivity (g. cal/sec/cm <sup>2</sup> /°C/cm)	.084	.50
Specific Heat (cal/gm/c)	.27	.40
Coefficient of Expansion (°C x 10 <sup>6</sup> )	6.4	6.0
Dielectric Constant (IMC)	9.2	6.4
Dissipation Factor (IMC, 25c)	.0003	.0001
Volume Resistivity ohm-cm x 10 <sup>-12</sup>	100.	100.

Composite material substrates can be divided into two groups: glazed substrates and metallized or multilayer substrates. Glazed substrates are used extensively for vacuum-deposited thin-film networks where ultra-smooth surface finishes are of prime importance. Metallized or multilayer type substrates and their construction, properties, and applications are discussed below in further detail.

### Multilayer Systems

**Thick Film Multilayer.** — Ceramic multilayer substrates can be fabricated using standard "thick film" processes; that is, screen printing and air firing of noble metal compositions. This process utilizes a fired alumina substrate on which gold-glass cermet conductors and glass or glass ceramic dielectric. Layers are sequentially screen printed and fired. The materials used for this concept are:

#### 1. Substrates

High purity alumina (96 percent  $Al_2O_3$ ) substrates are used almost exclusively because of their low cost, availability, good thermal conductivity and high strength. Beryllia substrates can be considered; however, their advantage of increased thermal conductivity (between the device and the substrate) is reduced when dielectric layers are applied. Additionally, beryllia is more costly, and little experience with the compatibility with thick film materials is available.

#### 2. Conductor Materials

Gold and gold platinum cermet pastes are used for conductors. Gold is used where high electrical conductivity, semiconductor die mounting, and ultrasonic or thermocompression bonding is required. Gold platinum is used where soldering or hermetic sealing is required.

#### 3. Dielectric Materials

Glass or glass-ceramics are used as the dielectric insulating layers between conductors. Connection from one conductive layer to another is made through openings or "vias" in the dielectric layer. The glass-ceramics contain a nucleating agent which causes the glass to crystallize upon the prescribed heat treatment. The resulting crystallized glass-ceramic generally has a higher melting point than the original glass and will not easily flow when refired during subsequent processing.

#### 4. Processing

The thick film process is a method in which specifically formulated pastes (inks) are applied to a ceramic substrate and fired at an elevated temperature to bond the material and obtain the desired properties. The most widely used technique for applying the pastes is the screen stencil printing process. Numerous variables affect the pattern quality and reproducibility; principal among them are the screen mesh size and ink viscosity. A 200-mesh stainless steel screen is used for most production printing of



thick film materials. This is based on a tradeoff between minimum line widths, current carrying capacity, screen wear life and screen costs. Control of ink viscosity and flow characteristics is the most critical factor affecting the printing operation. Pattern run-out of 1/2 mil per side is typical for most printing media. Recently, shear sensitive thixotropic media have become available for printing fine lines.

After printing, the patterns are dried and fired at temperatures from 750 C to 1000 C using an air atmosphere, continuous belt kiln. A continuous belt kiln is used to assure that once time-temperature profiles have been established, they can be adequately reproduced.

Monolithic Alumina Multilayer. — The monolithic alumina multilayer incorporates internal or buried metallization within the alumina ceramic substrate. The layer structure is produced by laminating green tapes of alumina which have been metallized or by sequentially screen printing metallizing layers and alumina dielectric layers and alumina dielectric layers on an alumina core substrate. In both methods, the metallized part is fired at temperatures in excess of 1500 C to mature the ceramic which results in a composite substrate having a continuous or monolithic alumina structure with buried metallization.

### 1. Substrate

The substrate of this multilayer is alumina with a continuous polycrystalline structure. This results in high strength, excellent dielectric insulation and excellent thermal dissipation properties. At this time, beryllia composites are not available commercially. However, the use of beryllia may warrant consideration for designs requiring very high thermal dissipation.

### 2. Conductor Materials

Two types of internal metallization are available: (1) refractory metals such as molybdenum, tungsten, and niobium; and (2) noble metals such as platinum. If the refractory metals are used, the final firing of the alumina (1500+ C) must be done in a neutral or reducing atmosphere to prevent oxidation of the metallization. Surface patterns of the refractory materials are normally nickel- and gold-plated to prevent corrosion and provide a surface suitable for subsequent joining processes. If platinum internal metallization is used, air firing thick film conductors such as gold, gold-platinum, gold-lead, and lead-silver can be used. Thick film resistors can also be applied to form hybrid circuits. External interconnection patterns can be formed by vacuum deposition and etching of gold over nichrome films providing the substrate surface has been polished to a suitable microinch finish.

### 3. Processing

The unfired composite substrates are built up by two methods. In one method, a thin sheet of alumina is made by doctor blading a slurry of material prepared with the proper organic additives. After drying,

conductor patterns are applied to the green tape by screen printing. Where required, holes can be punched in the green tape for interconnection of the metallized layers. The metallized tapes are then laminated together under moderate heat and pressure to form a multilayer composite substrate. A second method is used in which alternate layers of alumina and metallization are built up by screen printing on an unfired substrate.

After forming of the composite substrate, the part is fired to temperatures in excess of 1500 C. If the refractory metallization is used, a reducing atmosphere during firing is used to protect the metals from oxidation and produce the bonding reaction between the alumina and the metals. If platinum metallization is used, a normal air atmosphere can be used during the sintering process.

Summary. — The technologies described above are conveniently compared in tabular form in Table II.

TABLE II  
TECHNOLOGY COMPARISONS

	Thick-Film	Monolithic Alumina
1. Fabrication Process	Screen print	Laminated layers
(a) Basic	Sequential air firing	Single fire
(b) Exterior Conductor	Screen print or photo etch	Screen print or photo etch
(c) Processing Temp	780-850 deg C-Air	1600-1700 deg C-Reducing
2. Surface Finish	Fire glaze	8 microinch CLA
3. Line width/spacing	.005 in./ .005 in.	.004 in./ .004 in. for short distance only
4. Line Conductivity	.005 ohms/square	.01 ohms/square
5. Conductor Thickness	.0008 in. to .001 in.	.0003 in. to .0005 in.
6. Dielectric Thickness	.001 in. to .002 in.	.002 in. to .030 in.
7. Number Conductor Layers	Two/Side	Multiple
8. Packaging Considerations	Substrate only, must be repackaged	Integrated package and substrate

The thick film ceramic multilayer approach offers several processing advantages for the electronic systems producer. A reasonable capital investment will establish an in-house processing capability which will give the following results:

1. Immediate hardware with rapid turn-around time
2. A simple, low cost process
3. Design flexibility
4. Excellent circuit qualities

This general situation is in contrast to that of using the monolithic alumina multilayer where the user must procure parts from a ceramic supplier. This typically leads to long lead times, high tooling costs and loss of proprietary designs. The ideal situation perhaps would find the user evaluating designs and pre-production hardware using in-house thick film technology and subsequently purchasing high volume production parts in monolithic alumina. An alternate approach would be for the user to purchase a standard internal metallization grid pattern in monolithic alumina and then subsequently process the external interconnection pattern by thick film or vacuum deposition.

The potential use of thick film materials by the electronic systems producer makes an investigation of these materials and their processing parameters a timely investigation.

### Inorganic Micromultilayer Systems

Materials Survey. — The micromultilayer concept differs from the preceding technology essentially in process technique, employing vacuum deposition of conductors and insulators rather than screen printing. As would be expected, this necessitates a whole new set of criteria for the selection of materials. A compilation of this type of criteria for a number of materials is presented in Table III. Present recommendations, based on electrical properties, thermal expansion match and adhesion properties, are cobalt-iron or cobalt-nickel alloys for the conductor, and silicon monoxide for the dielectric. The monoxide would be converted, after deposition, to the dioxide by an ultraviolet-assisted oxidation.

Process Approach. — The inorganic micromultilayer concept would provide a reduction in the interconnection size comparable to that already achieved in the case of components by integrated circuits. Tests to determine the feasibility of a new method of making the interconnection through-holes were carried out. Thin layers of either permalloy or aluminum were successfully deposited on glazed Coors alumina substrates. The permalloy films (2 microns) showed evidence that corrosion of iron had occurred during the application of the photoresist (an experimental negative type photoresist manufactured by General Aniline), and ferric chloride etching. Because of this corrosion, further investigation of permalloy was discontinued.

TABLE III  
MATERIAL SELECTION CRITERIA

Material	Method of Deposition	Evaporation Temperature (C)	Formation Temperature (C)	Melting Point (C, 1 Atmosphere)	Source	Dielectric Constant	Dissipation Factor	Field Strength (V/CM)	Leakage Current or Resistance (amps or ohms)	Temp Coefficient	Remarks
Cerium Oxide	Resistive heating	1800 decomposes 1950	---	2600	BN lined carbon heater	3.9-6	---	---	---	---	---
Lead Titanate	Plasma	---	---	Self supporting	---	100	Low (No figure given)	$10^6$	---	---	Plasma or $PbTiO_3$ formed by glow discharge. Few details given.
Magnesium Fluoride	Resistive heating	---	---	1396	Mo	6.5	0.005-0.12	$2 \times 10^6$	$10^{-6}$ amps at $2 \times 10^6$ V/CM	---	Chaikin obtained unpredictable results. Maddocks had good results.
Magnesium Oxide	Pyrolytic deposition	---	65 C	2800	Magnesium Methylate	---	0.021-0.5	---	---	---	---
Niobium Oxide	Anodizing	---	---	1520	---	42	0.021-1.0	---	$1-10 \times 10^{-6}$ at 25 C	---	---
	Sputtering	---	---	---	Self supporting	23	0.07	---	---	885 PPM/deg C	Life test gave poor results; sputtering was in partial pressure of oxygen (45 Torr)
Silicon Carbide	Electron Bombardment	2000	---	2600(subl) Decomposes	Self supporting	---	---	---	---	---	Likely that the majority of the material ended up as $SiO_2$ .
Silicon Dioxide	Resistive heating	2300	---	1600	BN lined carbon heater	4.2	---	---	---	---	---
	Thermal Growth	---	1000 950	---	Grown on silicon	3.82	0.0601	$10^7$	$10^{-9}$ amp at 150 C and 50 V	250 PPM at 125 C, 100 PPM/deg C at 250 C	---
	Sputtering	---	---	---	Large plate of silicon dioxide	---	0.0003 and up	$3 \times 10^6$	$1-10^8$ meg $\Omega$	---	---
Alumina-Silicate Glass	Resistive heating	---	---	500 (Softening point)	---	5	0.007 at 50 MC	---	$10^{-11}$ amps	---	---
Aluminum Oxide	Resistive heating	---	---	2000	BN lined carbon heater	6.4	---	---	---	---	---

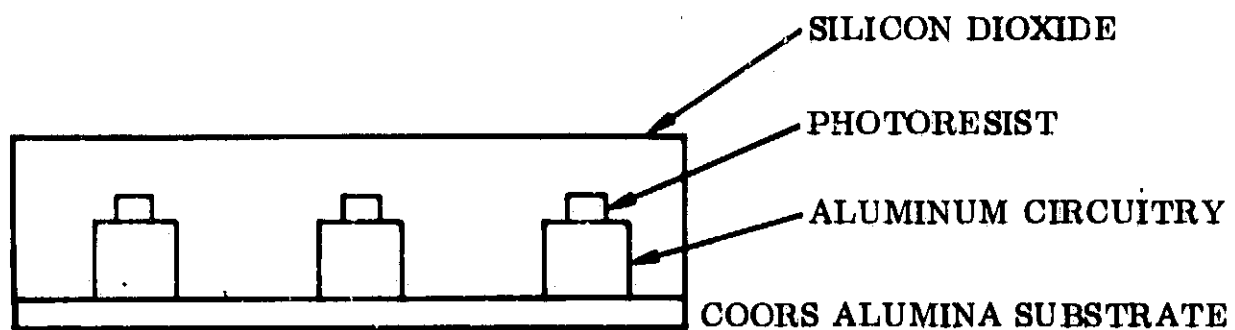
TABLE III (Cont)

Material	Method of Deposition	Evaporation Temperature (C)	Formation Temperature (C)	Melting Point (C, 1 Atmosphere)	Sources	Dielectric Constant	Dissipation Factor	Field Strength (V/cm)	Leakage Current or Resistance (amps or ohms)	T <sub>zmp</sub> Coefficient	Remarks
Aluminum Oxide (Cont)	Electron bombardment	1850	---	---	Self supporting	3.3-9.2	.05-.25				Rapidly dissolves tungsten (W used as preheater. Caused poor results)
	Anodizing	---	---	---	---	12	.1-.3		>10 <sup>14</sup> Ωcm		Al <sub>2</sub> O <sub>3</sub> was formed and had lower dielectric constant and much lower dissipation factor
	Reactive bombardment	---	---	---	---	4	.02-0.2 (at 1 MC)	6 x 10 <sup>5</sup>			Evaporation temperature should be much higher. These capacitors failed above 200 C.
Boron Nitride	Electron bombardment	1900	---	3000 (Subl.)	Self supporting						
Cerium Fluoride	Resistive heating	1450	---	1324	Tantalum boat	Thickness dependent 9.2-200	0.01-1.0	10 <sup>6</sup>	>10 <sup>6</sup> Ω		CeF <sub>3</sub> had a thickness dependent dielectric constant. High E/EO was obtained by evaporating from Ta boat. Evaporation from aluminum gave E/EO ~8.2. Very frequency dependent.
Silicon Monoxide	Resistive heating	---	---	---	1. Refractory Metal 2. Oxide Crucible 3. Drummer- lier source	5 (typical)	.007 and up	2 x 10 <sup>6</sup>	Low	600-700 PPM/deg C	Better results were obtained by slow evaporation (<5Å/sec). Annealing at 100 deg to 200 deg C in air seems to improve the capacitors.
	Resistive heating	2100	---	1900 (Subl.)	BN lined carbon heater	4.2					Undoubtedly mostly SiO <sub>2</sub> since N to O ratio of film was 1 to 10.
Silicon Nitride	Pyrolytic deposition	---	960	---	Silicon tetrahydride and nitrogen	12.7	<.0001	7 x 10 <sup>5</sup>	10 <sup>14</sup> Ω at 250 C		Functioned to 600 C. Some withstood 1000 C without permanent damage.
	Anodized	---	---	1470 decomposes	---	25		5 x 10 <sup>6</sup>	10 <sup>6</sup>	250 PPM/deg	
Tantalum Oxide	Reactive Sputtering	---	---	---	Large plate Ta	14	0.03				

TABLE III. (Cont)

Material	Method of Deposition	Evaporation Temperature (C)	Formation Temperature (C)	Melting Point (C, 1 Atmosphere)	Sources	Dielectric Constant	Dissipation Factor	Field Strength (V/CM)	Leakage Current or Resistance (amps or ohms)	Temp Coefficient	Remarks
Thorium Fluoride	Resistive heating	1160	---	1110	Radiant Heating	8.5-13	0.04-0.2	$7.3 \times 10^5$	$5 \times 10^{-6}$ A per capacitor at breakdown		There is good positive correlation between dissipation factor and dielectric constant.
Titanium Oxide	Anodizing	---	---	---	---	50	0.01-0.1		$10^{-9}$ amps at 100 C and 10V		Usually decomposes to TiO <sub>2</sub> (lower oxidation state)
	TiO <sub>2</sub> Evaporation	---	---	---	Carbon	28-100			$5 \times 10^4 - 5 \times 10^5$ Insulation Resistance		20 min oxidation in air at 500 C, or anodizing
	TiO Evaporation	1750	---	---	Tantalum Carbon	28-100			$10^{-5}$ /sq sheet resistivity		
	Reactive Ti Evaporation	---	---	---	Tantalum Tungsten	28-100	0.05				
	Reactive sputtering	---	---	---	Large Ti cathode	62	0.06				Cathode must be much larger than the source to substrate distance.
Titanium Oxide doped Sb <sub>2</sub> O <sub>3</sub>	Worked with bulk sintered pellets	---	Hot Fired	---	$10^4$ Thickness dependent	0.01-6.1			600K at 10V 200K at 30V	Zero. -50 to +100 C	1% Sb <sub>2</sub> O <sub>3</sub> worked best; Flat temperature characteristics -50 to +100 C
Tungsten Oxide	Resistive Heating	---	---	1473	Berillia Alumina	$10^3$					
	Anodizing	---	---	---	---	40			$10^6 \Omega$ -cm 250 C		
Ytterbium Oxide	Resistive Heating	---	---	---	BN Lined Carbon Heater	5.0					Very little information available.
Yttrium Oxide	Electron Bombardment	2450	---	2410	Self supporting						Very little information available.
Zinc Sulfide	Resistive Heating	1200	---	1020		8.2 10.0	0.01	$2 \times 10^5$			
Zirconium Oxide	Reactive Sputtering	---	---	2700	Large Zr Cathode	25					

Aluminum films (2 microns thick) then were deposited and satisfactorily etched with a proprietary etchant. After etching, the circuitry was cleaned and another application of the photoresist was made in an interconnection hole pattern so that dots of the resist remained where the through-holes were to be located, as illustrated below:



An insulating layer of silicon dioxide was then vapor deposited over the entire surface. Next, the substrate was heated at 200 C for one hour under a high intensity ultraviolet lamp to convert any silicon monoxide to the dioxide. Under this environment, the photoresist was decomposed with the evolution of nitrogen which fractured the overlying silicon dioxide. The feed-through holes were developed by soaking the substrate in acetone which softened and removed the photoresist and the fragile silicon dioxide. Adhesion of the silicon dioxide around the periphery of the substrate was marginal. This was traced to an oily residue left by the photoresist. The process approach admittedly is at a primitive stage of development but it would seem to warrant further development.

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## APPENDIX B.

# INVESTIGATION OF MULTILAYER PRINTED CIRCUIT BOARD MATERIALS MATERIALS REPORT

By J. E. Meinhard

Autonetics Division of  
North American Rockwell Corporation  
Anaheim, California

## INTRODUCTION

In accordance with the terms of the contract, this report assembles the properties and potential applications of materials considered over the past six months that show some promise of introducing improvements in the present practice of three-dimensional circuit technology. These materials are categorized according to their intended functions, namely: substrates, dielectrics for three-dimensional electrical isolation, and conductors. Both organic and inorganic substances are considered under each heading. In each case name, source, formula and general properties are listed, followed by a brief indication of the type of job for which the material is considered to be especially suited and any known or suspected peculiarities associated with the intended use.

At times the three-dimensional systems under consideration will not be novel in concept but will represent embodiments recently introduced and, as yet, incompletely optimized. In such cases the introduction of a single new material may culminate in a significant extension of system application. A potential representative of this category might be the utilization of crystallizable glass-ceramic as the z-direction dielectric on an alumina substrate. Almost no data for this system are available. Consequently its range of applicability will remain unknown until the system can be fully characterized.

A somewhat more innovative approach is to combine organic and inorganic materials in the same system. It is immediately apparent that ceramic layered on an organic substrate is unlikely to yield a workable system. This is not necessarily true of the reverse situation where, for example, a polyamide, or a polyamide/polyimide, is used for the z-direction dielectric on a ceramic substrate. Questions of materials compatibility must, of course, be thoroughly explored. Such questions relate not only to thermal expansion properties but to adhesion, potential delamination resulting from gas evolution during cure, etc. A major potential advantage of the system is the combination of the favorable mechanical properties of a ceramic substrate with the highly versatile properties of organic z-direction dielectrics. For example, circuit definition by photolithography is denied ceramic layer technology but not organic polymer layers.

At the other end of the innovative spectrum is the potential application of organic conductors in an organic materials environment. If workable this implies, but does not necessarily guarantee, the achievement of an ultimate level of materials



compatibility. This is a desirable goal because modern multilayer practice involves the interfacing of a large variety of solids - much larger, for example, than that employed in silicon planar technology. This gives integrated circuits a significant reliability advantage over multilayer boards. To achieve electronic conductivity (as distinguished from ionic or metallic conductivity) in organic substances, however, requires the introduction of certain molecular structures, specifically, extensive conjugation, or charge transfer, or both. In so doing it may turn out that adhesion to adjacent organic dielectrics is impaired, or that radical changes in thermal expansion properties are introduced, or that secure ohmic connection to external metallic conductors becomes difficult. These factors cannot be determined in advance and must await the synthesis and characterization of representative organic conductors tailored for utilization in a totally organic system.

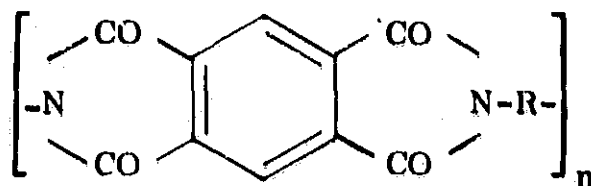
The materials tabulated below were selected for study on the basis of their applicability to one or more of the categories defined above.

## SUBSTRATES

Organic: Vespel

Source. - DuPont, Wilmington, Delaware.

Formula. -



where R is aliphatic, aromatic or both, and n is the unspecified number of repeating units resulting from the condensation of  $R(\text{NH}_2)_2$  with pyromellitic dianhydride.

General Properties. - Chemically inert, stable at high temperatures, mechanically tough but readily machinable, good strength at elevated temperatures, low vapor pressure, superior dielectric properties, adheres extremely well to vacuum deposited gold or copper.

Uses. - It approaches the toughness, and equals or exceeds the inertness, of many ceramic substrates without the necessity of incorporating an inorganic filler. Its superiority should lie mainly in substrate areas larger than those practically achievable by ceramics, or as a substitute for epoxy/glass where moisture imbibition or permeation is a problem.

Peculiarities. -

1. The chemical inertness of imide groups (the only residual functional groups) portends poor adhesion to overlying films of similar composition.

Good adhesion probably will require the retention (or introduction) of strongly polar groups in at least one of the two adjacent layers.

2. Thin Vespel, available in oriented fiber sheets, is difficult to lap smooth enough for vacuum metallization because of mechanical dislodging of fiber terminations. Substrates machined from block Vespel do not share this problem.
3. Vespel is ideally suited to vacuum deposition because of its low vapor pressure and high thermal stability. The virtual absence of significant outgassing under vacuum permits intimate, and probably interlocking, bonding of a metallization, which would account for the observed strong adherence.

#### Inorganic: Alumina Ceramic

Sources. — American Lava Corp., Chattanooga, Tennessee; Coors Porcelain, Golden, Colorado; Western Gold and Platinum Co., Belmont, California.

Formula. —

1. Thick film grade: 96%  $Al_2O_3$ ; 4% CaO, MgO,  $SiO_2$
2. Thin film grade: 99.5%  $Al_2O_3$

<u>General Properties</u>	<u>96% <math>Al_2O_3</math></u>	<u>99.5% <math>Al_2O_3</math></u>
Water absorption (%)	0	0
Specific gravity	3.70	3.89
Hardness (Rockwell 45N)	70	80
Thermal Exp. °C, 25-300 C ( $\times 10^{-6}$ )	6.4	6.0
Thermal conductivity, 25 C (Cal. cm/-sec. $cm^2$ . °C)	0.084	0.088
Flexural Strength (psi)	50,000	60,000
Surface Finish ( $\mu$ in - CLA)	<25	<8
Dielectric Strength (volts/mil)	500	500
Dielectric Constant (1 MC 25 C)	9.1	9.6
Dissipation Factor (1 MC 25 C)	0.0003	0.0002
Loss Factor (1 MC 25 C)	0.0027	0.0019



**Uses.** — Completely cured resin is electrically inert as well as chemically inert. Base solubility after partial cure permits etching through-holes by normal photolithographic method to establish electrical communication to an underlying layer.

**Peculiarities.** — Wets Vespel with difficulty if sprayed on. More viscous formulations (i. e., lower solvent content) are more successfully applied, e. g., by silk screen, painting, squeegee, etc. Adhesion to Vespel considerably reduced on complete cure; delamination aided by steam formation during cure as well as by removal of free carboxyl. Latter problem may disqualify its use on Vespel unless a way can be found to bond chemically, e. g., through amide groups, to the substrate.

#### Inorganic: Vitreous Glass

**Sources.** — E. I. duPont deNemours and Co., Electrochemicals Department, Wilmington, Del.; Electro-Science Laboratories, Philadelphia, Pa.; Electro-Materials Corp. of America, Mamaroneck, N. Y.

**Formula.** — Vendor Proprietary

Typically Lead-Boro-Silicate Glass

75% SiO<sub>2</sub>, 15% B<sub>2</sub>O<sub>3</sub>, 5% Al<sub>2</sub>O<sub>3</sub>, 5% PbO

**General Properties.** —

Dielectric constant, 1 kHz	8-10
Dissipation factor, %, 1 kHz	0.2
Insulation resistance	>10 <sup>9</sup>
Dielectric breakdown, volts/mil	300

**Uses.** —

1. Thick film crossover dielectric

**Peculiarities.** — Applied by screen painting. Melting range, 800 to 1000 C. Cannot be used in the same manner as ML varnish where an intermediate cure stage provides temporary sensitivity to etching.

#### Inorganic: Crystallizable Glass-Ceramic

**Sources.** — E. I. duPont deNemours and Co., Electro-Chemicals Department, Wilmington, Del.; Electro-Science Laboratories, Philadelphia, Pa.; Electro-Materials Corp. of America, Mamaroneck, N. Y.; Alloys Unlimited, Inc., Melville L. I., N. Y.

**Formula.** — Vendor Proprietary

BaO · Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> - Barium Feldspar

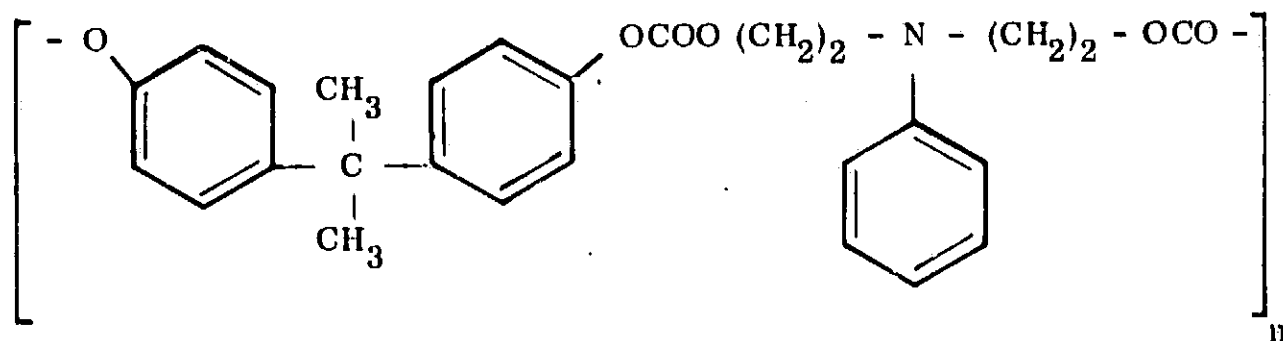
## CONDUCTORS

### Organic

#### Poly(phenyliminodiethanol-bisphenol A carbonate)

Source. — In-house, (Ref 1).

Formula. —



by interaction of bisphenol A with phosgene to form the chloroformate, followed by condensation with phenyliminodiethanol.

General Properties. — Soluble in methanol, indicating low molecular weight and only limited condensation.

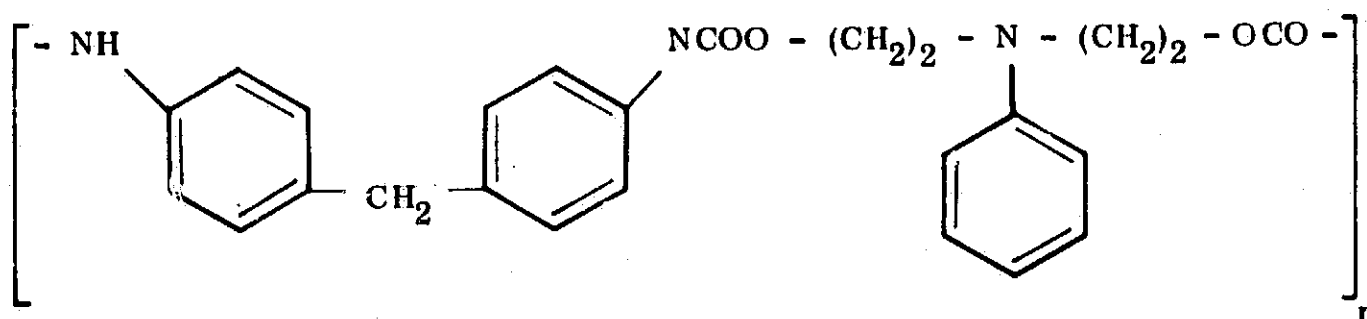
Uses. — Intended as the electron donor in charge transfer complexes with acceptors, such as tetracyanoethylene, tetracyanoquinodimethan (TCNQ), etc.

Peculiarities. — None noted. Approach abandoned due to lack of high molecular weight polymer.

#### Poly(phenyliminodiethanol-bisphenol F urethane)

Source. — In-house.

Formula. —



by reaction of phenyliminodiethanol with p, p'-diphenylmethane diisocyanate.

General Properties. — Hard, white polymer; softening point, 90-100 C. Sol. pyridine; insol. MIBK, MEK, benzene.

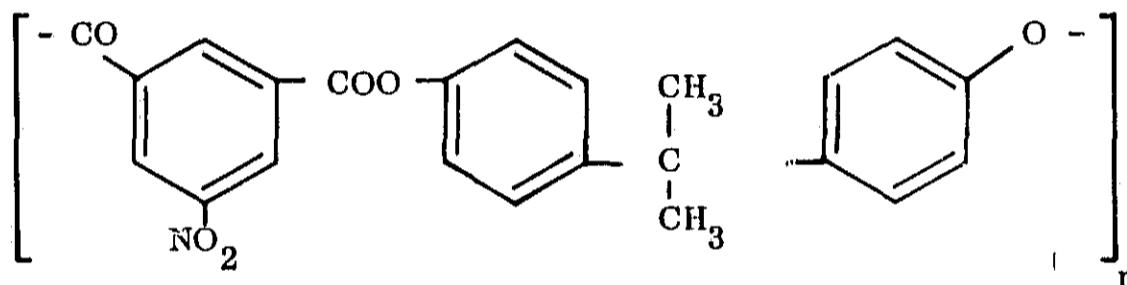
Uses. — Same as intended for previous polymer.

Peculiarities. — Forms orange-colored product with tetracyanoethylene. Electrical properties not yet determined.

Poly(bisphenol A-5-nitroisophthalate)

Source. — In-house, (Ref 1).

Formula. —



by interaction of bisphenol A with 5-nitroisophthalyl chloride.

General Properties. — Hard, white polymer; softening point, 130 to 140 C.

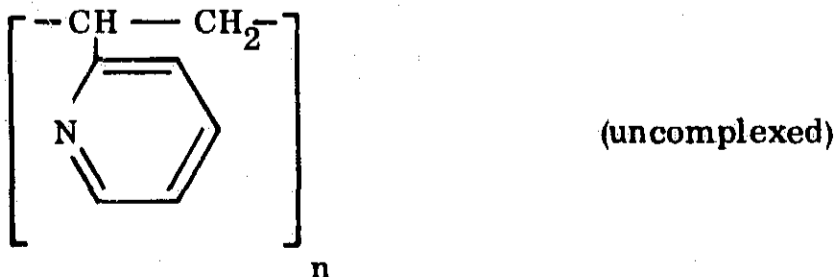
Uses. — Intended as a polymeric electron acceptor in charge transfer complexes with suitable donors that may, or may not, also be polymeric.

Peculiarities. — None noted; under further study.

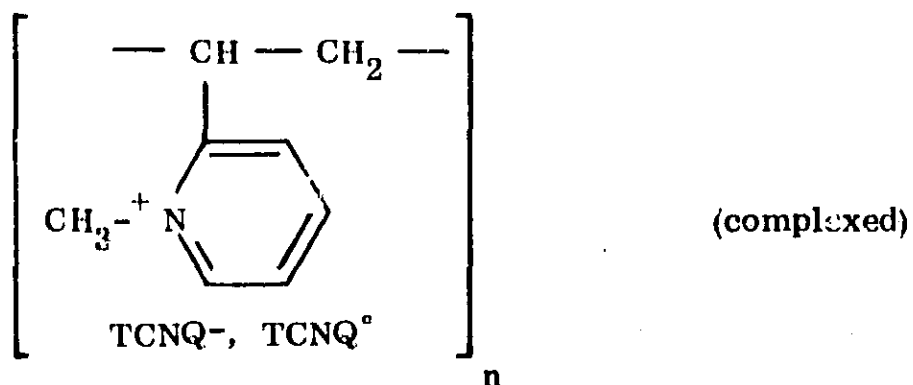
Poly(2-vinylpyridine) TCNQ complex.

Source. — In-house, (Ref 2).

Formula. —



by free radical-promoted bulk polymerization of 2-vinylpyridine.



by quaternization of polymer with dimethyl sulfate, followed by exchange of  $\text{SO}_4^-$  for  $\text{TCNQ}^- + \text{TCNQ}^0$ .

**General Properties.** — Initial polymer obtained as hard, brown solid; softening point about 50 C. Sol. methanol. IR disclosed ethylenic unsaturation completely used up. Quaternary readily formed but difficult to isolate from other ionic byproducts (sol.  $\text{H}_2\text{O}$ ; insol. alcohol).

**Uses.** — Intended as a charge transfer complex in which the polymer is the electron donor.

**Peculiarities.** — None noted; insufficient data.

**Inorganic:** Generally Metallic; No Innovations Apparent or Foreseeable in the Near Future

## REFERENCES

1. T. Sulzberg and R. J. Cotter, *Macromoles* 1, 554 (1968); *C&EN*, 23 December 1968, p 28.
2. J. H. Lupinski and K. D. Kopple, U. S. Patent 3,346,444, October 10, 1967.