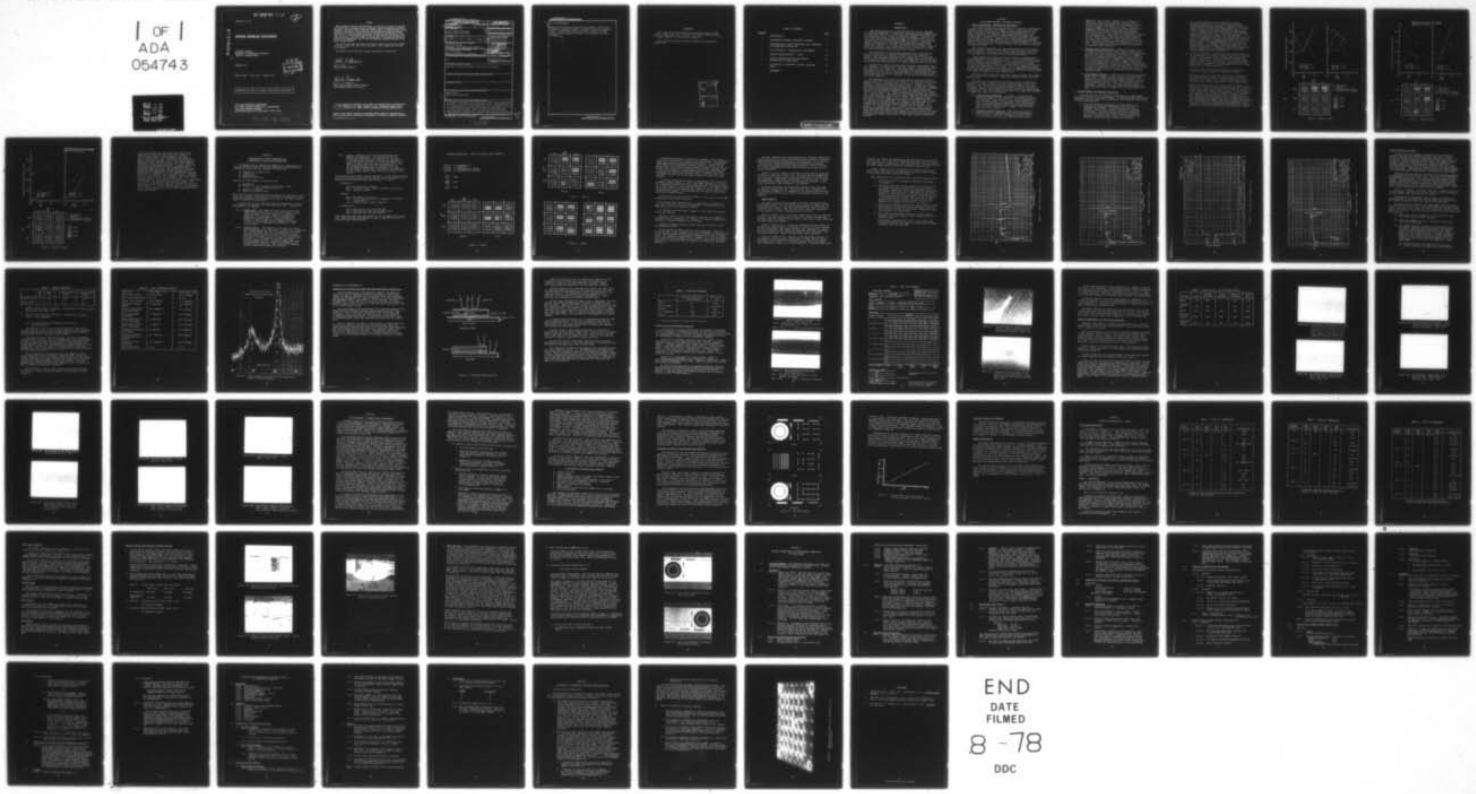
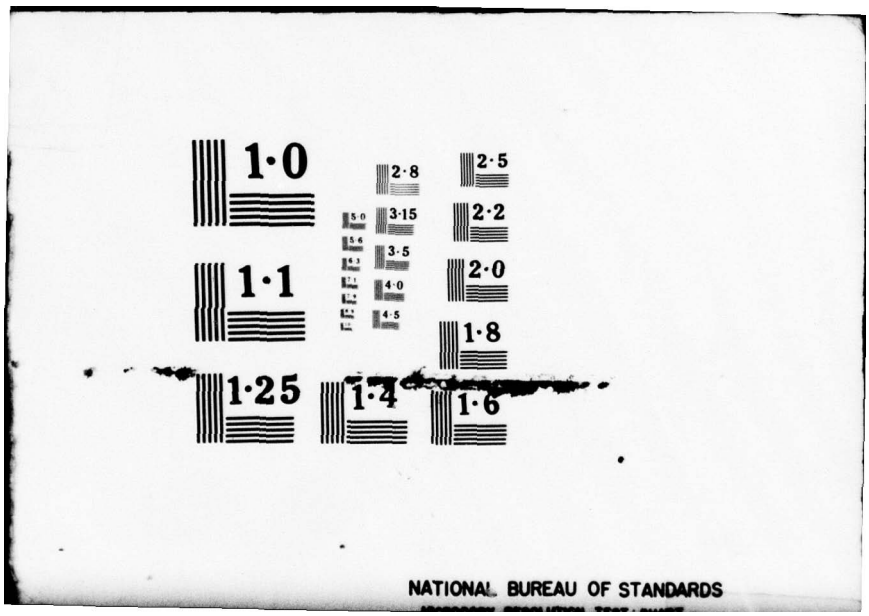
AD-A054 743 RAYTHEON CO SUDBURY MASS EQUIPMENT DEVELOPMENT LABS F/G 11/6
NICKEL BORON COATINGS.(U)
AUG 77 J BREEN, J CARR, G FIX, J JUDGE F33615-76-C-5255
UNCLASSIFIED AFML-TR-77-137 NL

1 OF 1
ADA
054743



END
DATE FILMED
8-78
DDC


1·0
1·1
1·25
2·8
3·15
3·5
4·0
4·5
5·0
5·6
2·5
2·2
2·0
1·8
1·4
1·6
NATIONAL BUREAU OF STANDARDS

FOR FURTHER TRAN

AMFL-TR-77-137

AD A054743

NICKEL BORON COATINGS

RAYTHEON COMPANY
MATERIALS ENGINEERING LABORATORY
SUDBURY, MASSACHUSETTS

DDC
RECEIVED
JUN 27 1978
F

AUGUST 1977

Final Report July 1976 - August 1977

Approved for public release; distribution unlimited.

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

78 06 26 022

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This final report was submitted by the Raytheon Company under Contract F33615-76-C-5255, Project 7371, Task 737102 with John C. Olson, AFML/LPJ as the technical monitor.

This technical report has been reviewed and approved for publication.

John C. Olson
Project Engineer AFML/LPJ

Dr. W. G. D. Frederick
Chief, Laser & Optical Materials Branch
Electromagnetic Materials Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify _____, W-P AFB, OH 45433 to help us maintain a current mailing list".

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

AIR FORCE/56780/7 April 1978 — 100

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: AFML-TR-77-137	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): NICKEL BORON COATINGS	5. TYPE OF REPORT & PERIOD COVERED: Final rept. Jul 76 - Aug 77.
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): J. Breen, J. Carr, G. Fix, J. Judge	8. CONTRACT OR GRANT NUMBER(s): F33615-76-C-5255
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Raytheon Company, Equipment Development Laboratories, 528 Boston Post Rd; Sudbury, Mass. 01776	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Project No. 7371, Task No. 737102
11. CONTROLLING OFFICE NAME AND ADDRESS: U.S. Air Force, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433	12. REPORT DATE: August 1977
	13. NUMBER OF PAGES: 71 (77 p.)
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): N/A	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Nickel Boron
Electroless Deposition

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Preliminary evaluation of nickel/boron alloys from commercially available electroless plating solutions has indicated potential applications of these materials as a replacement for gold in certain applications and as an additive metallurgy for printed circuit boards. Some of these alloys exhibit more than adequate solderability, abrasion and corrosion resistance coupled with acceptable formability. Analytical methods for

next page

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

78 06 26 022
406 335

No. 20 (Continued)

analysis of the boron content were developed. One of the commercial processes appears to possess excellent reproducibility. Diffraction studies indicate a highly stressed deposit whose epitaxial tendency can be modified by heat-treatment.

FOREWORD

This final report was submitted by Raytheon Company under Contract F33615-76-C-5255, Project 7371, Task 737102 with John C. Olson, AFML/LPJ as the technical monitor.

This technical report has been reviewed and approved for publication.

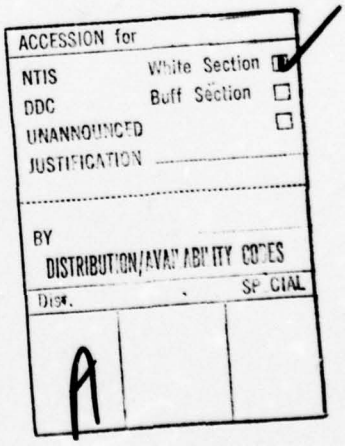


TABLE OF CONTENTS

Section		Page
1	INTRODUCTION	1
2	DEVELOPMENT SEQUENCE (TECHNICAL APPROACH)	2
3	INVESTIGATION OF BASIC PROPERTIES AND PARAMETERS OF NICKEL/BORON DEPOSITION	9
4	PCB PROCESSING - CHRONOLOGICAL DEVELOPMENT	38
5	TESTING PROGRAM/RESULTS - LEADS	45
6	PROCESS INSTRUCTIONS FOR ELECTROLESS DEPOSITION OF NICKEL/BORON	56
7	DISCUSSION OF PROCESSING PROBLEMS REQUIRING STUDY	68
	REFERENCES	71

PRECEDING PAGE BLANK-NOT FILMED

SECTION 1

INTRODUCTION

Gold plating alone or in conjunction with various subplates has been the workhorse in maintaining solderability and weldability on electronic leads (e.g., Kovar and other nickel/iron alloys) and on contact pins (i.e., brass and beryllium copper). While it is one of the more commonly used platings in the electronic industry, the high cost and the resultant attempt by vendors to economize by thinner coatings of poorer quality has lead users to seek less expensive substitutes. Typical candidates have included lower carat gold, rhodium, tin, nickel and various combinations. Many of these will perform a particular function as successfully as gold but none will perform all the functions as well.

The evaluation of nickel boron platings as a substitute for gold on electronics to enhance solderability while providing oxidation and corrosion protection was a major aim of the investigation. The secondary objective was to demonstrate the reliability of nickel-boron additive plating on high temperature printed wiring board polyimide base materials, as solder plate will not do the job.

Nickel-boron plating systems based on alkyl amine borane (see H.G. MacLeod, U.S. Patent No. 3,062,666 (1962)) or borohydride (see E.A. Sullivan, U.S. Patent No. 2,942,990 (1960)) reducing agents have been known for some time but problems of instabilities and lack of process control were not overcome because of the success of the Ni-P system and the lack of awareness of any potential advantages of these Ni-B deposits.

The appearance of commercial processes for the auto-catylytic deposition of Ni-B alloys has also lead to the suggestion that these deposits may have characteristics which are far superior in many respects to the more conventional Ni-P alloys. It had been claimed that these alloys have superior solderability, brazeability, oxidation and corrosion resistance, hardness, wear resistance, electrical conductivity and adhesion properties (see the manufacturers literature or an article by G.J. Estep in Electronic Packaging and Production, January 1974). That some of these properties had been achieved (e.g. high hardness) there is little doubt, but that all could be achieved in the same deposit did at first glance appear doubtful. The results of this investigation; however, do tend to bear out many of these earlier observations. For example, the solderability of nickel/boron is certainly superior to Ni/P or pure nickel. In addition in certain aspects (its tendency not to dissolve in the solder), its solderability may be superior to any other coatings. While some problems remain unsolved in introducing nickel-boron technology into the manufacturing operations, (see Section VII) there remains little doubt that it will become a factor not only on leads and polyimide based circuits but in many other areas of electronic hardware.

SECTION 2

DEVELOPMENT SEQUENCE (TECHNICAL APPROACH)

A. General Deposition - Cleaning and Initiation

The initial deposition investigations were directed at developing cleaning cycles for Kovar and copper. This is a most critical area when electroless deposition is involved because both adhesion and deposit initiation are dependent upon the cleaning cycles. With electro-deposition the required water-break-free and oxide-free surfaces may be obtained thru a number of cleaning methods, including simple abrasive cleaning. However, electroless deposition mandates that surfaces also be chemically active. A delicate balance occurs wherein the activity must be controlled such that oxidation of surfaces does not take place during transfer between the last cleaning step and the deposition bath.

The removal of ordinary soil was accomplished with hot alkaline cleaning methods. While a large number of such cleaners exist, and are satisfactory, the cleaner herein specified was chosen because it is also compatible with printed circuit board fabrication.

Oxide removal and surface activation of Kovar is accomplished thru simple pickling in hydrochloric acid. Too little pickling results in poor adhesion. Over pickling resulted in difficulty or failure to obtain coverage and poor adhesion. It is mandatory that rinsing following pickling be cold and that pickled work be rinsed sufficiently to reach the temperature of the rinse. At the low temperature, oxide formation during transfer to the deposition is apparently insignificant. Once in the deposition bath the surface of the work heats up so quickly that deposition appears to start immediately.

There are many methods for chemically removing oxides from copper. A great number were tried and, though they deoxidized well, they did not activate.

Throughout the investigation positive initiation of deposition solely on to copper surfaces by purely chemical means has not been possible. It is possible that nickel complexing agents other than those currently in the baths would permit auto-initiation directly on to copper. However, such investigations were beyond the scope of this investigation. Four (4) methods for initiation of electroless Ni/Boron on copper were found and investigated:

1) Strike Electro-deposition. By adding a suitable anode (stainless steel, nickel, platinum) to the bath and making the work cathodic at 2 volts for 1-3 seconds deposition will initiate. Deposition will continue autocatalytically when voltage biasing is disconnected. This method positively initiates deposition but has the disadvantage that each and every isolated piece of copper within the bath make electrical contact.

2) Palladium Chloride Catalysis. Immersion of the work in a very dilute (0.1 gm/gal of $PdCl_2$ in 25% hydrochloric acid) solution of catalyst followed by copious rinsing in cold running water prior to deposition will cause

deposition to initiate. However it is difficult to completely remove excess catalyst during rinsing. Minute particles introduced into the deposition bath continue to plate and deplete the bath. When the original copper is on a printed circuit the problem is compounded because the plastic substrate adsorbs catalyst and the result is severely treed deposits. The treeing can and does flake off resulting in severe bath contamination. Heavy particle contamination can not be removed during continuous filtration because the flow rates required to "move" the particles into the filter would result in entrainment of air into the bath. Entrained air causes auto decomposition of the bath. Heavy particulate contamination can be removed by frequent batch filtration.

3) Reducing Agent Catalyzation. Immersion of work into a 50% aqueous solution of the DMAB reducer supplied for the bath and then transferring directly to the deposition solution will cause deposition to initiate on copper. We have had approximately 50% deposition initiation on the first treatment and an aggregate of 90% initiation with a second treatment. However, approximately 10% of treated copper work will not initiate. This process has the disadvantage of increasing the DMAB concentration of the bath resulting in decreased stability. Additionally, on PCB's the DMAB absorbed on the substrate results in background plating with attendant particulate problems discussed above.

4) Auto-Catalytic Strip. A piece of any material previously plated with nickel/boron will serve as an Autocatalytic Strip (ACS). Properly cleaned copper immersed in the deposition bath requires only momentary contact with the ACS for deposition to initiate. This method induces no problems within the bath. The same ACS may be used repeatedly. However, as with strike electro-deposition, each individual piece of copper must be contacted by the ACS.

B. Accomplishment of Milestone Objectives

Coincidental with the foregoing investigations a preliminary evaluation of solutions was performed. It became quickly evident that the boron content of any given proprietary solution would fall within a narrow range because:

1) Solutions produced by Shipley and Allied Kelite are manufactured under patent agreement and licensing agreement with DuPont. Shipley manufactures one (1) solution, NiPosit 468, which is limited to a maximum of 1% boron. Allied Kelite has two binary solutions; one limited to less than 1% boron and one, Niklad 759 limited to 1% min-2% max. boron. DuPont markets one solution, Sylek 201 with a maximum of 3% boron.

2) The ligands employed in each proprietary solution provided greatest stability within the manufacturers recommended pH range of operation. Within this operating range % boron variation is confined between $\pm$ .1 to .2% Operation below the pH range gave plating rates so low as to be useless and with decomposition of DMAB reducer without reduction of nickel. At pH above the recommended range plating was fast, nodular and non-adherent. Temperature effects on plating rate track with pH variation i.e., low temperature low rate, high temperature high rate. However, the effect of temperature on boron % is slight and its effect on reducer decomposition is the reverse of the pH effect. For example, operating at low pH to increase boron content causes a very slow deposition rate. Raising temperature to compensate for this slow deposition rate increases the rate of DMAB decomposition without attendant deposition rate increase.

3) It was not possible to operate the baths enough outside of the recommended constituent concentrations to effect boron content. The premixed nickel concentrate contains the ligand or stabilizer. Increasing the % of nickel concentrate resulted in an inactive bath. Increasing the DMAB concentration resulted in rapid decomposition of the excess DMAB with no attendant deposition.

It can be said with absolute certainty, that the manufacturer recommended operating ranges are correct.

A solution was made up per the folmulation of Gorbunova.[1] This solution was reported to deposit films with boron content in the range of 6%. Films deposited were nodular and powdery and judged unapplicable to the investigation.

Deposition matrices were run on the three proprietary solutions, Dupont Sylek 201, Allied Kelite Niklad 759, and Shipley Niposit 468. Based on the matrix values and the solderability formability results (see Figures 1, 2, and 3), Niklad 759 appeared to be the best performer followed by NiPosit 468. Sylek 201 was the poorest from both deposition rate and solderability/formability results. Further studies of given portions of the deposition matrices showed that actually, for a given deposit thickness the Niklad and NiPosit were essentially equal as to formability/solderability, and larger quantities of these two proprietary solutions were ordered.

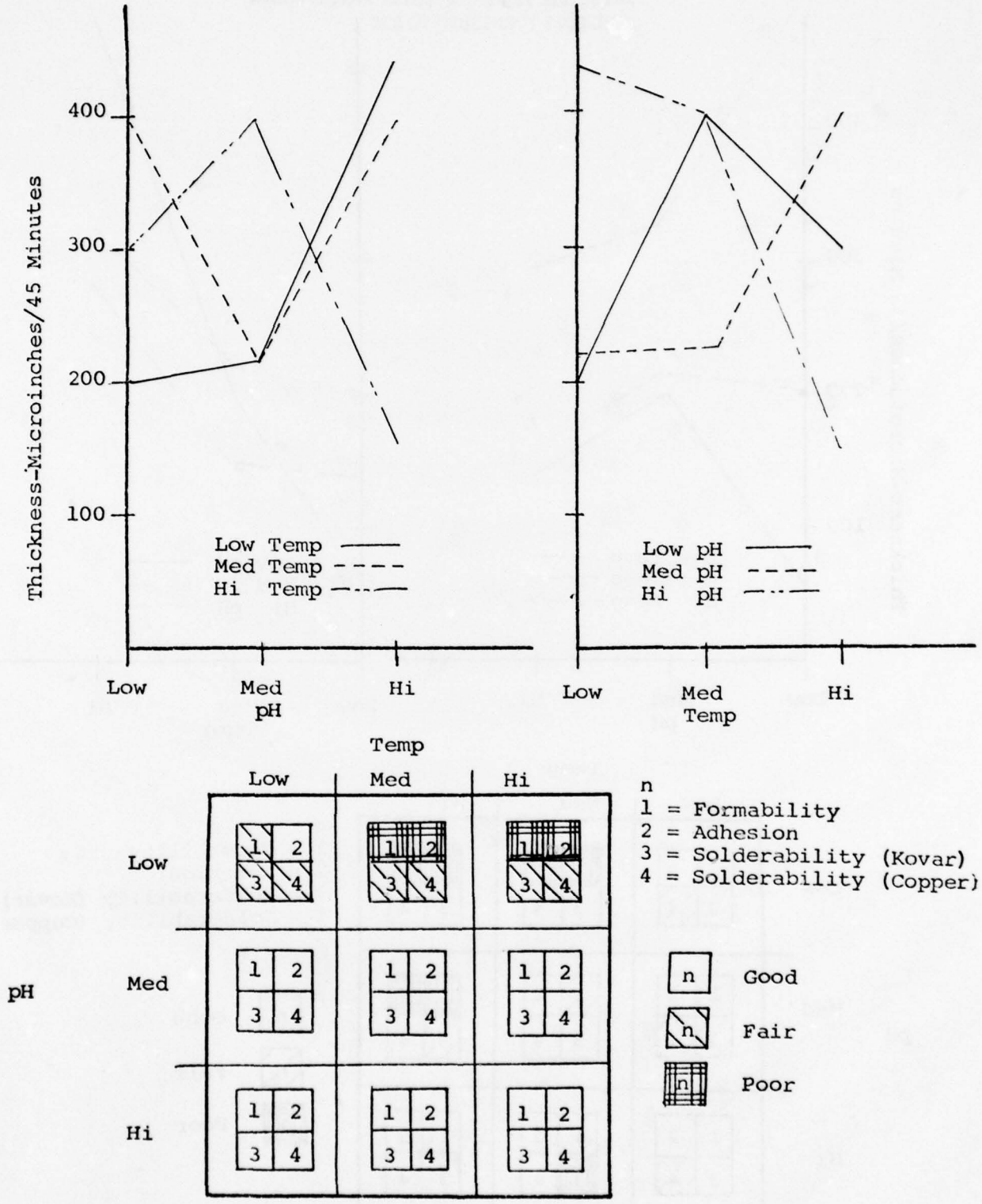
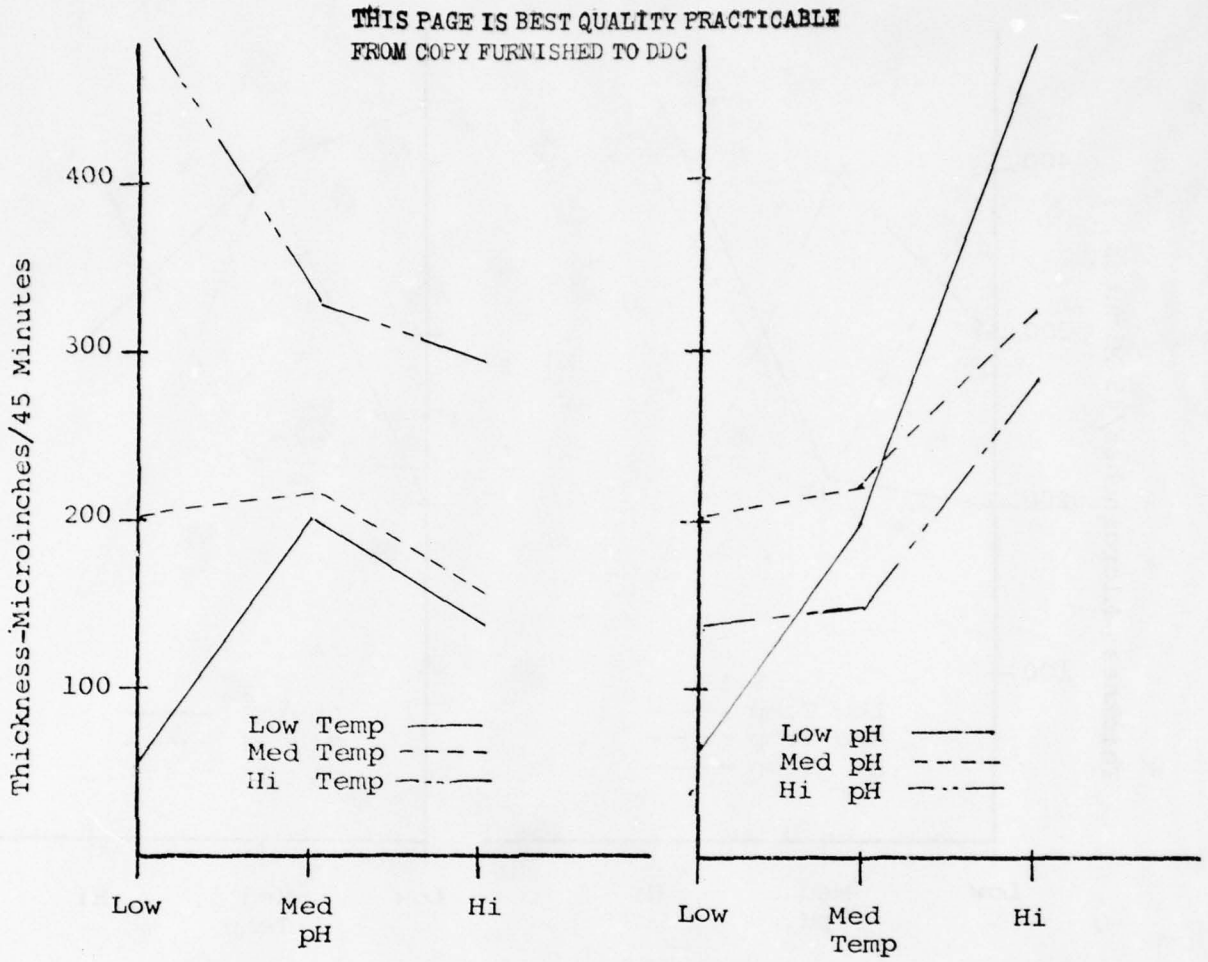


Figure 1. Dupont - Sylek

THIS PAGE IS BEST QUALITY PRACTICABLE
FROM COPY FURNISHED TO DDC



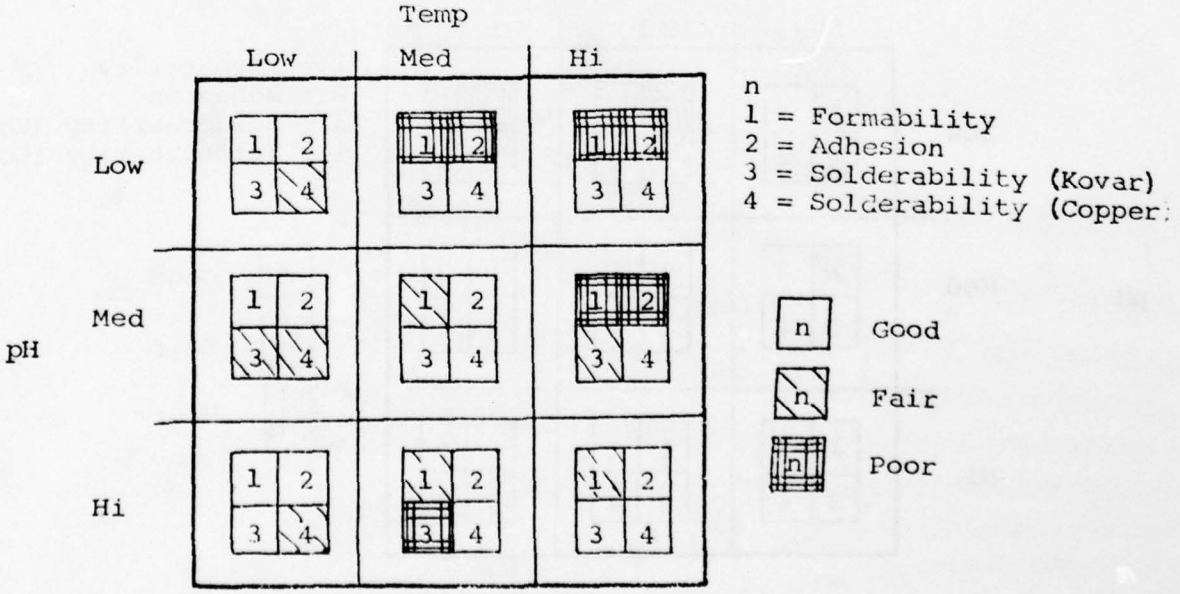
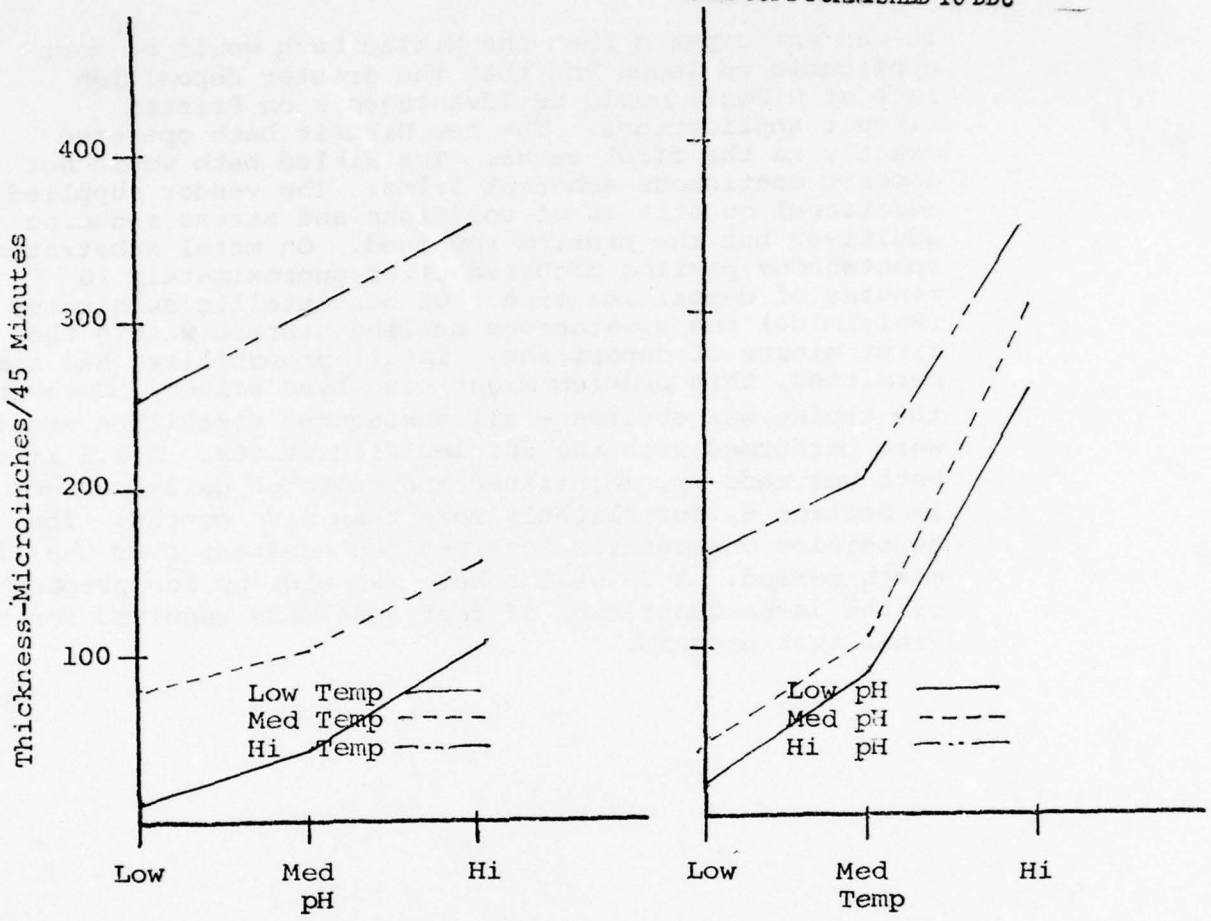


Figure 2. Shipley Deposit

THIS PAGE IS BEST QUALITY PRACTICABLE
FROM COPY FURNISHED TO DDC



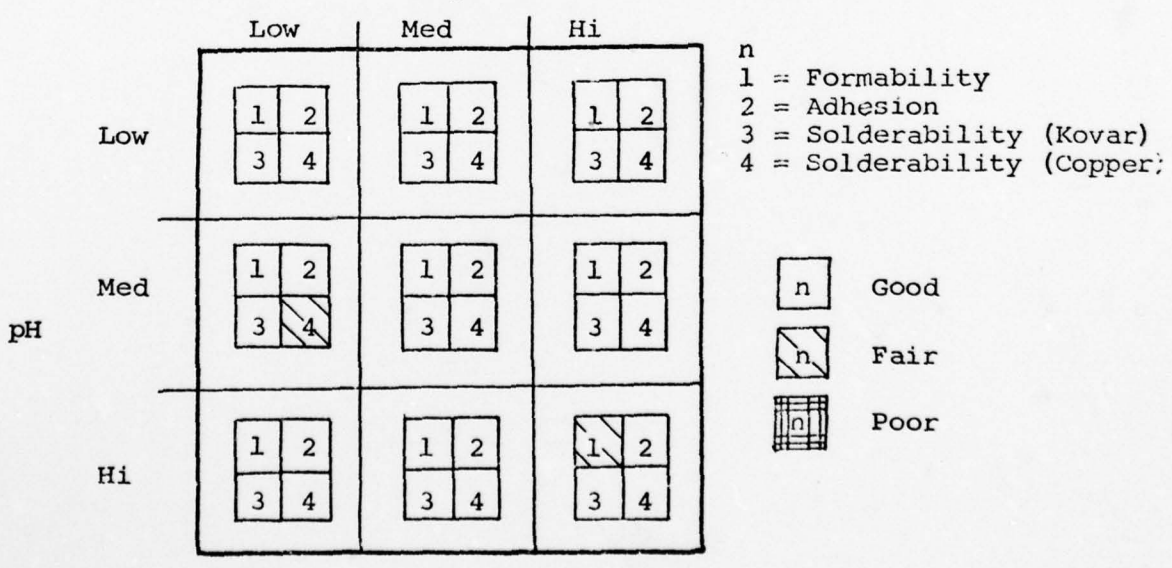


Figure 3. Allied - Kelite

It was anticipated that the Niklad bath would be most applicable on leads and that the greater deposition rate of NiPosit would be advantageous on Printed Circuit applications. The new NiPosit bath operated exactly as the first baths. The Niklad bath would not deposit continuous adherent films. The vendor supplied additional quantities of solutions and stress reducing additives but the problem remained. On metal substrates spontaneous peeling occurred after approximately 10 minutes of deposition time. On non-metallic substrates (Polyimide) the spontaneous peeling started within the first minute of deposition. In all probability, had time permitted, this problem might have been solved. However, the choice was obvious - all subsequent deposition studies were performed with the Shipley NiPosit 468. A 2.5 liter bath was made up, maintained and operated daily, as described in Section 6, for slightly more than five months. The deposition characteristics remained constant over the five month period. A 10 gallon bath was made up for preparation of the large quantities of test specimens required for the final test program.

SECTION 3

INVESTIGATION OF BASIC PROPERTIES AND PARAMETERS OF NICKEL/BORON DEPOSITION

The application of nickel/boron deposits as a replacement for gold on component leads for military electronics requires certain parameters. Among the more important of these are:

a) Adhesion to the base metal
b) Formability
c) Solderability
d) Long-term stability

Desired, but less important parameters are:

e) Weldability
f) Bondability (e.g. it should be possible to bond Aluminum/gold wires to it)
g) Abrasion resistance
h) Adhesion to sealing glass

After the initial studies were made on cleaning and activation of the base metal surfaces, solderability, formability and adhesion studies were made on deposits from solutions from each of the three sources: DuPont, Shipley and Allied Kelite.

A matrix was set up to show the effect of temperature and pH on the parameters of deposits from the three solutions. A summary of the results is as follows:

III-1. DuPont Sylek - The deposition rate variation with both temperature and pH variation are double valued in that linear parameter variation results in reversals of deposition rate variation. While the mechanical properties of these deposits may be excellent for mechanical applications, i.e., bearing surfaces, results on the as deposited films appear too random for the electronic applications considered in this investigation.

III-2. Shipley NiPosit - The deposition rate tends to diminish with increasing pH but definitely increases with temperature. The greatest deposition rate is obtained with this bath and the property of poor to fair formability at high deposition rate does not eliminate it from consideration for additive PCB fabrication. An area of investigation remaining is in the medium to high pH range where ductility appears better. Utilizing temperatures above the recommended range may produce thick deposits with somewhat better ductility. Heat treatment is expected to have a substantial effect on ductility.

III-3. Kelite - Deposition rate varies monotonically with both pH and temperature. The measured properties, formability (ductility) and solderability, are good at all operating conditions. The area of solderability rated fair was on the basis that flux type RMA did not result in 100% wettability but flux type RA did. The fair formability area (see the following chart for Allied-Kelite) showed very fine crazing at the most severe location of the bend. Obviously to be determined is the thickest deposit which will still maintain formability.

The following charts depict the data gathered. In all cases the values of pH and temperature utilized were the low, medium and high of the manufacturers recommended range (see Figures 4, 5, and 6).

Formability:

Good = No cracking or crazing
Fair = Crazing or minor cracks at highest stress point
Poor = General cracking

Adhesion:

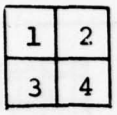
Good = No flaking or lifting
Fair = One or two flakes or minor separation at highest stress point
Poor = General flaking and/or separation

Solderability:

Good = Good wetting with flux type RMA
Fair = Required flux type RA for good wetting
Poor = Poor wetting with flux type RA

These parameters have been determined for the "as deposited" coating only. Heat treatment was expected to have a substantial effect on ductility and/or solderability.

DEPOSITION MATRICES -- Before and After Heat Treatment



1 = Formability
2 = Adhesion
3 = Solderability (Kovar)
4 = Solderability (Copper)



Good



Fair



Poor

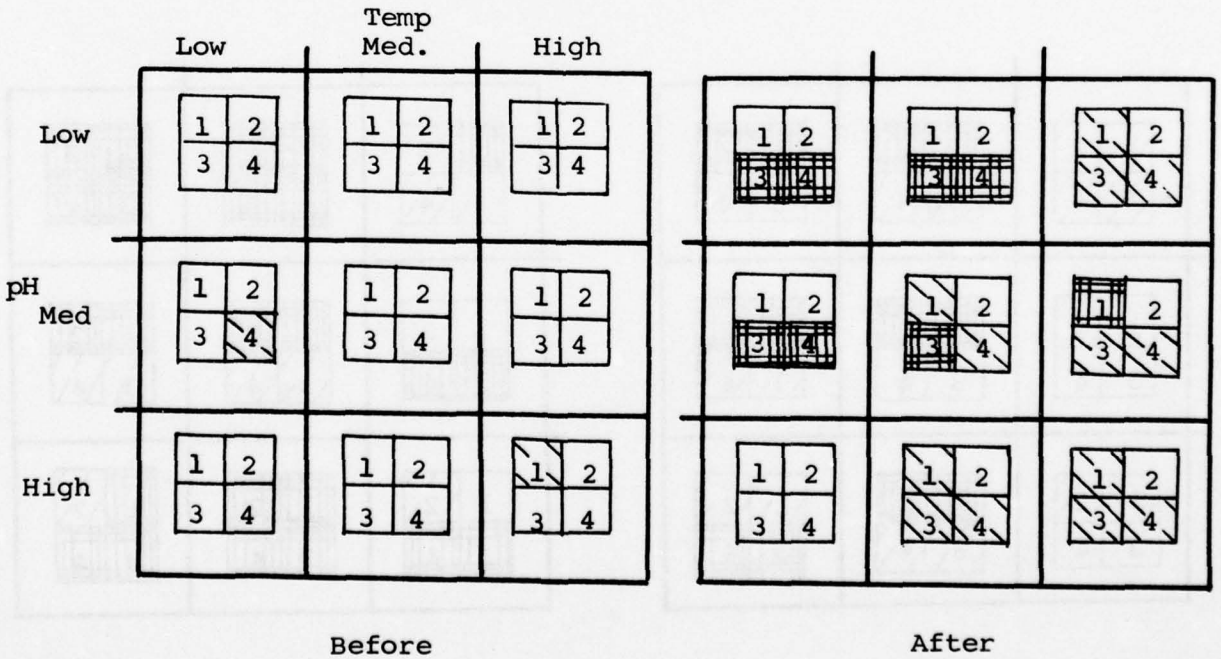


Figure 4. Kelite

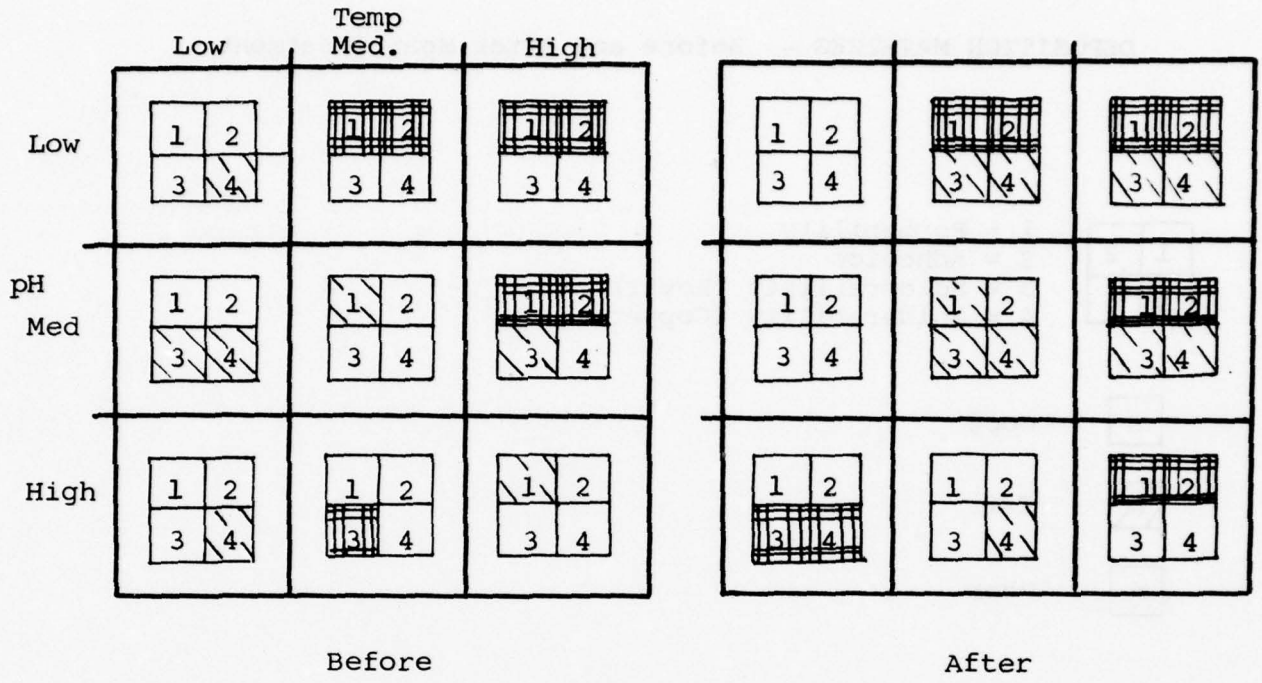


Figure 5. Shipley

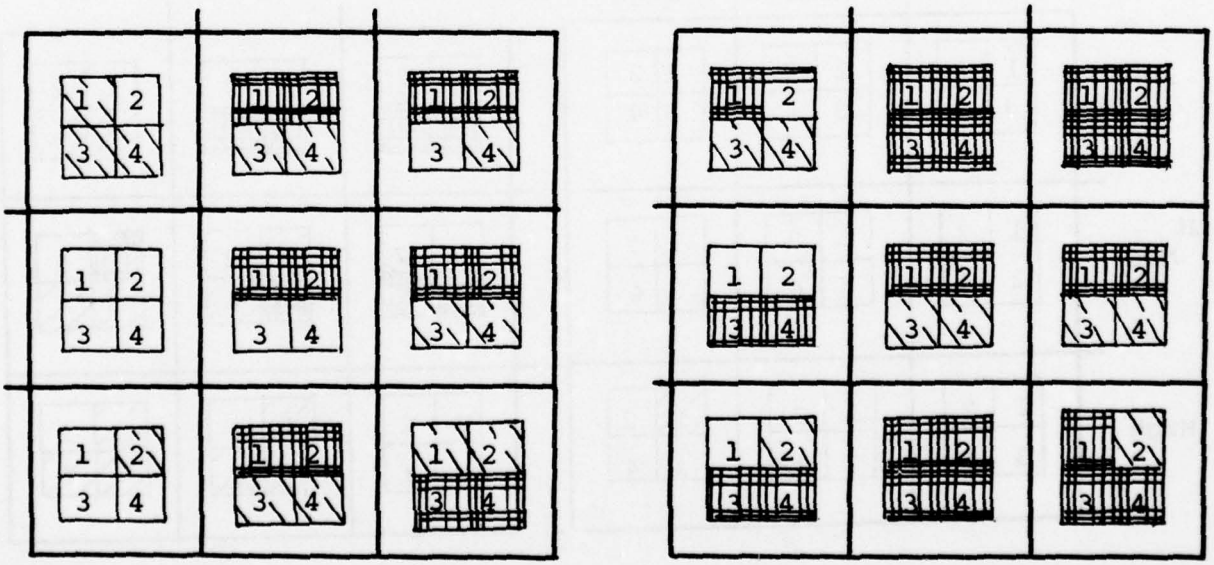


Figure 6. Dupont

Nickel/Boron deposits are alloys with somewhat varying composition, and, at equilibrium, having two or more phases. "As deposited" these materials are not normally at equilibrium. It has been well established that Nickel/Boron deposits respond to various thermal aging cycles. The manufacturers literature (DuPont, Shipley, Allied Kelite) and articles in the technical journals (R.F. Weightman and F. Perlstein, Hardness and Wear Resistance of Electroless Nickel Phosphorus and Nickel/Boron Deposits, Metal Finishing, Sept. θ974) give 400°C for one hour as the aging treatment to achieve maximum hardness.

It was our reasoning that aging at temperature would relieve the internal stresses inherent in most 'as plated' material and if aged at a temperature beyond that for maximum hardness, the ductility would be enhanced enough to allow improved formability of the leads. (This is an alloy with a face centered cubic matrix.) At the same time we recognized the danger to the solderability of putting a passivating film on the nickel surface.

On that basis we picked 550°C (1020°F) for two hours in a nitrogen atmosphere as the aging conditions.

The results were disappointing. An examination of Figures 4, 5, and 6 will show that there is no improvement in formability and in some areas there is a deleterious effect.

At the same time there were a number of areas where the solderability was lowered.

Obviously, 550°C is not high enough to improve the formability, and aging at this temperature, or higher, will require a reducing atmosphere; a neutral atmosphere is not enough.

Nickel and nickel alloys are stress relieved at 450°C to 700°C and annealed at 850°C.

We had hoped that 550°C would be a good compromise. This not being the case, it was necessary for us to re-evaluate the advisability of any heat-treatment on Nickel/Boron deposits used on any flat-pack leads. To achieve any improvement in formability, it may be necessary to go above 700°C and probably close to 800°C. There was some passivation of the surface at 550°C as shown by the lowering of the solderability.

Any heat treatment given these deposits for increased formability must be done prior to any glass sealing operation because the required temperatures are above those used for glass sealing. It is also obvious that the annealing temperature will passivate the surface necessitating a strong pickling using hydrochloric acid to restore the initial solderability of the surface unless it is done in a reducing atmosphere.

Further on in this report the problem of glass sealing leads with Nickel/Boron deposits is dealt with. The glass sealing temperatures will also tend to passivate the surface necessitating a strong pickling operation. Under these circumstances it might be well to apply the Nickel/Boron deposits after the glass sealing operation. This would preclude any heat treatment of the deposits.

To better understand the Nickel/Boron deposits Auger and X-Ray diffraction analyses were run. The Auger was run to determine if any variation existed in the chemistry of the deposits and the X-Ray diffraction was run to show the basic metallurgical structure of the deposits.

Auger Analysis

The actual analysis was performed at Physical Electronics Industries, Eden Prairie, Mn. The samples were prepared by depositing the Nickel/Boron directly on Polyimide substrates with forced air drying after hot water rinsing. The following charts show the composition of the deposit at various distances below the surface.

Figure 7 (Sheet 1 of 4) - Shows the composition of the as deposited surface. This was predominately nickel with a moderate oxygen peak and weak peaks for calcium, boron, carbon, sulfur and chlorine (chlorine and boron peaks superimpose).

Figure 7 (Sheet 2 of 4) - Shows the composition of the surface remaining after approximately 30 Angstroms of material had been removed by argon sputtering. The oxygen intensity was significantly reduced; Boron was slightly lower; carbon was reduced by one half; sulfur and chlorine almost gone. Argon, the sputtering medium appeared.

Figure 7 (Sheet 3 of 4) - Depicts a continuous scan (profile) of the principal (at this point) constituents: nickel, boron, oxygen, and carbon, as the depth of etching and surface removal proceeded from 30 Angstrom, shown as 0, to 1800 Angstroms. To obtain significant

readings, the carbon and oxygen have been multiplied by five and the boron by ten. It is seen that slightly deeper than 30 A^{O} the oxygen and carbon falls to essentially 0 and that the boron increases slightly and then remains stable through the remainder of the etching.

Figure 7 (Sheet 4 of 4) - Shows the full element trace at the depth, after profiling, of 1800 Angstroms below the initial surface. At this point only nickel and boron remain.

Some conclusions to be drawn from these traces and profiles are:

1. The boron content is uniformly distributed throughout the deposit.
2. The slight decrease in boron content in the final 30 A^{O} of deposition can be accounted for by the following mechanism: Deposition rate is approximately 8 Angstroms per second. This outer 30 A^{O} represents the last four seconds of deposition which is taking place from the thin film of plating solution remaining on the part while it is draining prior to rinsing. The thin film of liquid depletes very rapidly in Boron content such that all deposition is probably halted prior to rinsing.
3. The calcium, chlorine and sulfur are most probably introduced from the final heated rinse; although, in light of the presence of carbon in the surface, inadvertent handling may well have contributed.
4. The oxygen most certainly consists of oxides rapidly formed on the active freshly rinsed surface as well as absorbed oxygen.

   The thinness (approximately 30 A^{O}) of the oxygen rich surface accounts for our success in being able to solder acceptably with flux type RMA.

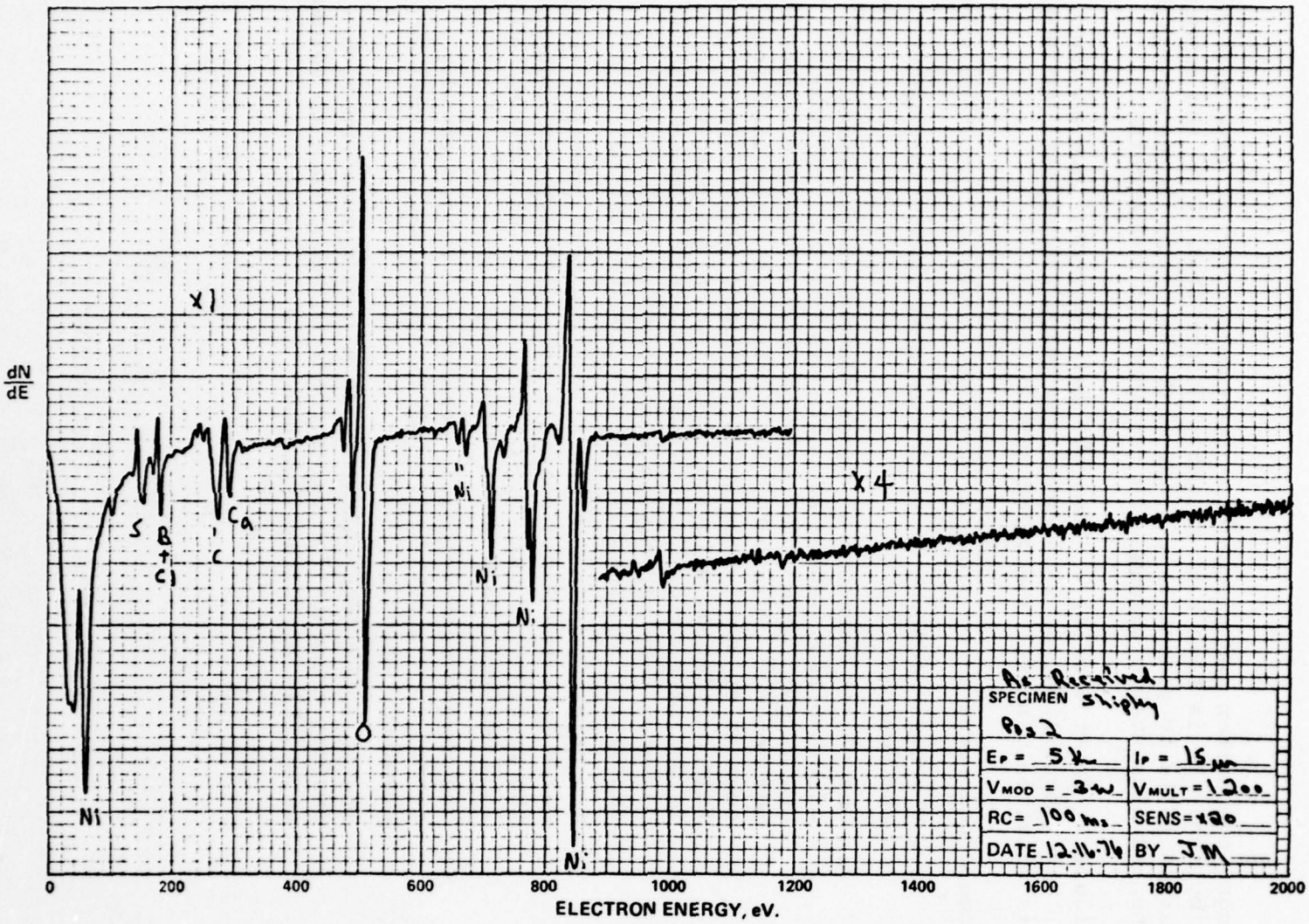


Figure 7. Auger Analysis (Sheet 1 of 4)

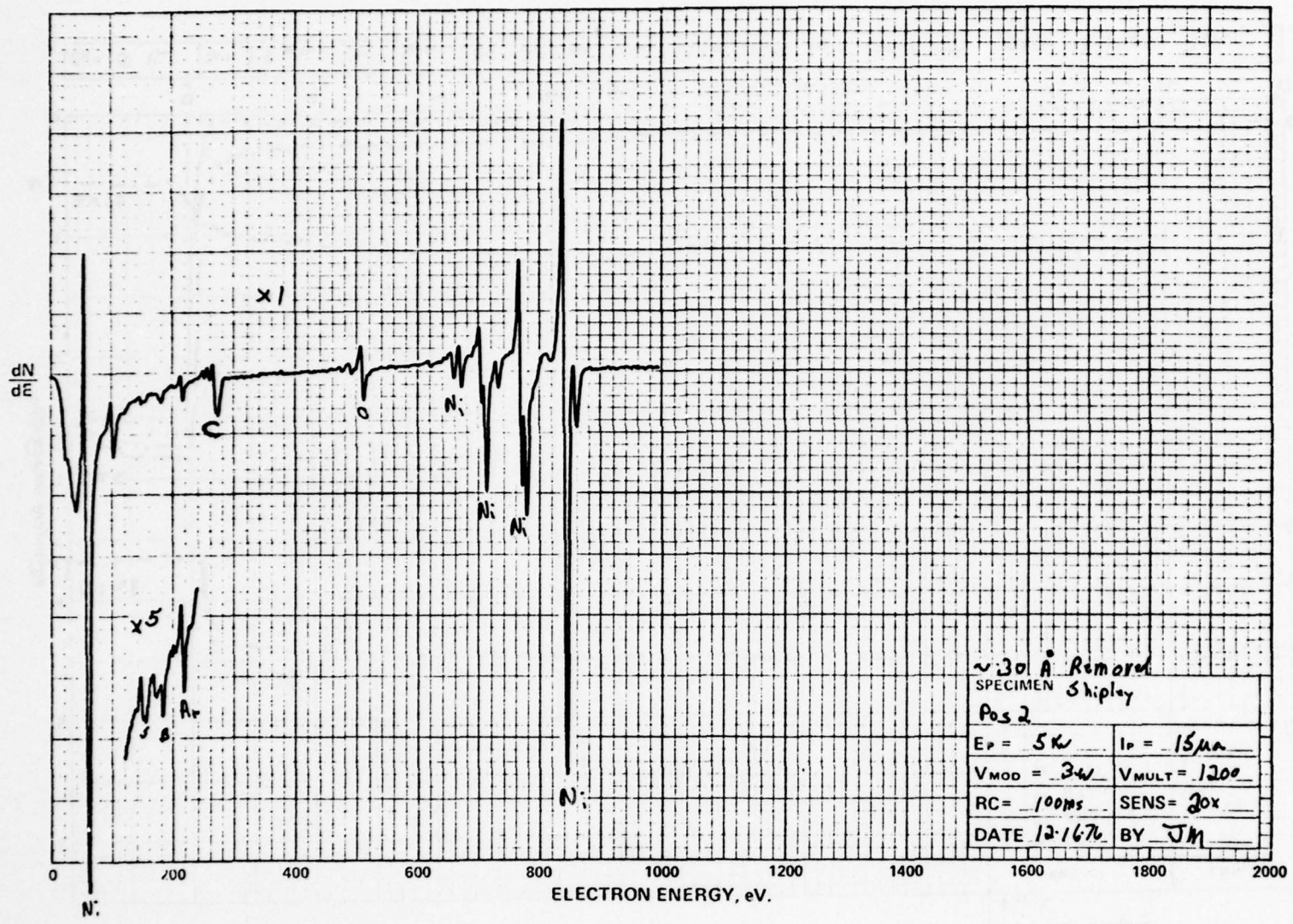


Figure 7. Auger Analysis (Sheet 2 of 4)

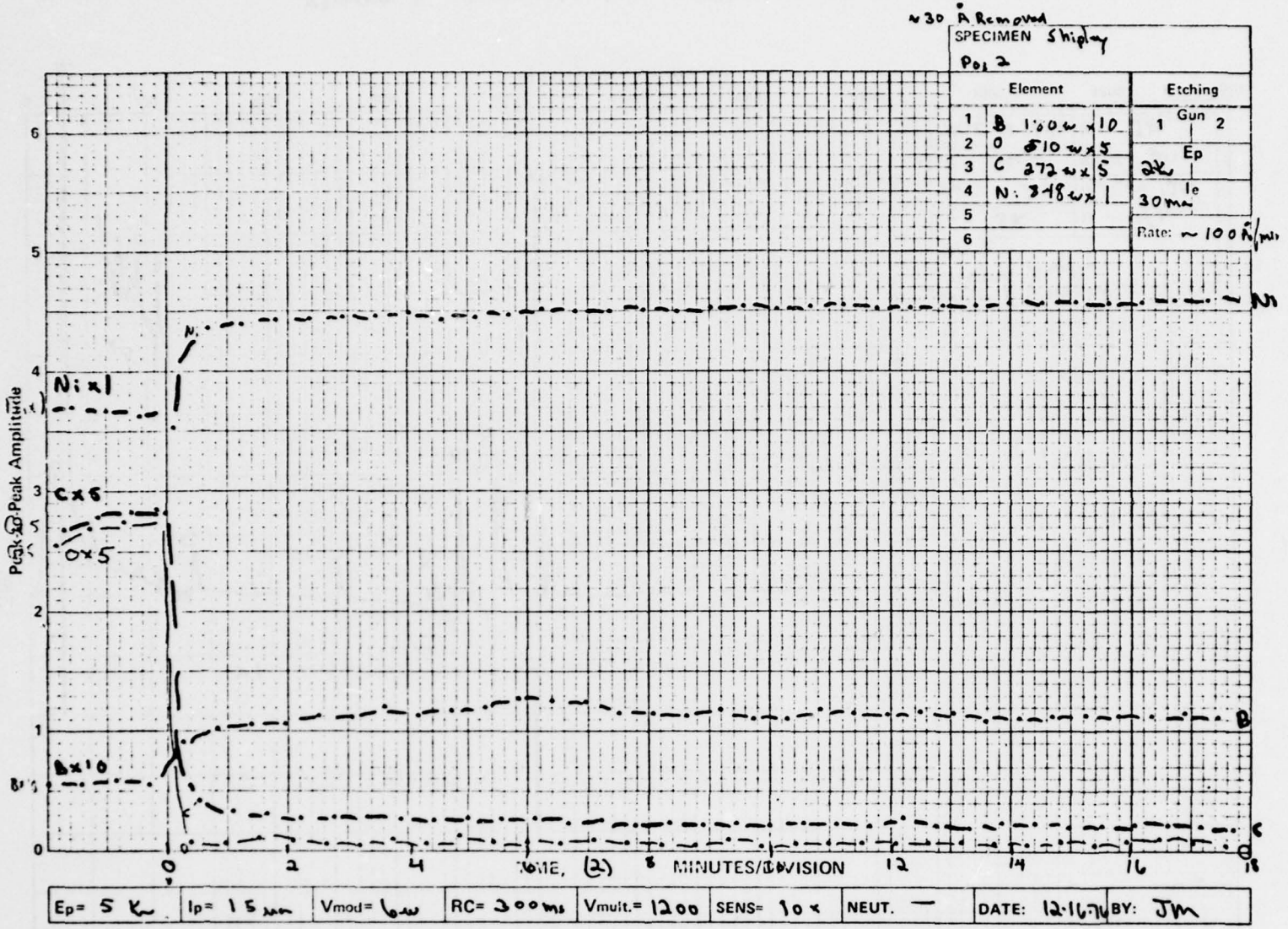


Figure 7. Auger Analysis (Sheet 3 of 4)

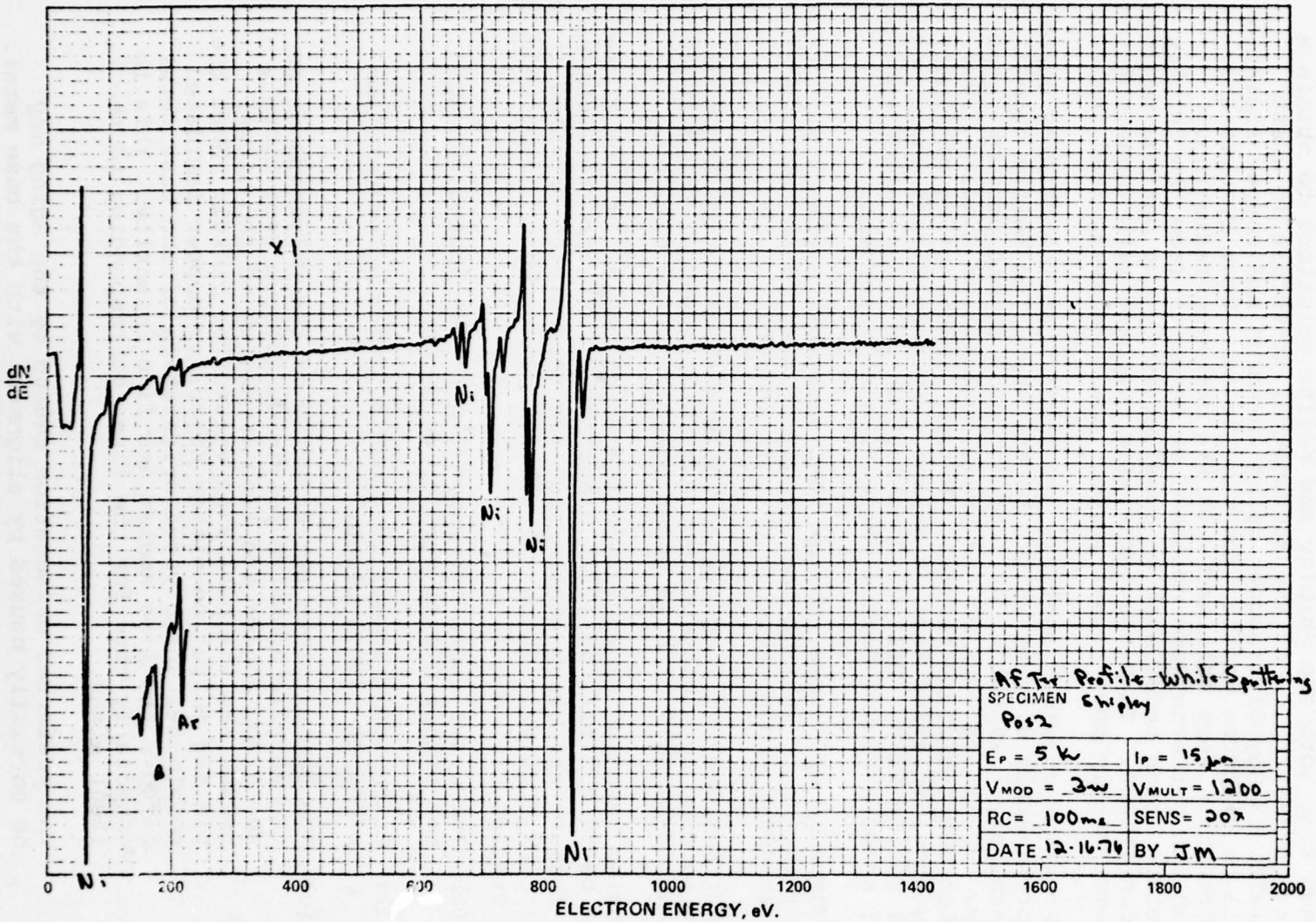


Figure 7. Auger Analysis (Sheet 4 of 4)

X-Ray Diffraction Studies

X-Ray diffraction analysis has been run on the deposits obtained from both the Shipley and Kelite solutions to obtain a greater understanding of the fundamental structure in these materials. X-Ray diffraction using chromium and copper radiation as well as electron diffraction were tried. Best results and sharpest lines were obtained with the chromium radiation. Diffraction patterns were obtained on deposits from the Shipley and Kelite baths under what we consider to be the optimum deposition conditions. These patterns were compared with those obtained for commercially pure nickel powder, and base Kovar lead frames.

Previous chemical analysis has shown that the Shipley deposit is approximately 0.3% by weight boron, while the Kelite deposit is approximately 1.2% boron, or 1.6% and 5.3% atomic percent respectively. Published work on the phase equilibrium diagram gives somewhat contradictory results. Hanson, Constitution of Binary Alloys shows an alloy that is essentially pure Nickel phase and Nickel Boride Ni_2B. Elliot, Constitution of Binary Alloy - Supplyment I shows a Nickel Boride phase Ni_3B also present.

There is of course, no law that says that a plated structure is at equilibrium. The fact that we get changes in the structure by aging at 400°C would indicate that it is not.

For purposes of comparison, Table 1 shows the relation of weight percent to atomic percent and the percent of the structure that should be Ni_2B or Ni_3B under equilibrium conditions.

Using chromium $K\alpha$ radiation the Bragg angle (2θ) for Nickel should be 68.55° for the (111) plane and 81.09° for the (200) plane. Table 2 shows the Bragg angles and line intensities obtained in the diffraction studies. There are several points that can be made from these studies.

(a) There are lines corresponding to the nickel but none for either nickel boride, or boron.

(b) Aging would appear to cause a preferred orientation along the (200) plane.

(c) The deposit when put directly on the polyimide or on the acrylic adhesive polyimide follows very closely the Bragg angles and line intensity of the nickel powder and the published values for nickel. When the plating is put on either Kovar, or copper laminated polyimide, the crystal orientation of the base metal affects the line angles and line intensity. This is especially true for the lines corresponding to the (200) plane.

The preferred orientation caused by the aging may be partially caused by alignment with the base metal.

TABLE 1. ATOMIC PERCENTAGES

	Wgt. %B	Atomic %B	At Equilibrium* % Ni_2B	At Equilibrium** % Ni_3B
Shipley Bath	0.3	1.61	4.86	5.19
Kelite Bath	1.2	5.26	15.8	20.8

* Based on phase diagram in Hanson - Constitution of Binary Alloys, McGraw-Hill, New York, 1958.

** Based on phase diagram in Elliott - Constitution of Binary Alloys, First Supplement.

(d) The lines show some broadening indicating a strained lattice.

The absence of any lines for nickel boride or boron would indicate that the boron is very finely dispersed in the structure. The line broadening would indicate that some had been dissolved in the nickel lattice, probably intersticially.

The Auger and X-Ray Diffraction both indicate a uniformly dispersed boron content. The line broadening is also an indicator of stress which is induced by the intersticially dissolved boron. Any aging probably causes a predisposition to precipitation of either boron or Ni_2B, thus the preferred orientation shown by X-ray diffraction. This would result in higher internal stress and probably accounts for the spalling on additive circuitry discussed in the Circuitry Section 4.

The similarity of the Bragg angle of the deposit to pure nickel when deposited on polyimide, especially when coated with acrylic adhesive, may be attributed to the softness of the surface on which the deposit is made, allowing the stress to be relieved causing the visual phenomena of "wrinkled" plating. Only by substantially overcuring the acrylic adhesive prior to deposition was it possible to eliminate "wrinkles".

Figure 8 shows a typical X-Ray diffraction pattern obtained. In this case it was on a Shipley deposit on the acrylic coated polyimide.

TABLE 2. X-RAY DIFFRACTION VALUES

Material	Bragg Angle (111)	Bragg Angle (200)
Pure Nickel Power	68.5° Strong	81.2 (Medium)
Published Data-Nickel	68.55°	81.09
Kovar (lead frames)	67.8 (Medium)	79.5 (Strong)
Shipley-As Plated Kovar	69 (Strong)	79.6 (Medium)
Shipley-Aged 400°C/ 1 Hr. over Kovar	68.8 (Medium)	79.5 (Strong)
Kelite-As Plated over Kovar	67 (Strong)	79.4 (Medium)
Kelite-Aged 400°C/ 1 Hr. over Kovar	73 (Medium)	81.4 (Strong)
Kelite-Aged 400°C/ 1 Hr. over Kovar	73 (Medium)	81.6 (Strong)
Shipley on Polyimide (As Plated)	69 (Strong)	81.2 (Medium)
Shipley on Acrylic on Polyimide (As Plated)	68.7 (Strong)	80.8 (Medium)
Shipley on Cu on Polyimide	69.4 (Medium)	78.2 (Strong)
Published Data-Cu	66.83	78.31

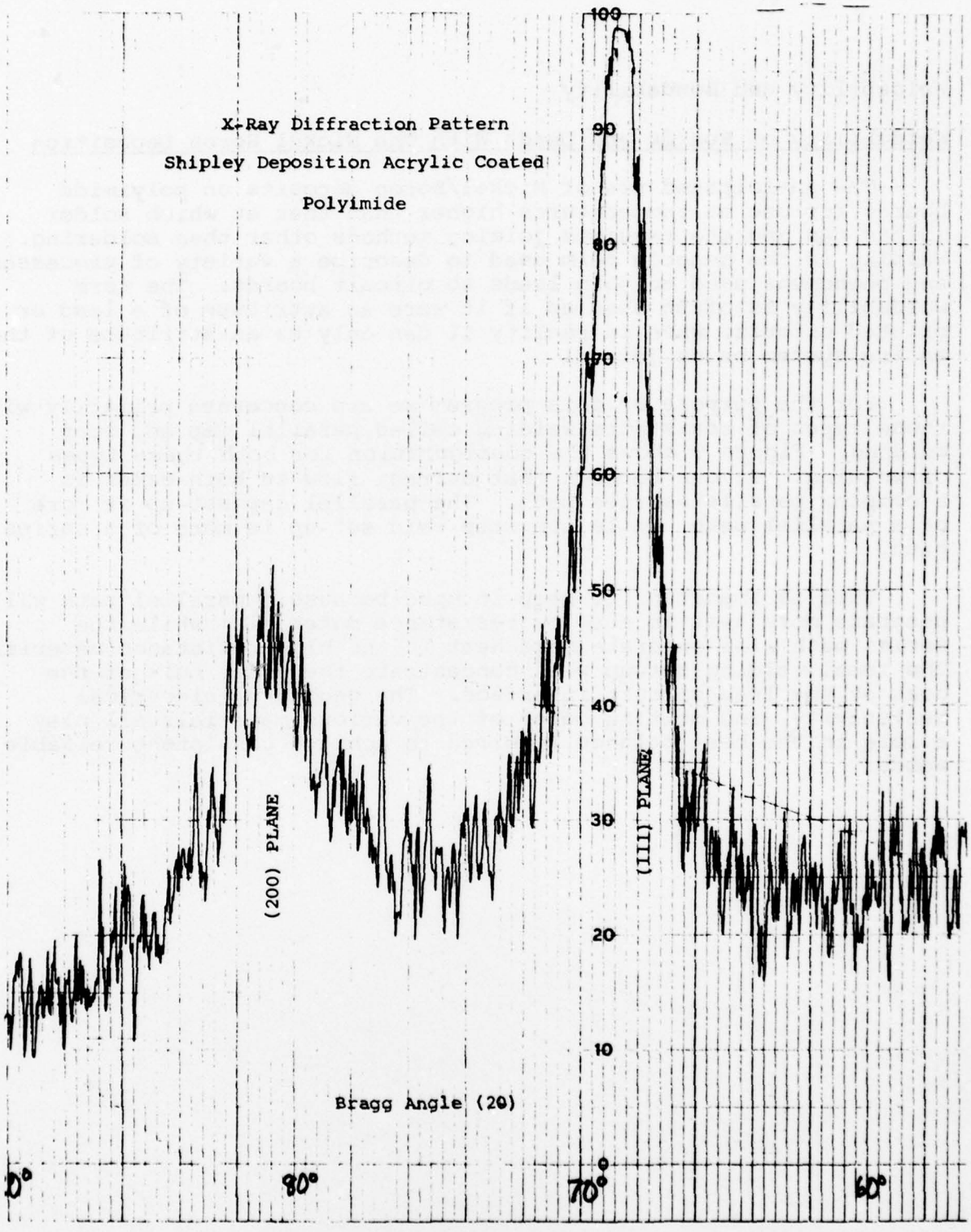


Figure 8. X-Ray Diffraction Pattern Shipley Deposition Acrylic Coated Polyimide

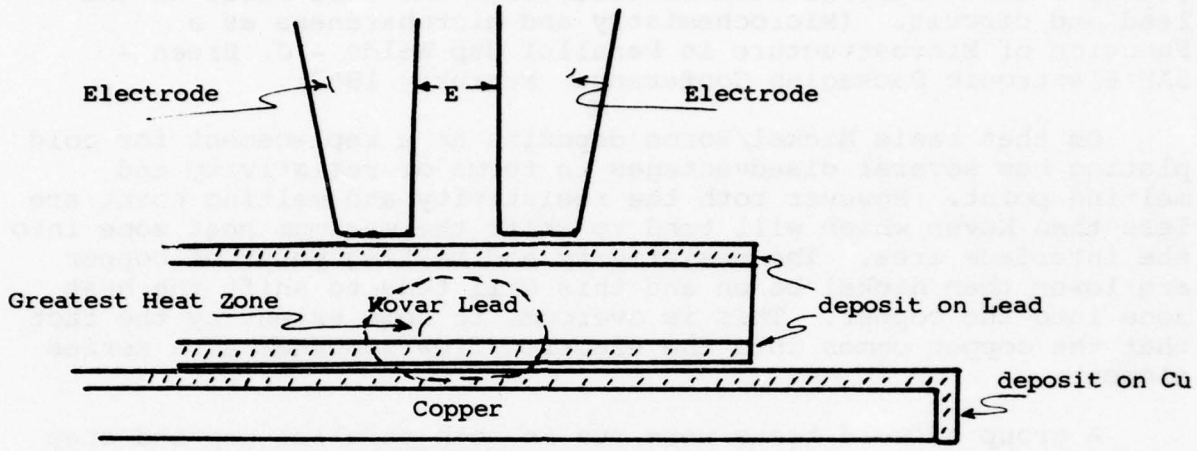
Weldability and Bondability

Weldability of Boards and Leads With The Nickel Boron Deposition

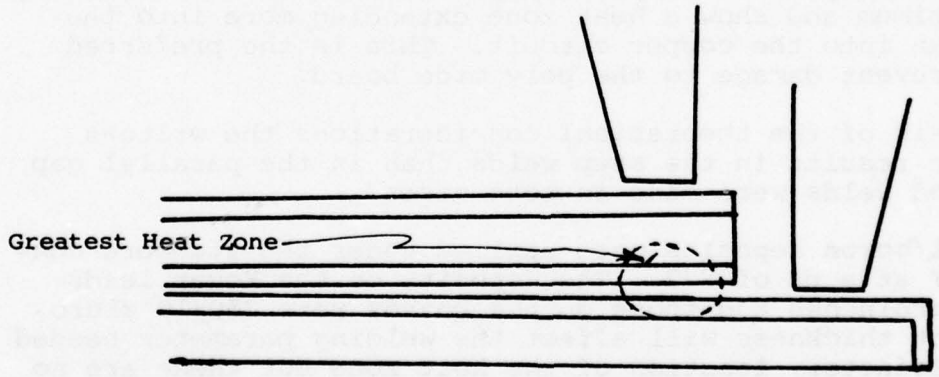
The anticipated use of Nickel/Boron deposits on polyimide boards for use at temperatures higher than that at which solder joints can operate requires joining methods other than soldering. Welding is the generic term used to describe a variety of processes and phenomena used to join leads to circuit boards. The term weldability is often used as if it were an attribute of a lead or printed circuit, when in reality it can only be an attribute of the entire system being joined.

For the purpose of this program we are concerned primarily with those types of resistance welding called parallel gap and step welding. Figure 9 shows the configuration for both these types of welding. It can be seen that current flow in both cases is a complex parallel-series path. The parallel gap set-up is more of a parallel path, while the step weld set-up is more of a series path.

This is important to keep in mind because a parallel path will generate more heat in the low resistance materials, while the series path will generate more heat in the high resistance materials. The ideal welding set-up will concentrate the great bulk of the heat at the lead/circuit interface. The geometry, electrical resistivity, and melting point of the various materials all play a role in the heat balance required to achieve consistent reliable welds.



PARALLEL GAP WELD



STEP WELD

Figure 9. Electrode Configurations

When we consider the role of nickel-boron deposits we are concerned with its electrical resistance and melting point compared to those of the other materials involved. Table 3 lists these physical properties for the materials involved.

Work published by this laboratory has shown that best welds are obtained when the plating on the lead and circuit melt and dissolve about half as much material from the base metal in the lead and circuit. (Microchemistry and Microhardness as a Function of Microstructure in Parallel Gap Welds - J. Breen - SAE Electronic Packaging Conference February 1967).

On that basis Nickel/Boron deposits as a replacement for gold plating has several disadvantages in terms of resistivity and melting point. However both the resistivity and melting point are less than Kovar which will tend to shift the maximum heat zone into the interface area. The resistivity and melting point of copper are lower than nickel boron and this will tend to shift the heat zone into the copper. This is overcome to some extent by the fact that the copper comes into the electric flow somewhat as a series element.

A group of weld tests were run in both parallel gap and step welding configurations. There was no attempt to optimize the weld schedule as this is a time consuming process, but only to demonstrate that satisfactory welds can be made without damage to the circuitry or polyimide board.

Figure 10 and 11 shows photomicrographs of satisfactory parallel gap and step welds respectively. These welds are slightly cooler than optimum and show a heat zone extending more into the Kovar leads than into the copper circuit. This is the preferred situation to prevent damage to the polyimide board.

On the basis of the theoretical considerations the writers expected better results in the step welds than in the parallel gap, but equally good welds were made in both cases.

The nickel/boron deposits were applied under the standard condition of 145^{o}F at a pH of 7.2. The deposits on the Kovar leads were 100$\pm$10 microinches and those on the boards were 250$\pm$10 microinches. Deposit thickness will affect the welding parameter needed to achieve satisfactory location of the heat zone but these are no serious problems provided the product is consistent. The work to-date shows that when the plating parameter are controlled the deposits are consistent.

TABLE 3. PHYSICAL PROPERTIES

	Electrical Resistivity (Micro-ohm-cm)	Melting Pt. (°C)
Kovar	49	1450
Sheet Nickel	9.6	1435/1446
Copper	1.7	1083
Ni-B Deposit*	15/40	1080/1425
Gold	2.35	1063

* Properties depend on %B and state of stress.

Bondability of Nickel/Boron Deposits

In the world of military electronics the assembly of flatpack circuits requires the bonding of aluminum or gold interconnect wires to the lead frames. At the present time this connection is usually made to a gold plated surface. Part of this study involved determining the feasibility of bonding to the nickel/boron deposits.

Using a K & L ultrasonic bonding machine and one mil (1% Si) aluminum wires, a brief study has shown that reliable consistent bonds can be made to flatpack lead frames with the nickel/boron deposit. (Shipley deposits, 100u inches made at 7.2 pH and 145°F). Table 4 shows the results of bond pull-tests run on a series of bonds. To put these values in perspective it should be kept in mind that the aluminum wire breaks at 14 $\pm$ 1 gm. After being subjected to the flatpack sealing which anneals the wire it will break at 4 $\pm$ 1 gm.

Figure 12 is a photograph of a typical bond. Figure 13 is a transverse metallographic section through a bonded area. These show typical deformation of the wire. There is a good metallurgical bond along the interface.

No claim is made that this is an optimum production schedule. The determination of optimum machine/material bonding parameters is costly and time consuming and beyond the scope of this study. However, it has been shown that bondability would not be a gating item in the use of these deposits.

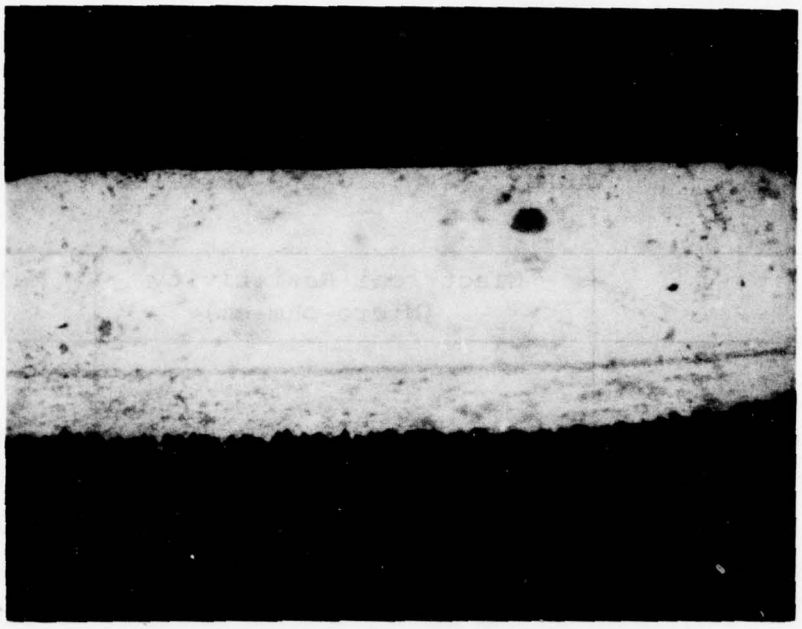


Figure 10. Photomicrograph of Parallel Gap Weld - Kovar Lead on Top
Note: Comparatively small amount of melting at interface -
Mag = 272x Etch = Acid Ferric Chloride

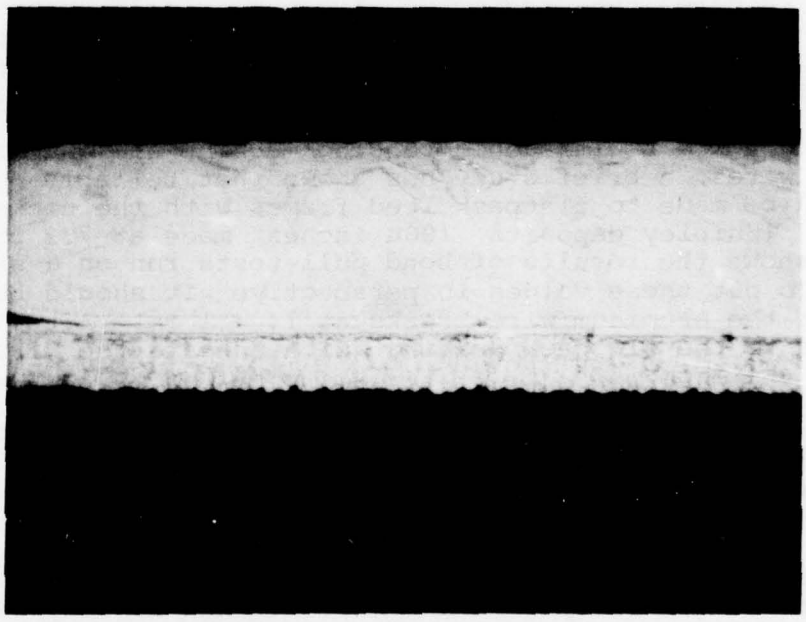


Figure 11. Photomicrograph of Step Weld - Kovar Lead on Top
Note: Melting at interface mostly on lead deposit and Kovar
Mag = 272x Etch = Acid Ferric Chloride

TABLE 4. WIRE BOND SCHEDULE

DATE:_____
ASSEMBLY LOT: #_____
PACKAGE LOT: #_____
WIRE LOT: #_____
DEFORMATION RANGE:_____

WIRE BOND SCHEDULE

OPERATOR 1	MACHINE 1

COMMENTS: NiB plating abraided

BOND SCHEDULE

MAT'L	BOND #	POWER	TIME(SEC)	FORCE (GR)	TOOL
CHIP	-	3.0	3.5	26	MS423-10-11
HEADER	-	2.5	3.5	26	

BOND DATA

SAMPLE	VISUAL		LEAD # 1	2	3	4	5	6	7	8	9	10
1		Gr	6.0	9.0	9.0	8.5	6.0	8.0	8.0	7.0	9.0	3.0
		M	1B	2H	1H	2H	1H	1H	2H	2H	2H	1H
2		Gr	9.0	9.0	7.5	5.5	7.0	11.0	8.5	9.0	7.0	7.5
		M	2H	1H	1H	1B	2H	2H	1B	1H	1H	2H
3		Gr	8.0	8.5	6.0	7.0	4.0	7.0	7.5	9.0	7.0	8.0
		M	2H	1H	2H	1L	1L	2B	2H	2B	1H	2H
		Gr	9.0	8.0	8.5	8.0	4.5	7.0	8.0	4.0	7.0	7.5
		M	1H	1H	1H	1H	1H	2H	2H	1H	1B	2H
		Gr										
		M										
		Gr										
		M										
		Gr										
		M										
		Gr										
		M										
		Gr										
		M										

BOND FAILURE (M) CODE B = Bond Break H = Heel Break L = Bond Lift S = Span Break

STATISTICAL DATA

ΣX	
ΣX^2	
$\bar{X}$	
$\sigma \cdot \left[\frac{\Sigma (X - \bar{X})}{n-1}\right]^{1/2}$	
$\bar{X} - 3\sigma \geq$	Gr

_____
Inspector

Reviewed By:

_____
R. H. LaBrie, Sr. Engineer
Quality Assurance Dept.

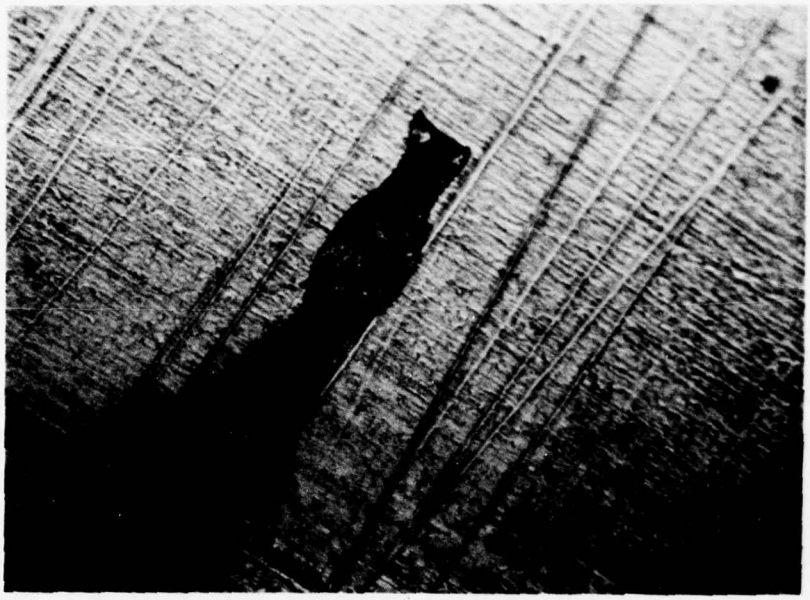


Figure 12. Optical Photo of Ultrasonic Bond. One mil (1% Si) Aluminum wire to Nickel-Boron deposit - Mag = 152x



Figure 13. Transverse Metallographic Cross-Section of Ultrasonic Bond. Good Metallurgical Bond along interface Mag = 790x

In any long-term study of this application, a number of factors will have to be considered. Aluminum forms hard, brittle intermetallic compounds with the transition elements (Fe, Ni, Co) as it does of course with gold. The size, distribution and presence or absence of a continuous network in the bond area will have to be determined.

Ultrasonic bonding, even more than welding or soldering, is a surface phenomenon. To achieve consistently good bonds for this study it was necessary to abrade the deposit surface. Cleaning with organic solvents was not sufficient.

The Auger analysis has shown that the top surface (5 to 30 Angstroms deep) does contain some impurities (0, Cl, S). This could be an area where more detailed studies will be needed in the future. But again it can be stated that bondability is not a gating item.

Abrasion Resistance of Nickel Boron Deposits

Abrasion tests were run comparing electroplated gold, electroplated nickel, electroless nickel/phosphorus and electroless nickel/boron, deposited on copper.

The plating samples were subjected to abrasion testing utilizing a Taber abrader, research model. All samples were abraded using Calibrase CS-17 abrasive wheels with a 1000 gram loading. The abrasive wheels were pre-treated per manufacturer's specifications, by facing on a S-11 abrasive disc for 25 wear cycles under a 1000 gram load, prior to the testing of each of the samples.

Table 5 shows the results of these tests. The nickel/boron deposits are clearly superior to all the others including the nickel/phosphorous deposits.

Figures 14 through 18 are metallographic cross sections showing the virgin deposits and the effects of the wear tests.

Failure of the gold and electrodeposited nickel occurred through completely removing the deposit and exposing the substrate. Failure of the much harder nickel/phosphorus and nickel/borons occurred by localized spalling exposing the substrate. This would be expected when using high loadings on a thin hard deposit plated over a soft substrate. The nickel/boron #1 (smooth) deposit was plated on a chemically polished copper surface etched to a light haze in ammonium persulfate. Ni/B #2 (rough) was plated on a chemically polished copper surface etched to a uniform matte finish in ammonium persulfate.

TABLE 5. Abrasion Test 1 Kg Load Wheel #CS-17

Plating	Cycles	Original Thickness	Final Thickness	Change of Thickness	Cycles/ 100 µ
Gold	290	130µ	0	130µ	223
Electro Ni	1220	140µ	0	140µ	871
Ni/P	4810	260µ	140µ	120µ	4008
Ni/B #1 Smooth	13975	280µ	150µ	130µ	10750
Ni/B #2 Rough	14150	300µ	130µ	170µ	8323

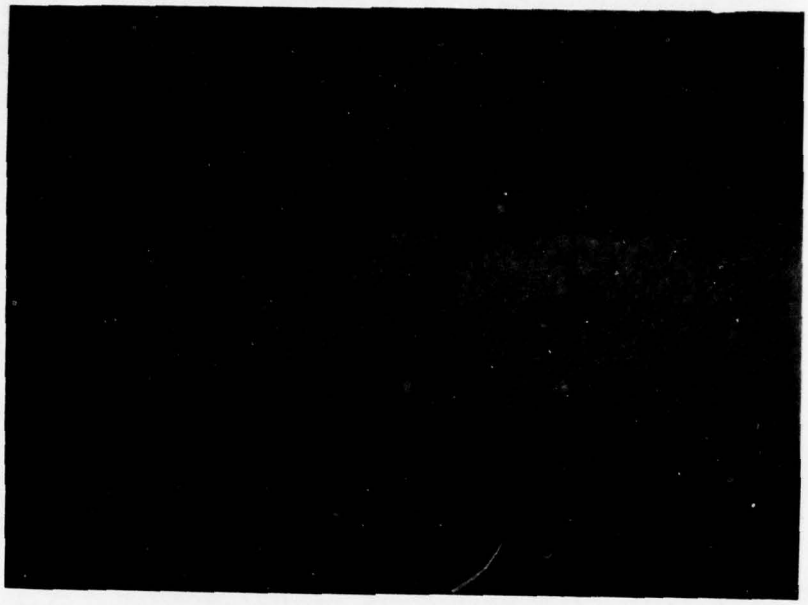


Figure 14A. Virgin Gold Plated Sample, Top layer is protective overplate of Ni for edge protection during polishing. Next layer is gold. Third layer is Ni subplate. Bottom layer is copper on PC board. Mag = 790x



Figure 14B. Gold Sample After Abrasion Test. Note gold layer is essentially gone. Mag = 790x



Figure 15A. Electroplated Nickel Sample - Virgin Section Top Layer, Ni-Bottom Layer Copper on PC Board. Mag = 790x



Figure 15B. Electroplated Nickel Sample After Abrasion Test. Note Nickel essentially gone. Mag = 790x



Figure 16A. Electroless Nickel (Ni/P) Sample - Virgin Section, Mag = 790x



Figure 16B. Electroless Nickel (Ni/P) Sample After Abrasion Test. Note deposit reduced to 140μ from 260μ by wear cycles.

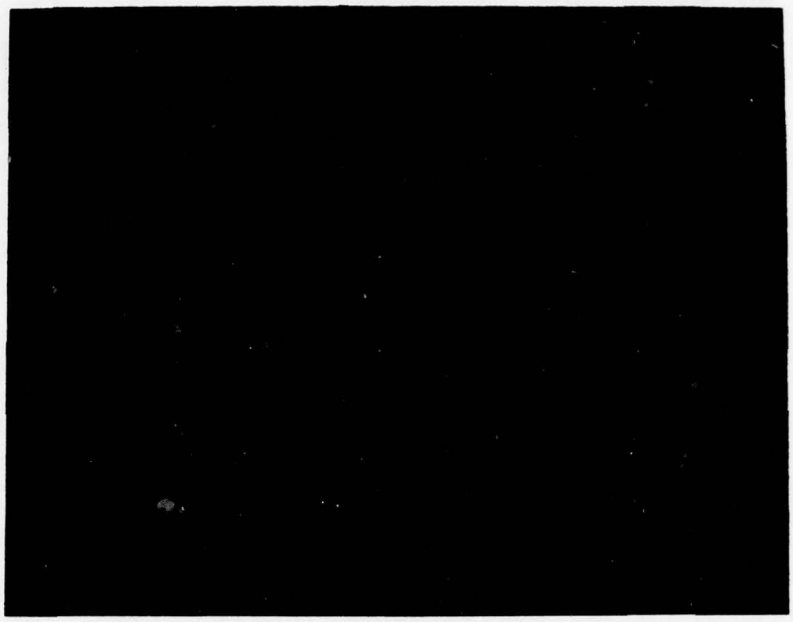


Figure 17A. Nickel-Boron Deposit - Virgin Section. Mag = 790x

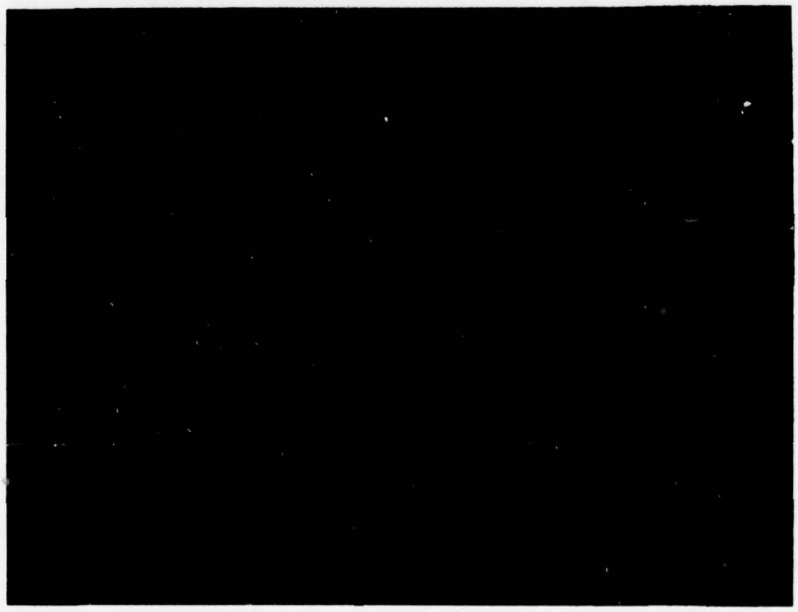


Figure 17B. Nickel-Boron Deposit After Abrasion Test. Note: Deposit reduced to 150μ from 280μ by 13975 cycle.



Figure 18A. Nickel-Boron Deposit - Virgin Sample. Mag = 790x

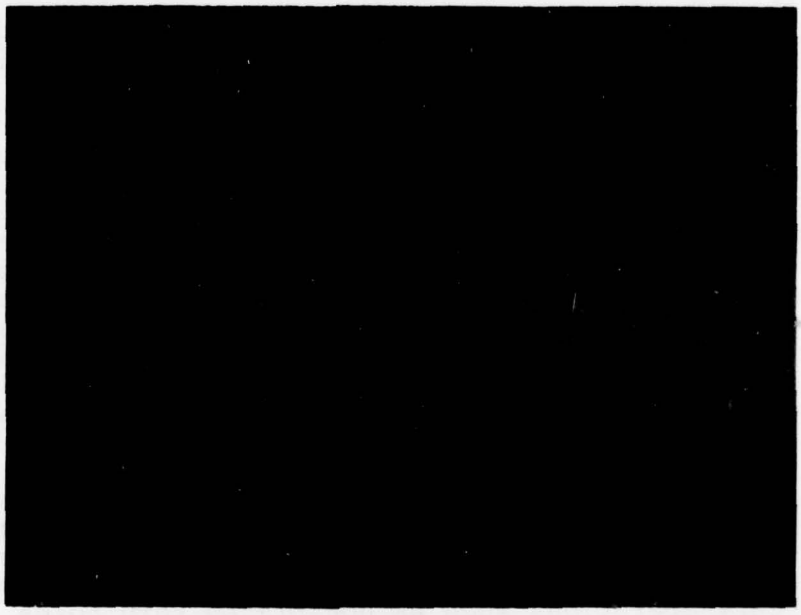


Figure 18B. Nickel-Boron Deposit After Abrasion Test. Note: Deposit reduced to 130μ from 300μ after 14150 wear cycles.

SECTION 4

PCB PROCESSING - CHRONOLOGICAL DEVELOPMENT

Processing cycles for both additive and subtractive printed circuitry were developed. Initial additive efforts were directed at metallization solely with nickel/boride. However, certain properties of the nickel/boride deposit, particularly stress and bulk resistivity, mandate the use of a copper under plate. Fortunately the procedures for deposition of nickel/boride on non-metallic substrates are identical to those for electroless deposition of copper on non-metallic substrates.

The polyimide material proved remarkably easy to sensitize and catalyze. No problems were encountered in obtaining rapid and complete coverage over the as supplied material. However, adhesion was poor. Attempts were made to partially hydrolize the surface of the polyimide with concentrated sulfuric acid, sulfuric/chromic acid and concentrated sodium hydroxide. Adhesion remained poor and use of sulfuric/chromic acid was found to inhibit catalysis. The polyimide material was remarkably resistant to degradation by these hot concentrated reagents thru-out immersion cycles and no evidence of surface roughening was found. Simple abrasion of the polyimide prior to catalyzation did result in sufficient adhesion to pass a standard tape test. However, even mild abrasion with pumice exposed the glass weave of the Micaply PG 418 material, hence, abrasion of unclad material was disgarded. A proprietary adhesive, Shipley Addiposit XP7604, was tried. This is a water based acrylic adhesive curing at 350^{o}F. Excellent adhesion of electroless deposits was obtained. However, the adhesive system would limit end use of the product to the 350^{o}F-400^{o}F range, a considerable sacrifice to the basic properties of polyimide which, alone, can operate continuously above 500^{o}F.

Laminated copper foil was removed from some of the Micaply PG 418-1/1 purchased for orthodox subtractive circuitry fabrication. Copper was removed mechanically by peeling and chemically by either ferric chloride of ammonium persulfate etching. In all cases the surface of the Polyimide was uniformly rough. (Actually a mirror image of the etched copper surface which had been laminated to it). No exposed weave was evident. Adhesion of the electroless deposit to these surfaces was sufficient to pass a standard tape test. Simultaneously with this development it was found that polyimide material with a micro-sanded surface was commercially available from Youngblood Associates. Additive work was continued with etched laminate because of the more than adequate supply on hand.

The system utilized for sensitization and catalyzation was the Shipley CuPosit series of baths used for electroless copper. This system has an advantage in that catalyzed substrates need not go directly into the deposition bath but may be dried and stored and/or have secondary operations such as non-plated thru holes fabricated. A simple water immersion is all that is required to activate the catalyzed surface for deposition. This system allows imaging of pre-catalyzed panels without the need for selective or photosensitizing. All imaging was done by silk screen methods and the choice

of resist proved critical. The materials first tried exhibited the effect of destroying the catalyst. The mechanism of this negative catalysis was not investigated but a switch to an air-drying acrylic resist solved the problem. Besides compatability with the catalyst system, the resist, "Nelco Blue", has the advantages of simple removal with cold solvents, such as MEK, and the images may be examined for defects under UV light. Its major disadvantage is brittleness after fully airdrying which can cause line edge roughness when touch up by scraping is required.

The first additive circuits were made utilizing both the adhesive coated unclad polyimide and the etched laminate (micro sanded). The adhesive coated panels were given varying degrees of pre-deposition cure with final full cure to be performed after deposition and resist removal. Deposition time were varied from a low of ½ hour (150-160 microinches) upwards. The results of this gave direction to all subsequent cycle development.

A. Adhesive coating was eliminated from further consideration:

   1. Coating plugged predrilled holes

   2. When drilled after coating, holes were crudded with soft gobs of stringy adhesive. Drilling swarf became embedded in the surface of the adhesive.

   3. Deposition on all but the fully precured adhesive was wrinkled. As deposit thickness increased wrinkling intensified. (This was later attributed to deposit stress).

B. Additive Circuits of Nickel/Boron only were determined unsatisfactory:

   1. Maximum thickness of deposit obtainable before resist breakdown and loss of detail was approx. 350 microinches. Circuit lines .025"wide exhibited electrical resistance of 1.67 ohms per lineal inch, a value at least one order of magnitude higher than practical for printed circuit applications.

   2. Tape testing caused some flaking of deposits at line edges.

   3. Deposits on etched laminate withstood immersion in 510° solder for 30 seconds with no failure. However, in attempting hand soldering operations it was found that the deposit spalled free of the substrate. This phenomenon occurred because the localized stress of differential heating in concert with the residual stress in the deposit exceeded the strength of the bond to the substrate. The residual stress was visually evidenced by wrinkling on the adhesive coated panels and confirmed during later x-ray diffraction studies.

Therefore, all subsequent circuitry consisted of nickel/boron deposited over copper. Only a few circuits were made by fully additive processes. All copper deposition was accomplished in high speed electroless baths and limited to an upper thickness of approximately 200 microinches. Resists can not withstand the electroless copper deposition hence the circuits were panel plated with copper. To gain its full advantage the nickel/boride coating must be deposited on all surfaces, including the vertical edge of the copper. Therefore, the panel plated copper was positively imaged and the circuit etched. Nickel/boron was then deposited on the etched circuitry. No problem was encountered in initiating deposition. On the contrary, Ni/B deposited everywhere. The residual catalyst on the panel caused complete coverage. The panels were again positively imaged and the undesired Ni/B removed with a ferric chloride etch. Circuits so fabricated were very satisfactory.

Solderability was very good. Hand soldering was performed with no spalling. The Ni/B proved an excellent barrier coating. Immersion in (or float on) 550°F solder for periods up to one (1) minute had no effect. Circuits fabricated of copper only dissolved drastically under the same conditions. Additive circuits were deemed feasible. However, the fabrication process as described is impractically cumbersome. In order to prepare sufficient circuits for the scheduled test program all subsequent circuitry was prepared by electroless deposition of Ni/B on to circuitry etched from copper clad laminate.

Initiation of Ni/B deposition was best accomplished by the autocatalytic strip method. However, initiating the numerous isolated portions of the circuitry was a tedious operation. The final process was evolved from some of the earliest findings, that Ni/B deposits could be dried and inspected and after simple cleaning, could be re-immersed in the bath for further adherent build up of deposit:

Nickel/Boron PCB Fabrication Outline:

1. Predrill all PTH
2. De-burr holes
3. Clean and deposit .15 to .20 mil electroless copper by the Standard Shipley Cuposit Process
4. Panel plate for one (1) minute (approx. 6 microinches) with Ni/B using autocatalytic strip for initiation
5. Dry panels and positively image
6. Etch circuit with Ferric Chloride
7. Remove resist
8. Clean panels and continue Ni/B deposition to a minimum of 150 microinches

This sequence of operations worked well with only one significant problem: On approximately 50% of the circuits fabricated the exposed polyimide surface became autocatalytic with resultant treed or "Blushed" deposition. Yield of good circuitry was increased by operating the nickel/boride bath with a more restricted concentration of DMAB reducing agent. The manufacturer's recommended range is 80% to 105%. Best yield was obtained between 80% and 95%. Because of the yield problem only 128 acceptable PC patterns were fabricated.

However, it was possible to submit 50 specimens to each required test by sectioning out specific portions of the patterns for specific tests. For example (see Figure 19) the large circles and line grid were separated from the thru-hole circuitry for the insulation resistance test series. The circuitry portion was utilized for continuity testing.

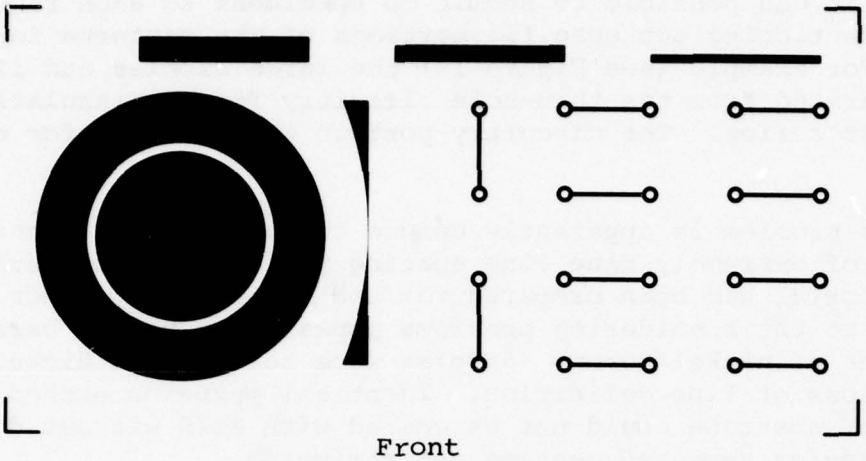
This problem is apparently unique to the polyimide substrate. A series of extremely fine line spacing patterns on standard G-10 epoxy material had been prepared for and by another project. A solution to their soldering problems appeared to be the barrier properties of nickel/boron. Samples were coated with nickel/boron with no loss of line definition. Identical patterns etched on the polyimide substrate could not be coated with Ni/B without double imaging and/or repeated coating and stripping.

Analysis for Boron in Electroless Ni/B Deposits

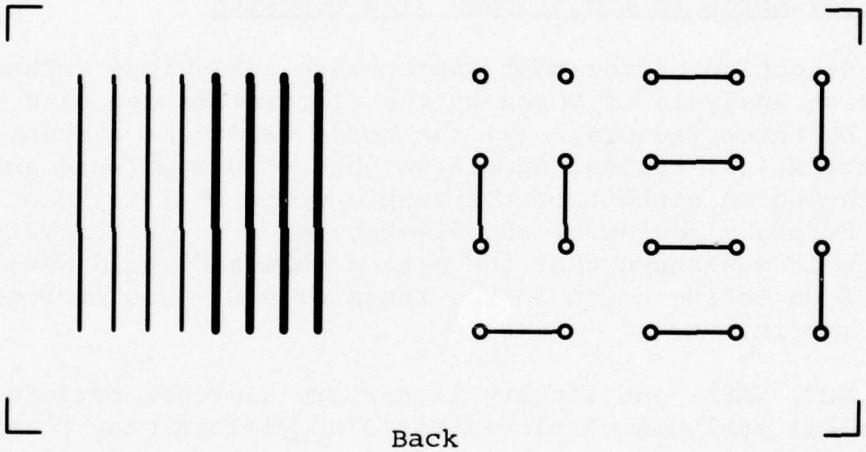
The selection of the most appropriate analytical method for the quantitative analysis of boron in the electroless deposits was constrained by three factors: (1) the boron was to be present in a nickel matrix, (2) typical sample weights of 0.5 mg were anticipated, and (3) the boron content of the sample would be less than 2% by weight. Before a review of the literature on boron analysis had been undertaken it was known that the method selected would have to be capable of detecting boron in the range of 0.0 - 5.0 micrograms from a nickel matrix.

The DCC, NASA, and library literature searches performed for the "chemical analysis of nickel borides" yielded many references but few were applicable to the analysis of boron. Singularly, the most useful reference has been "Analytical Chemistry of Boron," (Ref. #2). Of the numerous methods for the analysis of boron found in the above reference, the curcumin-oxalic acid colorimetric complex seemed best suited to our required sensitivities.

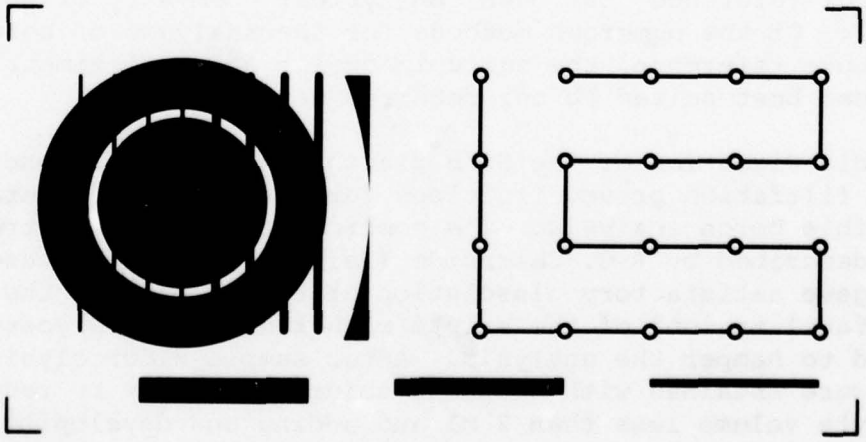
Acidic digestion of the Ni/B plating and subsequent neutralization and filtration proved fruitless for obtaining an accurate and reproducible boron analysis. The combination of the electrolysis method, described by R.C. Chirnside (Ref. #3), with the curcumin reagent gave satisfactory dissolution of the sample but the subsequent "stabilization" of the solute with the caustic glycerol solution was found to hamper the analysis. After sample electrolysis, tangible results were obtained with standard solutions simply by reducing the electrolyte volume less than 2 ml and adding and developing the



Front



Back



Composite

Figure 19. PCB Test Pattern

curcumin color. Using this procedure, however, a non-linear Beer's law relationship was generated. The only known variable among the standard solution was the reduced electrolyte volume, so following the volumetric reduction each standard sample was adjusted to a 2 ml volume with deionized water. This standard solution treatment yielded a linear Beer's law relationship (Figure 20) which was utilized for all subsequent analyses.

Electrolysis of the Ni/B plating on a copper substrate yielded quantitative boron results of approximately 20% of those reported by the plating solution manufacturers. Due to the copper substrate of these samples the electrolysis was not carried to complete sample solution, to avoid possible copper interferences, and it was hypothesized that the low boron analysis was most probably the result of the preferential electrolysis of the nickel over the nickel boride.

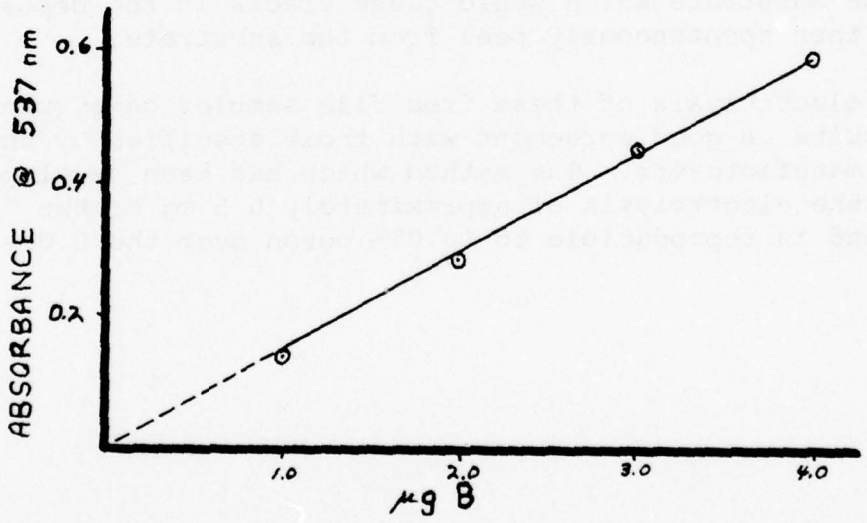


Figure 20. Linear Beer's law relationship between absorbance and boron content.

Chemical Analysis of Deposit

These difficulties encountered in obtaining meaningful analysis with partial solution of the sample necessitated the development of a process for preparing free films of the plating which could be completely electrolyzed. The problem was to deposit Ni/B on to a substrate with sufficient adhesion to prevent spontaneous flaking of the stressed deposit yet deposit to a thickness which would permit removal of "sheets" of the somewhat brittle material.

Sample Preparation

The method developed was to polish a piece of polyimide substrate to a high gloss with a water slurry of 1.0 micron alumina. This produced a high gloss water wettable surface which was then catalyzed in Shipley Catalyst 9F for 2 minutes followed by 5 minutes in Shipley activator 19. Following activation the specimens are allowed to dry in ambient air and then immersed in the Ni/B deposition solution. Continuous deposits of approximately 80 microinches were formed. The deposits were air dried. Film specimens were removed by simple flexure of the substrate which would cause cracks in the deposit. The deposits then spontaneously peel from the substrate.

The electrolysis of these free film samples gave quantitative boron results in good agreement with those specified by the plating solution manufacturers. The method which has been developed only requires the electrolysis of approximately 0.5 mg of the "free film" sample, and is reproducible to ±0.03% boron over the 0.0 - 1.5% range.

SECTION 5

TESTING PROGRAM/RESULTS - LEADS

High Temperature Aging

One hundred specimens of each thickness were aged at 200°C and 300°C in still air. Tables 6, 7, and 8 show the results after 168, 366 and 500 hours, respectively. Plating thickness of 50, 100 and 150 microinches, plated from a Shipley bath at 145 ± 5°F and 7.2 ± 0.1 pH, were tested. Ten gold plated lead frames (5 each at 200° and 300°C) were used for controls.

Visually all the specimens, except the 150 microinch specimen aged at 300°C, looked good. These specimens had a spotty discoloration from the first examination at 168 hours.

The solderability after the high temperature aging was reasonably good. As might be expected, the 300°C aging had a more adverse effect than the 200°C aging.

Time is a factor but a secondary factor compared to temperature. If we assume that the solderability is reduced because of surface reactions with the atmosphere then the rate of these reaction decreases with time.

In like manner the effects of plating thickness, above a minimum thickness, would appear to be minor. The 100 microinch specimen was only slightly superior to the 50 microinch specimen. This would go along with the idea that aging at these temperatures effects solderability because of surface reactions. These tests would indicate that the nickel boron deposits will retain their solderability under reasonable aging conditions.

Moisture Resistance

One hundred specimens of the three thickness were subjected to ten days moisture exposure per Mil-Std-883, Method 1004. Ten samples each of gold plated and ten plated lead frames were used as a control sample. All specimens were given a 90° bend around a 0.063 inch radius prior to exposure.

This is a ten day cyclic humidity test.

Visually the samples all looked good. There was only slight discoloration and no build up of corrosion products. Solderability of all specimens was poor. Neither RMA or RA flux was effective for solderability. The control samples retained their solderability. The nickel boron deposits can be made solderable by the activated cleaner used prior to plating or by dipping in a 25% hydrochloric acid solution. Obviously the heavy moisture puts a passivation film on the surface.

Long term storage of nickel boron deposits will require a moisture controlled atmosphere.

TABLE 6. AGING AT TEMPERATURE

Plating Thickness	Type Lead	Aging Temp.	Aging Time	Type Flux	Solderability
50μ in.	FP	200°C	168 hrs.	611	good
"	TO	"	"	"	good
100μ in.	FP	"	"	"	good
"	TO	"	"	"	fair (non wetted areas)
"	"	"	"	711	fair
150μ in.	FP	"	"	611	OK
50μ in.	FP	300°C	"	611	fair
"	"	"	"	711	good
"	TO	"	"	611	fair (non wetted areas)
"	"	"	"	"	"
100μ in.	FP	"	"	"	fair - good
"	"	"	"	711	good
"	TO	"	"	611	fair
"	"	"	"	711	fair - good
150μ in.	FP	"	"	611	fair
"	"	"	"	711	fair

Visually all specimens looked good except slight discoloration at 300°C for 158μ specimens.

TABLE 7. AGING AT TEMPERATURE

Plating Thickness	Type Lead	Aging Temp.	Aging Time	Type Flux	Solderability
50μ in.	FP	200°C	336	611	good
"	TO	"	"	"	fair
"	"	"	"	711	good
100μ in.	FP	"	"	611	good
"	TO	"	"	611	fair/good
150μ in.	FP	"	"	611	fair/good
50μ in.	FP	300°C	"	611	fair
"	"	"	"	711	fair/good
"	TO	"	"	611	poor
"	TO	"	"	711	fair
100μ in.	FP	"	"	611	fair/good
"	FP	"	"	711	good
"	TO	"	"	611	poor
"	"	"	"	711	fair
150μ in.	FP	"	"	611	fair/good
"	"	"	"	711	fair/good

Visually all specimens looked good except 150μ specimens at 300°C had some discoloration.

TABLE 8. AGING AT TEMPERATURE

Plating Thickness	Type Lead	Aging Temp.	Aging Time	Type Flux	Solderability
50 μ in.	FP	200°C	500 hrs.	611	fair
"	"	"	"	711	fair/good
"	TO	"	"	611	fair/good
"	"	"	"	711	fair/good
100 μ in.	FP	"	"	611	fair/good
"	"	"	"	711	good
"	TO	"	"	611	fair/good
"	"	"	"	711	good
150 μ in.	FP	"	"	611	good
50 μ in.	FP	300°C	"	611	fair
"	"	"	"	711	good
"	TO	"	"	611	fair
"	"	"	"	711	fair to good
100 μ in.	FP	"	"	611	fair
"	"	"	"	711	fair/good
"	TO	"	"	611	poor/fair
"	"	"	"	711	fair/good
150 μ in.	FP	"	"	611	poor to good
"	"	"	"	711	fair to good

Visually all specimens looked good except the 150μ ones at 300°C which had spotty discoloration.

Salt Spray Exposure

One hundred specimens of each thickness were subjected to 24 hours salt spray per MIL-STD-883, Method 1009.

Visually all specimens, including the gold plated control samples, showed evidence of base metal corrosion. The tin plated control samples had the best visual appearance but were heavily discolored.

None of the nickel boron deposits was solderable with either RMA or RA flux. The gold and tin control samples were solderable. The tin samples were best. Washing the nickel boron deposits in water with a mild detergent did not restore the solderability. The moisture apparently passivated the surface and the presence of the chloride ions did not reactivate it. The attack on the base metal indicated some porosity in the deposit including the gold deposits but not the flowed tin.

Again these tests would indicate the need to store nickel boron deposits in a moisture controlled atmosphere to preserve long term solderability.

Thermal Shock

Thirty six nickel boron plated flat pack frames were glass sealed in flat pack cases. These were leak tested and subjected to thermal shock per Mil-Std-883, Method 1011 (-64°C to 200°C).

No leaking occurred at any of the glass seals. No oxidation or surface treatment was given the deposits in the seal area. The presence of boron could well be a factor in producing a good seal.

Lead Fatigue

Thirty six T.O. can samples with each of the three plating thickness were soldered to two sided boards along with five gold and five tin plated control samples.

The boards were vibrated at resonance for 10^6 cycles at 5 g's with no failures. The test was repeated at 10 g's and again at 40 g and 70 g with no failure. In all 4×10^6 cycles were run with no failure. No cracking or peeling of the deposits or any cracks in the solder joint appeared. See Figure 26.

Conclusions

These extensive series of tests at three plating thicknesses show that the nickel boron deposits have good long term stability in air but that the air environment should be controlled for moisture if long term solderability is to be retained. Solder joints which will withstand extensive vibration, and reliable glass seals can be made.

Testing Program and Results Printed Circuits

A. Thermal Stress (Solder Float) per Mil-P-55640A, Para. 4.7.14 Boards were conditioned at 140°C ± 5°C for 1 hour. Boards were cooled to room temperature and then floated on an SN 63 solder bath maintained at 288°C ± 5°C for 10 seconds. After cooling to room temperature circuit continuity was checked and random holes were sectioned and examined. All specimens were acceptable. (See Figures 21, 22, and 23.)

Additional stress testing over and above that required: Sample boards with no pre-conditioning were fluxed and floated on SN 63 solder bath maintained at 288°C ± 5°C for 1 minute. No failures occurred.

B. Peel Strength per Mil-P-13949, para. 4.7.2.6 were performed on boards processes thru all plating solutions. Testing was performed on the etched peel test strips of .150 wide, .100 wide and .050 wide.

Results: Average peel strength per inch width

	.150 strip	.100 strip	.050 strip
As fabricated	10.75 ppi	12.50 ppi	10.40 ppi
After thermal Exposure	8.71 ppi	9.85 ppi	8.74 ppi

C. Moisture Resistance Mil-P-SS110 para. 4.9.8

All specimens passed

D. Insulation Resistance Mil-P-SS110 para. 4.9.4

All specimens passed

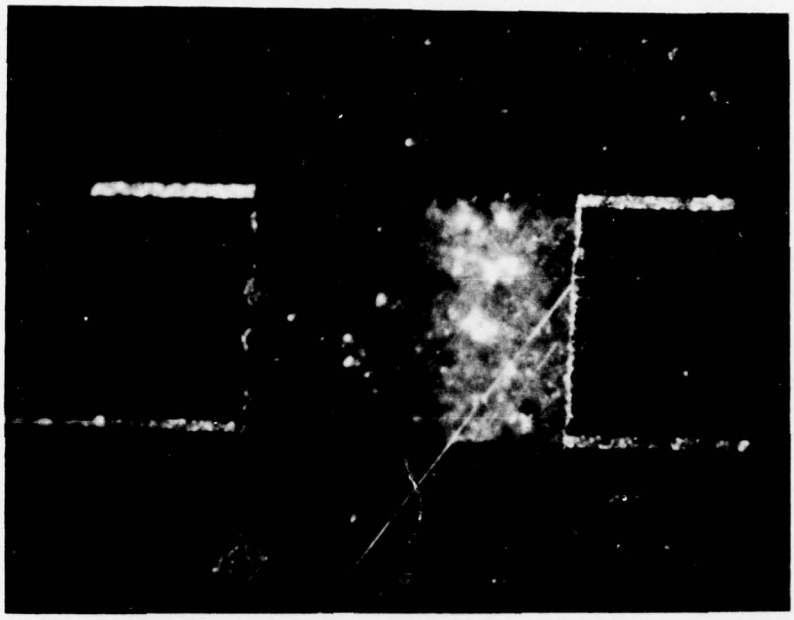


Figure 21. Section of as plated hole. Note thin electroless deposition in hole.

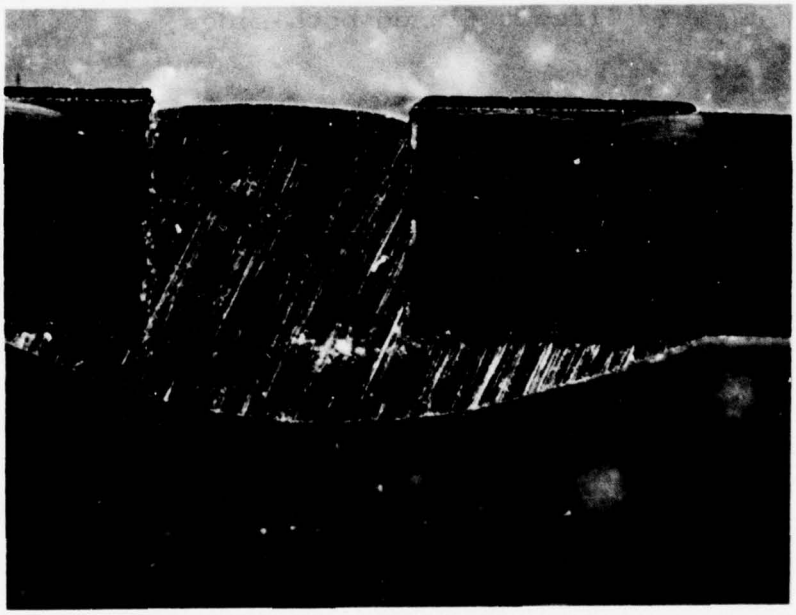


Figure 22. Section of hole after thermal stress. Circuit fluxed on bottom side only.

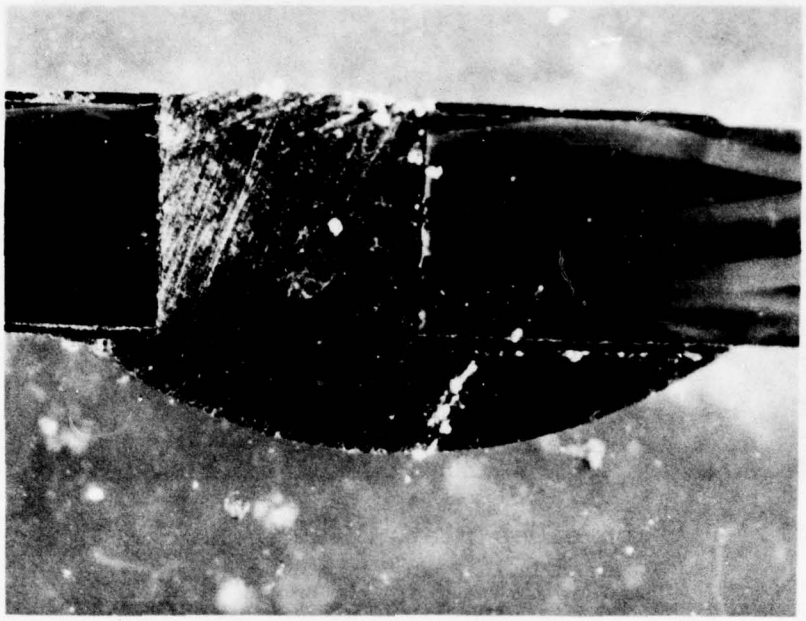


Figure 23. Section of hole after thermal stress. Circuit fluxed both sides.

E. Solderability - This parameter was evaluated by soldering methods normally used in production of PCB assemblies. Hand soldering and dip soldering with and without components on circuitry and large simulated ground planes was evaluated on a continual basis since the first PCB's were fabricated. Evaluation was performed on freshly made circuitry and on circuitry stored in open racks in uncontrolled lab environment up to 5 months. These methods were used, instead of the Mil-P-55110 pattern and fixture, to give a more accurate indication of potential production problems particularly on thru hole soldering and large ground plane wetting and delamination problems.

All soldering tests on PCB's were made using Alpha 611 Type RMA Resin Flux. This is the standard flux within Raytheon, and many other manufacturers, used when soldering electronic assemblies to Mil-Std-275.

No soldering difficulties were encountered. Ready solderability coupled with insolubility of the Ni/B deposit in solder are the most exciting properties found. A yellow/blue discoloration which developed upon storage required no special treatment. Such surfaces wetted as well as fresh deposits. Most striking is the wicking of solder up thru plated holes, with and without components. Standard tin/lead coated PCB's can give false indications in this test because, even with defects which prevent solder wicking up the hole the tin/lead coating will melt and give the appearance of solder flow. Solder wicked up the Ni/B holes. There was no evidence of outgassing when the circuits were kept in contact with the solder pot or soldering iron for periods of up to one minute. Upon removal of the circuitry from the solder pot the solder showed little tendency to flow back down the holes. These findings are most remarkable considering that the thru hole copper plating was done by electroless methods only and copper thickness was 150-200 microinches rather than the 1000 microinches which would be present in normal production holes.

Leads soldered into holes and onto fine lines were removed and reinstalled by hand soldering to simulate touch up operations. No limit was found to the number of times a joint could be made and remade. When the solder itself became dross-laden from repeated heating simple wicking and additional fresh solder returned the joint to acceptable conditions.

This abilitiy to solder and resolder, while due in the most part to the barrier property of the Ni/B deposit is further enhanced by the heat resistance of the polyimide material. No instances of circuit delamination were produced by soldering operations.

F. Salt fog per Mil-P-28809 para 4.8.6

Circuitry made by the "strike before etch" method exhibited significant corrosion of fine line circuitry. Circuitry made by the "strike after etch" method showed insignificant discoloration on massive areas only. See photomicrograph Figures 24 and 25.

G. Continuity per Mil-P-55640 para 4.7.8

All tests circuits passed

Testing beyond requirements - The current carrying capacity for the above test is calculated from the thickness (cross sectional area) of copper at the most restricted part of the circuitry.

The copper thickness in the holes was 150 microinches and the calculated current for test purposes was 0.6 amperes. It was decided to test the current carrying capacity to destruction of the circuitry. The circuit used was the series of 20 holes on the test pattern. Current was increased at the rate of 1 amp/minute. At the 6 amp level localized heating was visually evident as a growing discoloration along paths. Current was left at the 6 amp level for 12 minutes. The polyimide material charred substantially as evidenced by blackening thru the board. However, the circuit continued to function. After 12 minutes degradation appeared to stabilize and current was again increased at 1 amp/minute. As current level reached 9 amperes the circuit ceased functioning. Voltage level at 9 amperes was 2.5 volts. Only one hole of the 20 failed. Upon sectioning of the barrel of the hole from the pad of the annular ring, no delamination was found in any of the charred areas. Delamination did occur when the circuit was cut for sectioning.

Aside from the good current carrying capacity shown in indications are that Ni/B circuitry on Polyimide can be operated in temperature regims well above the limitations of soldered joints on copper.

I. Plated thru hole vertical sections:

All specimens were acceptable before and after stress tests.

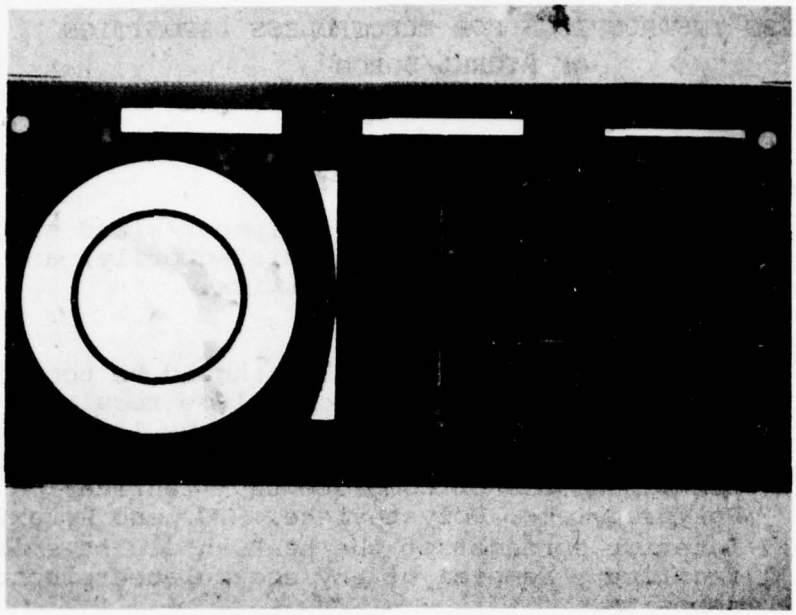


Figure 24. Salt spray nickel/boron strike prior to etching.

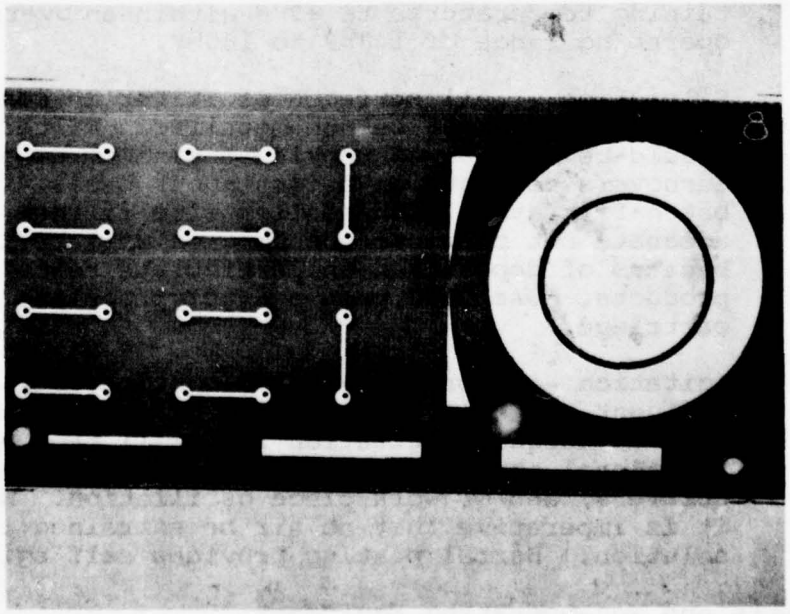


Figure 25. Salt spray exposure nickel/boron strike after etching.

SECTION 6

PROCESS INSTRUCTIONS FOR ELECTROLESS DEPOSITION
OF NICKEL/BORON

1.0 Solution Make-up: The following equipment/s and steps are required to make up and operate, satisfactorily, a nickel/boride (electroless) deposition solution.

1.1 Equipment

1.1.1 Deposition Tank - The tank should be non-metallic. Where, because of solution volume required, a metal tank must be used the tank must be lined. The lining must be pin hole free. Materials suitable for lining and/or complete tank fabrication are: Polypropylene, Polyethylene, PVC, and Pyrex. Interior surfaces of the tank should be smooth to facilitate removal of any accumulated electroless deposits.

1.1.2 Heater - The preferred heating system is the double boiler type. The solution must not be directly heated by immersion heaters or any sytem which results in subjecting the solution, or localized portions of the solution, to temperatures in excess of 175°F. Heating system must be capable of maintaining temperatures to $\pm 2^{\circ}F$ within an overall operating range of 140°F to 160°F.

1.1.3 Filtration - All surfaces of filter in contact with solution must be non-metallic. Filter capacity should be such as to provide a minimum of 5 tank turnovers per hour on a continuous basis. Daily batch filtration with smaller size filters is adequate but chemical consumption will be increased because of deposition on particulate reaction products. Use CPVC pump and polypropylene filter cartridge.

1.1.4 Agitation - A properly sized continuous filter with effluent properly directed and dispersed should provide adequate agitation for still tank operation. Additional agitation may be obtained with non-metallic stirrers, and/or work piece oscillation. However, it is imperative that no air be entrained in the solution. Barrel plating provides self agitation.

1.2 Materials and Non-Operating Equipment

1.2.1 Shipley NiPosit 468 A
1.2.2 Shipley NiPosit 468 M
1.2.3 Shipley NiPosit 468 B (1 year Shelf Life)

Materials and Non-Operating Equipment (continued)

1.2.4 Reagent Grade Ammonium Hydroxide (NH_4 OH)
1.2.5 Reagent Grade Sulfuric Acid (H_2 SO_4)
1.2.6 DeIonized Water 1 meg ohm minimum
1.2.7 pH Meter with Sensitivity of .05 pH units
1.2.8 Buffer Solution pH 7.0
1.2.9 Liquid measuring utensils (non-metallic) capable of measuring and dispensing specific volumes within 2%

1.3 Make-up - See Safe Handling Precautions 1.4

1.3.1 Fill tank with 5% solution of sulfuric acid in deionized water. Allow to stand and leach 24 hours minimum.

1.3.2 Drain leaching solution. Rinse tank with deionized water. Repeat rinsing until pH of rinse waste rises to a minimum of 6.0.

1.3.3 Place in tank 88.5% of final volume of water turn filter pump on. Then add, in sequence, allowing ample time for mixing between each item addition:

NiPosit 468 A	4.0% of final vol
NiPosit 468 M	5.0% " " "
NiPosit 468 B	2.5% " " "

*Note - Although the manufacturers literature allows wider operating ranges for temperature and pH than herein after specified the formability of the deposit in lead applications is directly related to deposit thickness, deposition rate and deposit composition. pH and temperature exhibit the greatest influence upon these parameters.

1.3.4 Adjust pH to 7.2 $\pm$ 0.1. Raise pH with additions of 25% Ammonium Hydroxide Solution in D.I. water. Lower pH with additions of 25% Sulfuric Acid in D.I. water.

1.3.5 Heat solution to the operating range of 145° - 150°F. Mark solution level on tank. Maintain this operating level at operating temperature with D.I. water. Tank must be at operating level and temperature when maintaining pH or with drawing samples for analysis.

1.4 Safe Handling Precautions

1.4.1 NiPosit 468 concentrate A & M contain nickel salts and have approx. respective pH values of 4.5 and 8.3. Repeated contact with skin may produce a dermatitis known as "Nickel Itch". Rubber gloves and eye protection should be used.

1.4.2 CAUTION! - NiPosit 468 B contains dimethylamine borane, a strong reducing agent. Its pH is approx. 8.5. Contact with acid can produce flammable toxic gas. Dried residues can be ignited by excessive heat or contact with acids and/or oxidizing agents. Material used to wipe up spills, and filter cartridges, must be rinsed thoroughly with water before disposal. Ingestion and/or contact with eyes, mucus membranes and/or broken skin can be harmful. Eye protection, rubber gloves and protective clothing should be worn.

1.4.3 The mixed plating (deposition) solution has hazard and toxicological properties of a Watts type bright nickel bath.

1.4.4 Ammonium hydroxide solution is caustic and evolves irritating toxic fumes. Rubber gloves and eye protection should be worn. Solutions should be handled only in adequately ventilated areas (Fume Hood etc).

1.4.5 Sulfuric acid solutions are caustic. Concentrated sulfuric acid is a vigorously dehydrating caustic. Admixture with water is accompanied by evolution of heat. Rubber gloves and eye protection must be worn. When diluting concentrated acid ALWAYS add acid to cold water. Add slowly and with thorough agitation to avoid vigorous evolution of heat.

2.0 Maintenance and Control

2.1 Periodic Analysis Frequency - Analysis Per 4.0

2.1.1 Analysis for metal content and DMAB content shall be preformed at the start of each shift, and calculated additions made.

2.1.2 Analysis for metal content shall be preformed, during daily operations each time ½ sq. ft. of work per gal. has been processed for 1 hour.

Example:
Tank Size 10 gal.
Work Load 2½ sq. ft.
Deposition Time ½ hour
Analyze after each 4 loads

For these periodic operational analysis the addition of DMAB concentrate required shall be considered equal to the metal concentrate addition calculated.

2.1.3 pH shall be measured and adjusted at the start at each shift and between each work load.

2.1.4 Additions and pH adjustments must not be made while work is in the tank.

2.1.5 Tank and solution shall be cooled (allowed to cool) during inoperative periods of more than one (1) eight (8) hour shift to minimize consumption of DMAB and build up of reaction products.

2.1.6 Weekly batch filtration into a spare tank is recommended to permit and facilitate removal of heavy particles and any deposition on vessel walls. The most serious effect of these particles and deposits is to greatly increase consumption of addition agents.

2.1.7 Maximum permissible work load shall be ½ sq. ft. surface area per gallon of solution.

3.0 Deposition on Kovar and Similar Iron/Nickel Alloys

3.1 Materials

3.1.1 Cleaner

Shipley AlChelate	1 part by volume
D.I. Water	6 parts by volume
Sodium Hydroxide	6 oz. per final gallon

Operate at 175-185°F

3.1.2 Pickle
Concentrated hydrochloric acid; Reagent Grade
operate at 175-185°F

3.2 Operation Sequence

3.2.1 Soak clean parts in cleaner (3.1.1) for 30 seconds minimum to 60 seconds maximum.

3.2.2 Rinse thoroughly in running water. *Note - Hot running water is most efficient, however cold water will suffice.

3.2.3 Pickle in HCL (3.1.2) until the first even coating of bubble forms on parts. Time 10-15 seconds.

3.2.4 Rinse in running cold water a minimum of 1 minute.

3.2.5 Immediately transfer work to deposition tank. Start timing when first gas bubbles are seen evolving from work. Deposition rate from the solution made up, operated and maintained per this instruction is 6 micro-inches per minute. Maximum thickness which will retain acceptable formability characteristics is 130 microinches.

3.2.6 When time/thickness has been attained rinse parts in cold running water for a minimum of 2 minutes.

3.2.7 Force dry parts with air not exceeding 130°F. Brown/blue stains on parts after drying indicate insufficient rinsing in step 3.2.6. Such stains may be removed by a 10 second dip in 30-50% hydrochloric acid solution followed by rinsing and drying per 3.2.6. *Note increase rinsing time if stains occur. Be sure water is less than 65°F.

4.0 Analysis, Quantitative, Wet Methods

4.1 Determination of Nickel Content (Concentrate A)

4.1.1 Reagents

4.1.1.1 Ammonium Hydroxide, Conc. Reagt. grade

4.1.1.2 0.05 M Ethylene-DiAmine-Tetra Acetic Acid, Sodium Salt (18.69 gms. per liter)

4.1.1.3 Murexide Indicator

4.1.2 Procedure

4.1.2.1 Pipette 10 ml. sample of bath into a 250 ml. Erlenmeyer flask

4.1.2.2 Add approx. 100 ml. D.I. water

4.1.2.3 Add 25 ml. concentrated Ammonium Hydroxide

4.1.2.4 Add ½ gm. murexide indicator

4.1.2.5 Titrate with 0.05 M EDTA to the end point color change of from rose color to violet.

4.1.3 Addition Calculation

(100 - % concentration) x gal. of tank x 1.9 ≐ ML NiPosit 468 A reg'd

4.2 Determination of DMAB Content (Concentrate B)

4.2.1 Reagents

*4.2.1.1 0.1M (0.6N) Potassium Iodate (KIO_3) solution with 3-5 ml. 25% NaOH per liter.

*4.2.1.2 10% Potassium Iodide (KI) solution with 3-5 ml. NaOH per liter.

4.2.1.3 4M Sulfuric Acid (H_2SO_4) solution

4.2.1.4 0.1M Sodium Thiosulfate ($Na_2S_2O_3$) solution.

4.2.1.5 Starch Indicator solution

*Discard KIO_3 and KI solutions if they become yellow in coloration.

4.2.2 Procedure

4.2.2.1 Pipette 10 ml. sample of bath into a 250 ml. erlenmeyer flask.

4.2.2.2 Pipette 5 ml. 0.1 M KIO_3 solution into flask.

4.2.2.3 Add 20 ml. 10% KI solution.

4.2.2.4 Add 20 ml. 4 M H_2SO_4 solution.

4.2.2.5 Swirl gently and wash down flask walls with 20-30 ml. D.I. water from wash bottle.

4.2.2.6 Titrate with 0.1 N Thiosulfate solution to a pale yellow color.

4.2.2.7 Add 4-5 ml. starch indicator solution.

4.2.2.8 Titrate with Thiosulfate solution to a clear end point.

4.2.3 Calculations

(ml KIO_3 x N KIO_3) -(ml. $Na_2S_2O_3$ x N $Na_2S_2O_3$) x 49.1 = % DMAB Conc.

4.2.4 Additions

(100-% DMAB) x 1.9 x gal. of tank = ml. NiPosit 468 B reg'd.

*Note - Make additions only when no work is in tank.

If Nickel or DMAB are either, or both, at less than 80% concentration make additions in multiple steps of no greater than 20% and allow 10 minutes agitation between successive additions.

**Note - Always add NiPosit 468 A first and allow thorough mixing before adding NiPosit 468 B.

5.0 Deposition on Copper and/or Copper Alloys

5.1 Materials

5.1.1 Cleaner
Shipley Al-Chelate per 3.1.1

5.1.2 Ammonium Persulfate etch - Solution life 48 hours

Ammonium Persulfate	1 lb.
Water	1 gal.
Sulfuric Acid	2 oz.

room temperature,
discard etch when it shows a light blue color

5.1.3 Pickle #1
10% Sulfuric Acid Solution

5.1.4 Pickle #2
5% Sulfuric Acid Solution

5.1.5 Sensitizer
A. 0.1 gm/gal $PdCl_2$ in 25% HCL Solution

or

B. 50% Solution of NiPosit 468 B in water

or

C. Auto-catalytic strip (see 5.2.9 C)

5.2 Procedure

5.2.1 Soak clean work in cleaner (5.1.1) for 1-3 minutes.

5.2.2 Rinse thoroughly in room temperature running water (1-2 minutes).

5.2.3 Immerse in persulfate etch (5.1.2) for a minimum of 5 seconds.

*Note-Time in etch will affect surface finish. 5-10 seconds should maintain any original brightness. Longer times produce progressively more haze and eventually a uniform matte surface. Where an ultra bright finish is required, etch may be diluted 50% with water.

5.2.4 Rinse thoroughly in cool or cold running water.

5.2.5 Immerse in pickle #1 (5.1.3) for 30 seconds to destroy any persulfate residues.

5.2.6 Rinse in cold running water. Inspect work for water breaks. Repeat 5.2.1 thru 5.2.6 until no water breaks are evident.

5.2.7 Immerse in pickle #2 (5.1.4). Work may be stored in pickle #2 for up to 48 hours prior to deposition. For immediate thru put a 15 second immersion is sufficient.

5.2.8 Rinse for a minimum of 1 minute in cold running water.

5.2.9 Sensitize: Copper and copper alloys are not auto-catalytic for nickel boron deposition. However, once deposition has started the reaction becomes auto-catalytic.

Deposition may be initiated in at least three (3) ways:

5.2.9 (continued)

A. Immerse part in $PdCl_2$ (5.1.5 A) solution for 3 to 5 seconds. Rinse in running cold water for a minimum of 3 minutes. Then place in plating solution.

or

B. Immerse part in dilute DMAB solution (5.1.5 B) for 10-20 seconds. Transfer work directly to plating solution.

*Note: with either method A or B it is suggested that a separate small tank of plating solution be used to initiate deposition. Once initial coverage has been completed work may be transferred directly to the final deposition bath.

or

C. Auto-catalytic strip (5.1.5 C). Any piece of material (Kovar, Copper, etc.) which has been previously plated with nickel boron will serve as an initiator of the deposition process. Immerse part in plating solution and contact it with the auto-catalytic strip. Within 10-15 seconds coverage will be complete and strip may be removed.

5.2.10 Deposition rate is 6 microinches per minute. Start timing when initial coverage is complete.

5.2.11 When thickness has been attained rinse in cold running water and dry per 3.2.6.

6.0 Deposition on Printed Circuitry (Polyimide Substrate)

*Note: To gain full advantage of the nickel boron the final deposit must be done, in the case of subtractive circuitry, after etching. With polyimide substrates complete additive processing is not recommended because the processing required for adhesion results in lower physical properties of the substrate - particularly in operating temperature range. It is recommended that PCB mfgr. start with thin copper laminate, approx. ¼ oz., and that the circuitry be pattern plated. Regardless of system used, the PCB's presented for Ni/B plating will have all circuits defined and isolated prior to final Ni/B plating.

6.1 Process

6.1.1 Solution make up shall be per 1.0.

6.1.1 (continued)

After make up solution shall be operated with a dummy work load of ½ sq. ft. per gal. for ½ hour. Solution shall be analyzed per 4.0 and the following operating conditions maintained.

Replenish Nickel to 100% concentration
Replenish DMAB to 95% concentration

Bath must be operated at a DMAB concentration not exceeding 95% to minimize auto-catalyzation of the polyimide.

6.1.2 Initiation of deposition may be accomplished as detailed in 5.2.9. However, due to the ease with which the substrate becomes auto-catalytic only 5.2.9 C is recommended.

A novel method has been found to be successful. Prior to final imaging the complete panel is flash plated with Ni/B. Then the pattern is imaged and etched with ferric chloride. After removal of imaging resist a light scrubbing with Ajax scouring powder followed by a 10 second immersion in pickle #2 (5.1.4) is all that is necessary to prepare for the final plating build up.

6.1.3 Deposition rate is 6 microinches per minute. When thickness has been attained rinse work thoroughly in cool/cold running water. Force dry work with cold air.

Procedure for Determination of Boron Content in Nickel/Boron Deposits

1.0 Equipment

- 1.0.1 Microbalance
- 1.0.2 Platinum crucible; 25 ml., Tall form
- 1.0.3 DC Power Supply; 40V, 3A
- 1.0.4 Spectrophotometer
- 1.0.5 Polyethylene Beakers - 50 ml.
- 1.0.6 Polyethylene Pipete
- 1.0.7 Water Bath
- 1.0.8 Volumetric Flask, 1 liter
- 1.0.9 Platinum Wire Electrode

1.1 Reagents

- 1.1.1 Sulfuric Acid, 0.02 N (Electrolyte)
- 1.1.2 Curcumin reagent per 2.1
- 1.1.3 Methanol
- 1.1.4 Hydrochloric Acid
- 1.1.5 Oxalic Acid
- 1.1.6 Mercury
- 1.1.7 DeIonized Water
- 1.1.8 Boric Acid
- 1.1.9 Curcumin

2.0 Preparation of Standard Solutions

2.1 Curcumin Reagent

2.1.1 To 700 ml of methanol (1.1.3) add 25 ml hydrochloric acid (1.1.4), 15 grams oxalic acid (1.1.5), 75 ml water (1.1.7) and 0.35 grams of curcumin.

2.1.2 Mix until all solids are dissolved.

2.1.3 Store reagent in polyethylene bottle.

2.2 Boric Acid Standard

2.2.1 Dissolve exactly 0.5715 grams of dry boric acid in deionized water in 1 liter volumetric flask. Dilute to 1 liter.

2.2.2 Pipette 10 ml of this solution into a 1 liter volumetric flask and dilute to 1 liter. This standard solution contains 1 microgram of boron per ml.

3.0 Determination Procedure

3.1 Electrolysis of Sample

3.1.1 Place 2 ml mercury (1.1.6) and 15 ml of 0.02 N sulfuric acid (1.1.1) into platinum crucible (1.0.2).

3.1.2 The crucible shall be attached to the negative (cathode) terminal of the power supply (1.0.3)

3.1.3 Weigh a free flake of the nickel boron deposit on the microbalance (Typical flake approx. 500 micrograms).

3.1.4 Attach weighed flake to positive (anodic) terminal of power supply.

3.1.5 Set power supply to 4 volts open circuit and immerse approx. ½ of the flake into the electrolyte taking precaution not to touch either the crucible or mercury pool.

3.1.6 Electrolyze until the immersed portion of the sample breaks free.

3.1.7 Remove stub of flake from attachment to anode lead. Rinse well with DI water. Dry and weigh. Sample weight is the original flake weight minus stub weight.

3.1.8 Continue electrolysis of sample, using platinum wire (1.0.9) as anode, for 15 minutes.

3.2 Analysis

3.2.1 Transfer the electrolyzed electrolyte to a 50 ml polyethylene beaker (1.0.5). Wash crucible and mercury pool 3 times with D.I. water. Transfer washings, quantitatively, to the polyethylene beaker.

3.2.2 Evaporate the contents of the beaker to dryness on the water bath operated at $58^{o} \pm 1^{o}C$.

3.2.3 To the dried residue add 2 ml deionized water and 5 ml of the prepared curcumin reagent (2.1.3).

3.2.4 Evaporate this solution, on the water bath at $58^{o} \pm 1^{o}C$, to dryness until no odor of hydrochloric acid can be detected.

3.2.5 To the dried residue add 50 ml of methanol.

3.2.6 Transfer the resulting solution to a 1 cm cuvette and measure absorbance on the spectrophotometer at 537 nanometers wavelength.

Note: A blank sample should be run with each analysis.

3.3 Calibration

3.3.1 Place 15 ml of 0.02 N sulfuric acid into each of 5 separate polyethylene beakers.

3.3.2 Add boric acid standard solution (2.2.2) to each beaker:

Beaker	Ml Standard
1	1
2	2
3	3
4	4
5	5

3.3.3 Perform all steps from 3.2.2 on.

3.3.4 Plot the absorbances obtained in step 3.2.6 for each concentration of boron. This plot is used to determine boron concentration, in micrograms, of the deposit sample.

SECTION 7

DISCUSSION OF PROCESSING PROBLEMS REQUIRING STUDY

A. Printed Circuit Fabrication

The following two problems encountered and worked around during this investigation must be solved to permit large scale fabrication of nickel/boron on polyimide printed circuits:

1) The property of the polyimide to become autocatalytic during the deposition must be overcome. Potential areas of investigation include etching media and/or post etching dips which will totally passivate the polyimide surface. The polyimide also exhibits this property in electroless copper deposition. The only positive observations were that as line-to-line spacing increased the onset of the phenomenontook longer to occur and that if it did not start during the first 10 minutes of deposition it did not start at all. More preplexing is the fact that the phenomena occurred randomly on identically processed circuits. While this was a laboratory scale investigation time constraints precluded individual processing of circuits and processing was scaled to a minimum batch size of six (6) circuits per chemical operation.

2) Initiation of Ni/B deposition onto copper was reduced to an individual panel problem during this investigation. A number of mechanical means to avoid individually contacting each panel with the ACS are obvious. However, a major drawback to large scale production of typical PCB is present in the etch removal of the thin Ni/B strike from the unimaged areas. The Ni/B strike dissolves at a much faster rate than the copper. After removal of the resist it was noted that the area of strike remaining on the .025 wide lines was a band approximately .010 wide. On a typical high density circuit with line width varying down to a minimum of .010 this strike would have been lost resulting in isolated areas requiring re-initiation of deposition with the for subsequent plating thickness build up. The solution to this problem requires the development of:

   a. A method of copper sensitization not subject to deterioration during etching which would promote deposit initiation in:

   b. A solution of reduced stability to promote initiation of deposit on a sensitized material low in the electromotive series yet not so unstable as to initiate deposition on:

c. Polyimide substrate desensitized to counteract problem #1.

In addition to these two major problems minor problems in the machining and drilling of polyimide were encountered. During the early investigations drilling was performed with a template and carbide drills, in the lab on an ordinary drill press. Hole quality was poor and burring and copper delamination was prevalent on the exit side of the hole. The larger "production" run of circuits for the test schedules was drilled on tape controlled equipment in our PCB shop. Hole quality was slightly improved but delamination of copper on the exit side of the holes caused a significant amount of scrap.

B. General Parameters to Optimize Assembly

1. Optimize welding schedules to take full advantage of the high temperature capabilities of the polyimide substrates. Establish trade-offs for cost of various deposition thickness to ease of welding.

2. High temperature solders for nickel-boron should be investigated. Such solders would enable use of circuitry at higher temperatures yet permit field repairs.

3. Porosity in the deposit, particularly the thinner deposits, was evinced in salt spray exposure. It would be desirable to investigate pre-deposition treatments and/or solution modifications which would permit thin plating without porosity.

4. Wire bonding schedules should be developed and a study made of possible intermetallic growths.

5. Heat treatment at temperatures up to 800^{o}C in vacuum or forming gas atmosphere should be studied. Successful heat treatment could permit the use of heavier pore-free deposits for increased corrosion resistance yet maintain both formability and solderability.

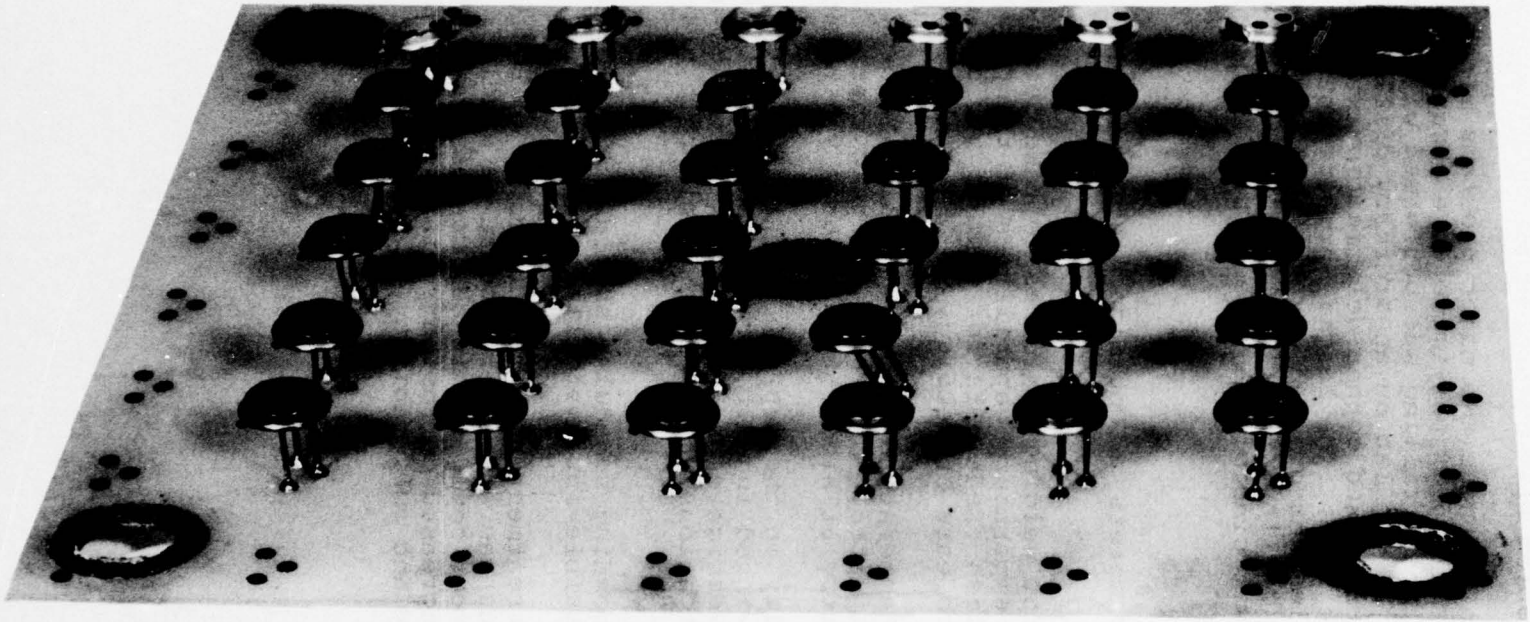


Figure 26. Vibration Test Fixture after completion of all Vibration Cycles

REFERENCES

1. Gorbunova, K.M., Ivanov, M.V., and Moiseev, V.P., J. Electrochem Society, 120, 613 (1973).

2. Nemodruk, A.A. and Karolova, Z.K., "Analytical Chemistry of Boron," Ann Arbor-Humphrey Science Publishers, London, 1969.

3. Chirnside, R.C., Cluley, H.J., and Proffitt, P.M.C., Analyst 82, 18, 1957.

*U.S.Government Printing Office: 1978 — 757-080/483