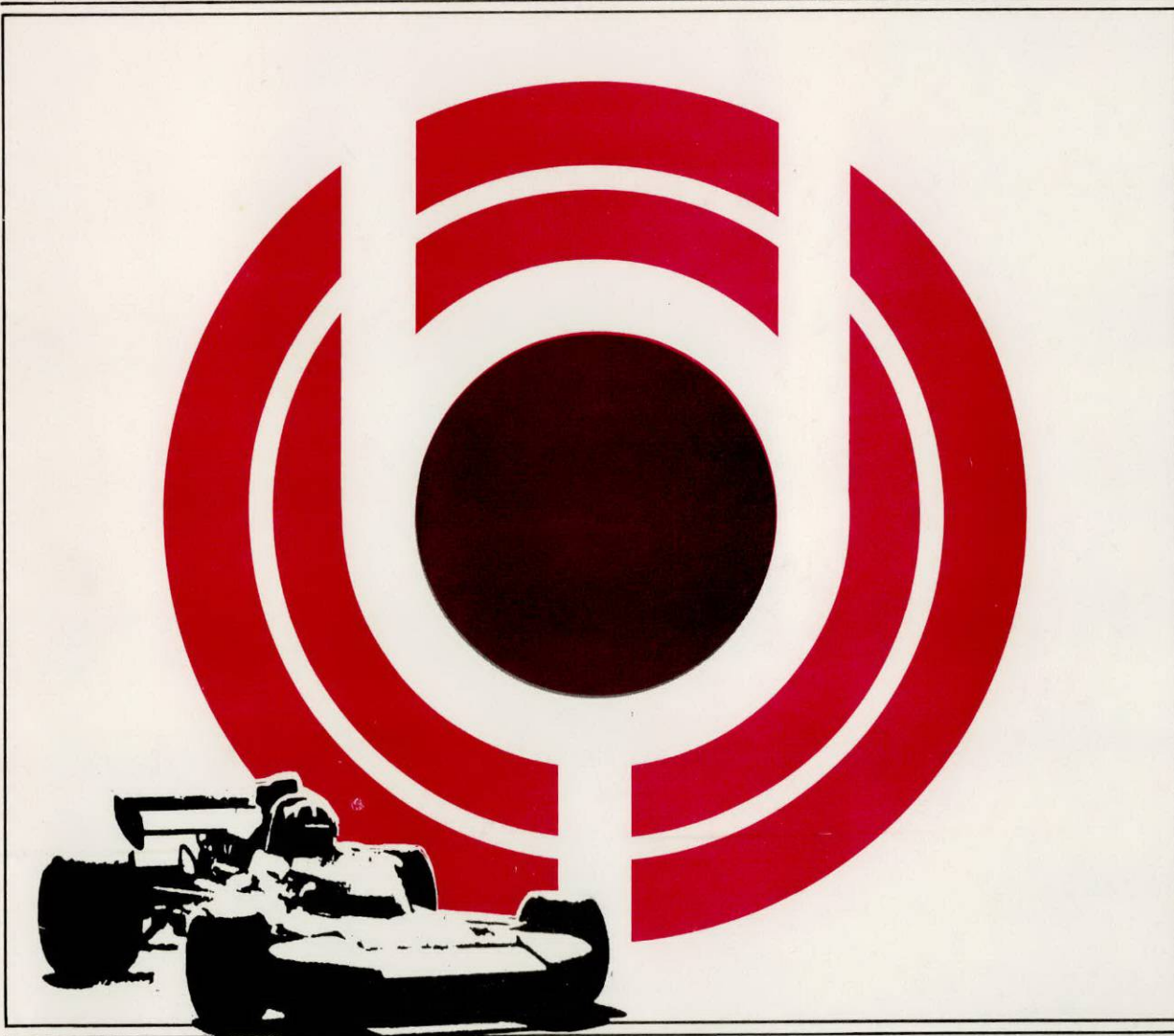




**American
Electroplaters'
Society
SUR/FIN '83**

**70th
Annual
Technical
Conference**



**June 27-30, 1983
Hyatt Regency Indianapolis and
The Indiana Convention - Exposition Center
Indianapolis, IN**

Session D - Electronics I

AMERICAN ELECTROPLATERS' SOCIETY, INC.
70TH ANNUAL TECHNICAL CONFERENCE - INDIANAPOLIS, IN
ELECTRONICS I
SESSION D

Page No.

Role of Cobalt in Acid Gold Plating.....D-1

Daniel Becker and Alan Blair, Engelhard Industries,
East Newark, NJ

Engineering Grade Thermoplastics & Additive Plating.....D-2

David C. Frisch, PCK Technology Div., Kollmorgen Corp.,
Melville, NY

Tensile Testing of Printed Circuit Board Elements.....D-3

M. Parente and Dr. Rolf Weil, Stevens Institute of
Technology, Hoboken, NJ and Dr. Milan Paunovic, PCK
Technology Div., Kollmorgen Corp., Melville, NY

Automatic PCB Plating Machinery.....D-4

Joseph N. Simonin, International Automated Systems, Inc.,
Corydon, IN

Gold Distribution on Printed Circuit Board Edge Connectors.....D-5

Dr. Paul Watson, Plessey Research (Caswell) Ltd., Towcester
Northants, U.K.

New Procedures for Predicting Solderability Performance
of Electroplated Tin Deposits.....D-6

William T. Hobson, Naval Avionics Center, Indianapolis, IN
and Bance F. Hom, Indy Electronics Inc., Manteca, CA

D-1

Electronics I Session D

Role of Cobalt in Acid Gold Plating

Daniel Becker and Alan Blair
Engelhard Industries
East Newark, NJ

Role of Cobalt in Acid Gold Plating Systems

by Alan Blair
Dan Becker
Engelhard Corporation
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Introduction

The role of cobalt in acid hard gold plating systems has been the object of considerable study since they were first introduced in the late 1950's.¹

The introduction of these processes marked the most significant change in the technique of electrodepositing gold since Wright and Elkington's work around 1840.²

Gold's physical and chemical properties make it an ideal material for certain electronic uses, particularly in its electroplated form. Its electrical and corrosion resistant properties were augmented by wear resistance when transition metals, such as cobalt, were co-deposited at levels of 0.1-0.3% in deposit. This codeposition causes spectacular changes in deposit character and electrolyte performance. Deposits are transformed from dull, equi-axed or columnar structures into bright, laminar ones and cathode efficiency is significantly decreased, becoming much more current density dependent.

Analysis of these deposits soon revealed that other elements, such as carbon, were codeposited with the transition metal, and so-called "polymer" was isolated.³

Carbon inclusions were determined to have emanated from the cyanide ligand in potassium gold cyanide and were found to be located near cobalt inclusions within the deposit⁴. Eisenmann⁵ suggested the presence of cobalt cyanoaurate in these deposits and other workers,^{6, 7, 8} have studied this possibility more closely. The hypotheses presented appear to explain both the inclusion levels of the various elements involved and the modification of grain growth.

On a more practical plane, studies have been performed to establish the influence of the chemical form in which cobalt is introduced to the electrolyte and the ultimate influence this has on the deposit.⁹

The object of this paper is to extend this last mentioned work and to present a more complete illustration of this chemical influence within a simple citrate system.

Experimental

Previous experiments⁹ have indicated that cobalt, when introduced to a citrate-based electrolyte, will produce hard deposits unless the cobalt complex used has a very high stability constant (e.g., $K_3\text{Co}(\text{CN})_6$; $K_1 = 10^{-32}$).¹⁰

It was decided to investigate the influence of cobalt complex and its concentration on cathode efficiency, cobalt in deposit, and deposit microhardness.

The electrolyte used throughout was:

Gold as potassium gold cyanide	8.0 g/l
Potassium citrate	100 g/l
Citric acid	76 g/l
pH	4.2
Temperature	35°C
Current density	10 A/ft ²

Cobalt was introduced as either the sulfate, cyanide ($\text{Co}(\text{CN})_2$), cyanoaurate or as a proprietary complex. Deposits containing up to 0.2% by weight cobalt were aimed for and the influence of cobalt concentration in solution is presented in Tables 1, 2, and 3 and on Figures 1, 2, and 3.

It should be noted that complex D, potassium cobaltous trisauricyanide, is only sparingly soluble in water, however, it dissolves slowly in an electrolyte. It must be assumed that a chemical change occurs under these conditions and that cobalt is present as citrate, cyanide, and a low concentration of potassium cyanauroate.

Results

As expected, cobalt concentration in solution influences cobalt in deposit much more when the complex is weak. Stronger complexes can be used over a much larger concentration without significantly changing deposit composition. Conversely, cathode efficiency remains almost unchanged by cobalt concentration in solution for stronger complexes. Naturally, this means that cathode efficiency is generally higher at low concentrations of weak complexes. When cobalt concentration is kept constant, other variables such as current density, solution pH, and temperature all influence codeposition of cobalt and cathode efficiency to a greater degree with a weak cobalt complex.

Deposit microhardness increases as cobalt concentration is increased, in line with higher deposit levels of cobalt. Again, the trend is less marked for stronger cobalt complexes than for weaker ones. Since all the deposits are of a similar nature, it is possible to apply a general comment - as deposit microhardness increases, ductility decreases. It is not safe to assume that wear resistance improves with harder deposits since the type of wear can change (adhesive wear versus abrasive wear). Much work has already been published on testing this property of gold deposits.¹¹

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Table 1
% Cobalt Codeposited Vs. Co in Solution

<u>Cobalt</u>	<u>% Codeposit</u>	<u>PPM Co</u>
<u>Proprietary</u>	0.12	100
	0.16	200
	0.19	400
	0.31	800
	0.33	1000
	0.40	1500
<u>Cobalt Sulfate</u>	0.05	16
	0.09	32
	0.13	64
	0.16	100
	0.20	125
<u>Cobalt Cyanide</u>	0.07	50
	0.11	100
	0.14	150
	0.16	300
<u>K Co(Au(CN)₂)₃</u>	0.09	50
	0.10	100
	0.12	150
	0.14	200
	0.16	300

Table 2
Cathode Efficiency Vs. Co in Solution

<u>Cobalt</u>	<u>PPM Co</u>	<u>% Efficiency</u>
<u>Proprietary</u>	100	46
	200	50
	400	47
	800	46
	1000	47
	1500	40
<u>Cobalt Sulfate</u>	16	71
	32	60
	64	52
	100	47
	125	43
<u>Cobalt Cyanide</u>	50	67
	100	58
	150	52
	300	46
<u>K Co(Au(CN)₂)₃</u>	50	63
	100	60
	150	60
	200	61
	300	49

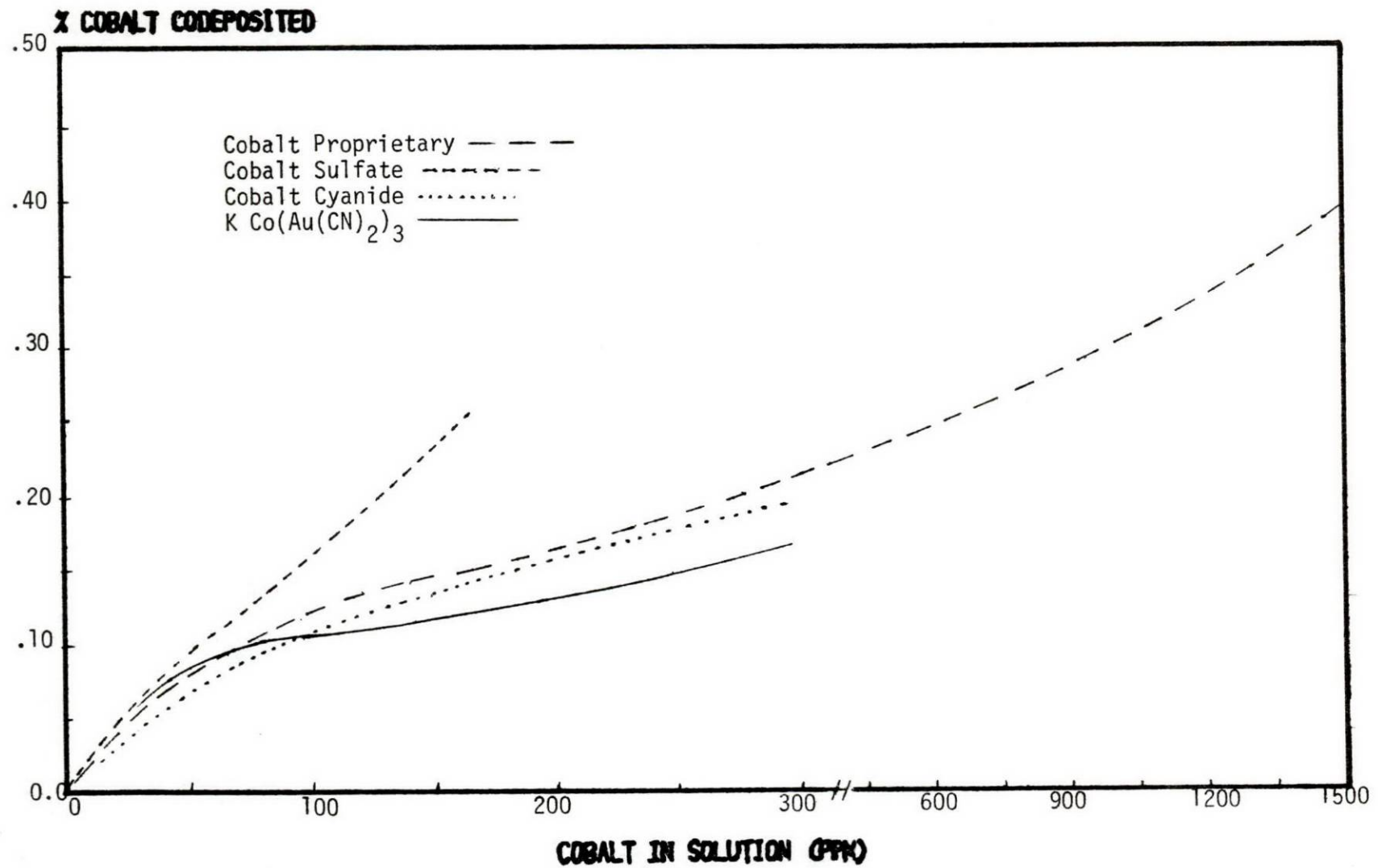
Table 3

Knoop Hardness vs. % Co in Deposit

<u>Cobalt</u>	<u>Knoop Hardness</u>	<u>% Co in Deposit</u>
Proprietary	130	0.12
	135	0.16
	138	0.19
	156	0.31
	160	0.33
	180	0.40
<u>Cobalt Sulfate</u>	141	0.05
	175	0.09
	188	0.13
	187	0.16
	195	0.20
<u>Cobalt Cyanide</u>	143	0.07
	152	0.11
	162	0.14
	181	0.16
<u>K Co(Au(CN)₂)₃</u>	138	0.09
	156	0.10
	160	0.12
	157	0.14
	168	0.16

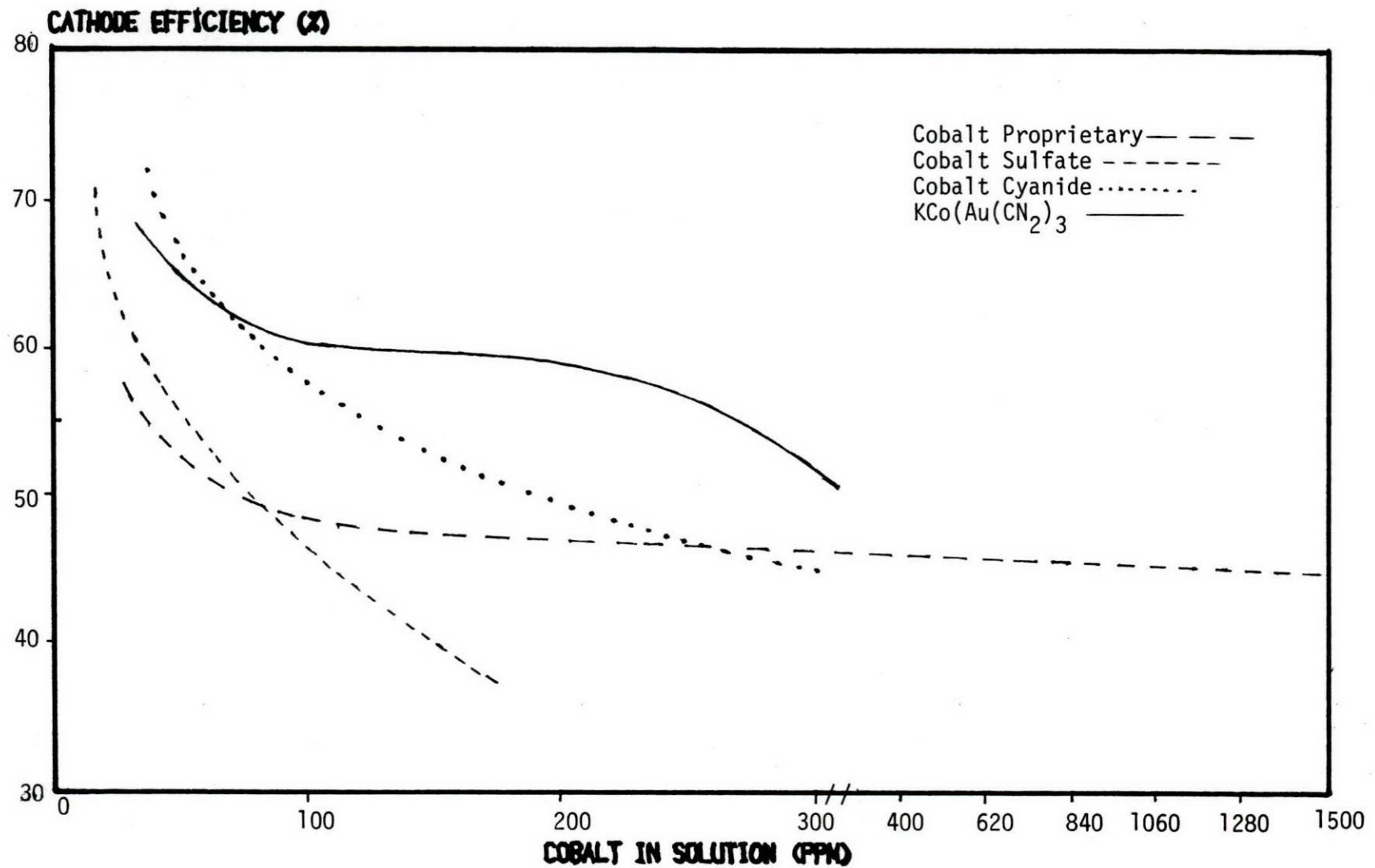
% CO CODEPOSITED VS. Co IN SOL'N

Figure 1



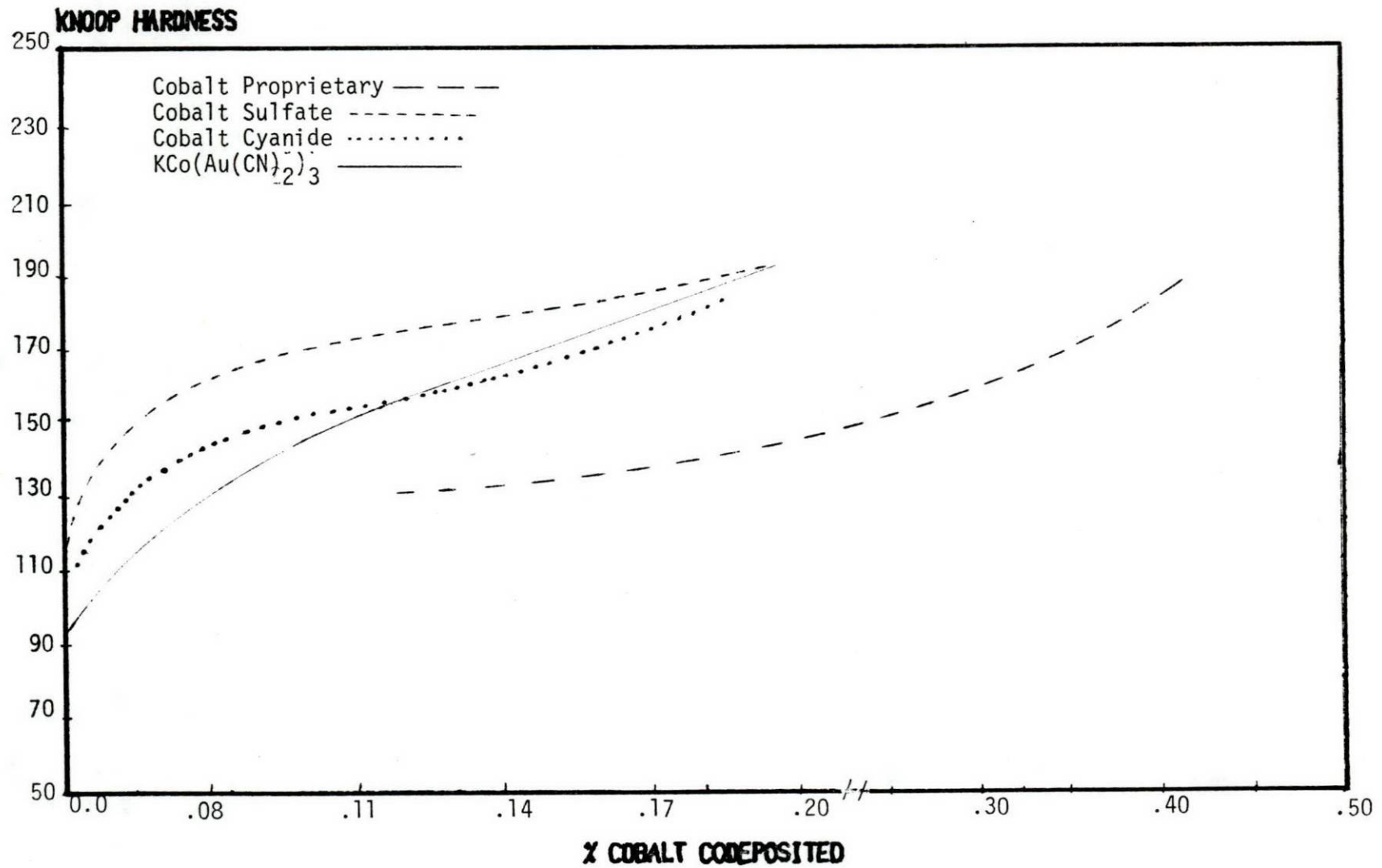
CATHODE EFF. VS. Co IN SOL'N

Figure 2



KNOOP HARDNESS VS. % Co IN DEP

Figure 3



Electronics I Session D

Engineering Grade Thermoplastics & Additive Plating

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ENGINEERING GRADE THERMOPLASTICS & ADDITIVE PLATING

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The primary support base for essentially 100% of all printed wiring boards for almost thirty years has been thermosetting resin-laminated plastic sheets. Regardless of the resin chemistry; i.e. phenolic epoxy or polyester, the common link between all these materials is the use of reinforcement fabrics such as cellulose paper or woven glass cloth and their batch processing steps of resin impregnation, slitting, stacking, laminating and final trimming. All told, there are at least five discrete operations required to fabricate a "C"-staged rigid sheet or panel.

As an alternative approach to batch techniques, continuous processes have been considered as potential methods to improve on the efficiency and economy of press laminating. However, these concepts have had limited commercial success.

Recent break-throughs in the development of engineering grade, high temperature thermoplastic resins, suitable for printed circuit applications, have generated considerable interest because of their non-lamination manufacturing methods. Being hot melt processable resins, thermoplastic sheets may be produced by either "in-line" continuous extrusion or injection molding techniques. Regardless of the process used, modest to significant price reductions may be realized over conventional premium grade laminate materials. For applications requiring dielectric properties that are superior to that of epoxy-glass laminates but sensitive to the higher costs of PTFE-glass RF or microwave substrates, the low loss characteristics of selected speciality thermoplastics offer performance at economical savings. Also for products requiring base substrates thermally stable over a broad temperature range, high temperature thermoplastics again present alternatives to the more costly polyimide-glass type laminates.

Finally, in addition to the economic benefits realized in manufacturing thermoplastic substrates, their inherent unclad "As Fabricated" construction is ideally suited for PC metalizing by semi-additive plating methods. Fine line, high density patterns with reliable plated through hole interconnections can be produced at additional savings as compared to the subtractive or conventional approach. Semi-additive circuits differ from their subtractive counterparts in a variety of features including; minimal to no undercuts of conductor traces, rework capability during fabrication (recycle drop-outs) and lower manufacturing costs due to reduced

consumption of plating and etching chemicals.

Materials

Two thermoplastic resin systems are commercially available that meet the general criteria for printed wiring board fabrication including:

- Compatibility with PTH "additive" chemistry
- Machinable on existing equipment
- Plating adhesion $\geq$ 6.0 lbs/inch
- Wave and hand solderable

Of the two materials, the first to be available was UDEL® Polysulfone, marketed by Union Carbide Corporation (PSF). Standard grades being made are: Pl700 and Pl720 (unfilled) and P8000 (mineral filler).

The second material to date proven suitable is available from General Electric Co. under the trade name ULTEM® Polyetherimide (PEI). As is the case with PSF resins, ULTEM is offered in an unfilled grade (1000) and 20% glass reinforced alternative (2200).

Both of these materials are classified under the general heading of amorphous thermoplastics. This means that they have no crystalline form. They do not have a melting point. Rather they gradually become softer and softer until, finally, they are recognized as being a liquid. Their characteristics allow them to be processed on conventional extrusion equipment.

Because of their improved thermal characteristics, the PSF and PEI resins are known as "high temperature" engineering grade thermoplastics as their heat deflection (HDT), and glass transition (Tg) temperatures are far greater than for conventional thermoplastic resin materials like polycarbonate and ABS.

It is these features that result in the ability of UDEL and ULTEM plated products being suitable for mass soldering procedures.

Furthermore, the Underwriters Laboratories Inc. has extended "Recognition" ratings to these materials for maximum operating temperatures in excess of that assigned to the more commonly used circuitry substrates such as epoxy-glass (FR-4). Table I shows the thermal ratings for the UDEL and ULTEM materials.

An added performance benefit of the high Tg values is the low thermal expansion coefficient at elevated temperatures. As shown in Figure A, their Z-axis expansion is lower than for

conventional epoxy-glass and PTFE-glass laminates. Plated-through hole reliability is enhanced by the reduced change in thickness versus temperature profiles of PSF and PEI.

The key electrical properties for printed wiring board applications include excellent volume and surface resistivities, as well as a low dissipation factor and stable dielectric constant over a broad frequency and temperature range, as shown in Figures B, C and D.

Although not directly interchangeable with conventional microwave substrates, both the UDEL and ULTEM offer improved characteristics over higher loss materials like epoxy-glass (FR-4) or polyimide-glass. Furthermore, where design proves compatible with PSF and PEI, significant economic benefits may be realized. Cost savings become particularly important with higher volume commercial and consumer products.

The economic factors for considering polysulfone and polyetherimide become even more attractive when comparing differences between clad and unclad sheeting. Because semi-additive plating does not require a pre-clad base material, "as extruded" sheet products are used, thereby eliminating secondary "off-line" lamination processes which add unwarranted additional cost to bare substrates.

As shown in Table II, PSF and PEI offer economic advantages over conventional PTFE-glass, while approaching FR-4 prices.

Manufacturing Thermoplastic Sheets

The reason for the economy of engineering thermoplastics is the extrusion processes. Unlike laminates which are fabricated in batch quantities, extrusion is a continuous process wherein resin, supplied as a solid plastic pellet, is heated in a chamber to its melt viscosity (600°F to 800°F), forced through a narrow opening or gap in a die in continuous film or sheet until finally being sheared into full-sized sheets or panels and stacked for delivery. A complete extrusion line is illustrated in Figure E.

Tight tolerancing is routinely achieved on the order of ± 0.003 "; however, ± 0.002 " is obtainable. Custom extruders such as Westlake Plastics, Lenni, Pennsylvania and Rowland Inc., Berlin, Ct., have production experience in processing high quality UDEL and ULTEM sheets.

Semi-Additive

Plating directly onto "as fabricated" thermoplastic sheets has been routinely accomplished by semi-additive techniques. With proper pre-plate chemical treatment, conventional plating

catalysts and electroless copper (or nickel) platings adhere with great tenacity. Finally, after etching, peel strengths commonly exceed quoted 6 lbs/inch minimum values, averaging 10 to 12 lbs. on both the surface and in the hole walls.

The essential step to achieving strong plating-to-substrate is in the "adhesion promotion" (surface treatment) chemistry which creates a microporous topography on the surface and in the drilled holes, providing anchors for subsequent electroless metallization.

Process

The semi-additive process is composed of a sequence of manufacturing operations starting with the selection of the appropriate base material, proceeding through surface pretreatment, electroless and electrolytic plating and concluding with a quick etch of the background electroless copper.

The following is the entire manufacturing process from the raw material stage to the finished product. Each of the individual manufacturing steps will be highlighted to detail their procedure.

- Stress Relief - extruded materials require heat treatment to relieve internal stresses induced during their fabrication. This is normally performed by baking the sheets in a convection oven at the temperatures at or just below the resin's heat deflection temperature (HDT). Typical baking times of 3 to 6 hours are recommended by the resin suppliers depending upon the sheet thickness. Furthermore, fixturing between metal platens is suggested to avoid heat-induced distortion. An alternative to this lengthy procedure has been developed wherein the extruded unclad sheets are exposed to either an infra-red or microwave radiation (Frisch et.al., Patent No. 4,339,303).^{*} This new technique eliminates both the need for elaborate fixtures while shortening exposure times to between 15 to 20 minutes.
- Form Pattern and Pilot Holes - thermoplastics require more attention to avoid overheating. Heat dissipating entry and back-up foil has been found to yield acceptable results with good quality, smear and burr-free holes. Figure F illustrates a typical drilled hole in PSF sheet.

Subsequent to drilling, the sheets are resubjected to the stress relief process. This step is essential since the materials will be exposed to stress cracking agents during the following adhesion pretreatment steps.

^{*} Assignee is Kollmorgen Technology Corporation

- Adhesion Promotion and Copper Reduction - to ensure a strong bond between the substrate and the electrolessly deposited copper, it is necessary to pre-treat in an oxidizing solution. This step is commonly referred to as "Adhesion Promotion, Pretreatment or Conditioning". The oxidizing agent is an acidic chrome solution.

The Adhesion Promotion process sequence encompasses:

Solvent Swell
Conditioner
Acid Predip
Adhesion Promoter
Dragout Rinse
Neutralization
Water Rinse

In-process quality control testing of a chemical and topographical nature ensures the reliability of the process. Examples of an adhesion promoted ULTEM substrate are shown in the photomicrographs of Figures G, H, and I. Hole walls replicate the surface topography by virtue of the homogeneous nature of the extruded substrates. Figure J illustrates a UDEL Polysulfone adhesion promoted drilled hole. The microporous (etched) texture is uniform throughout the hole wall as shown in the SEM photograph of Figure K at 700X magnification.

The panel is then catalyzed by depositing either a noble metal, usually palladium, or a non-noble metal complex on the surface and on the hole walls. This step is common to conventional (subtractive) circuit board manufacture.

The final step in this sequence is to deposit a micron thin layer of electroless copper on the surface and in the holes. The copper should be thick enough to withstand subsequent imaging and plating operations. Typically, 25 millionths to 100 millionths of an inch are deposited.

Copper reduction consists of the following steps:

Cleaner Conditioner
Activate and Rinse
Accelerate and Rinse
Electroless Copper

- Screen or Photoprint Plating Resist - The methods, materials and equipment required in this step are common with subtractive circuit manufacture. However, these thermoplastics are attacked by chlorinated hydrocarbons; consequently, semi-aqueous or full-aqueous resists are recommended in lieu of methylene chloride strippable products.

- Electroplated Copper - A 10% thicker plating deposit is advised if subsequent metal etch resists are not used.
- Optional Overplates - If required, overplating of tin-lead or nickel-gold can be used; however, a copper-only board may be manufactured without plating a metal etch resist.

The following illustrates the relationship between the total build-up of copper on a circuit conductor and the background electroless flash that has to be etched.

	<u>Surface</u>	<u>Background</u>	<u>Ratio (S/B)</u>
Conventional 1 oz.	2.7 mil	1.4 mil	1.92
Conventional ½ oz.	2.0 mil	0.7 mil	2.84
Semi-Additive (unclad)	1.3 mil	0.1 mil	13.00

The higher comparative thickness ratio of semi-additive permits the elimination of overplate etch resists while preserving the integrity of plated conductors and holes.

- Strip Plating Resist - The equipment-stripping mediums and procedures are identical to the subtractive process. Remember, semi-aqueous and fully-aqueous resists are highly recommended.
- Quick Etch of Copper Flash - The thin background electroless copper only requires a "quick etch", thereby reducing the cost and quantity of etchants with increased through-puts. Etching a maximum of 0.1 mils produces no observable undercut of the conductors, resulting in accurate fine line patterns.

A typical plated-through hole interconnection is shown topographically in Figure "L" and cross-sectionally in Figure "M".

Final secondary operations such as solder masking, nickel-gold plated contact fingers and nomenclature (legend) markings are compatible with PSF and PEI. Thermally-cured masks such as PC-501, as well as UV curable systems, have been used to produce semi-additive thermoplastic boards with excellent results.

Physical Properties

In-house quality control, independent laboratory and customer testing has shown semi-additive thermoplastic circuits to be of good quality. To date, several environmental evaluation tests have been performed on PSF, grade P1720. This program and its results were reported on at the Fall 1981 IPC meeting in Dallas, Texas (IPC Technical Paper TP-382).

Essentially, the test boards passed extremes of cycling temperature, thermal shock, hot oil immersion, thermal aging and plated through hole bond strength retention. Similar testing of ULTEM 1000 circuits is planned.

Additionally, PCK has been granted Underwriters Laboratories printed wiring board process "Recognition" on UDEL Polysulfone grades P1700 and P1720 (reference: file #E-76278) as follows:

Minimum Line Width: 0.010"

Maximum Unpierced Area:

P1700-2.0 inch dia. @245°C/5 secs.
0.5 inch dia. @260°C/5 secs.

P1720-2.0 inch dia. @260°C/5 secs.

Maximum Operating Temperature - 140°C

Minimum Thickness: 0.060"

Submission of the ULTEM PEI is now in process with similar ratings anticipated.

Soldering Recommendations

Since the processing of thermoplastic extruded additive circuits is in its infancy, experience relating thereto is being acquired at a rapid rate. PSF and PEI are known to be attacked by chlorinated hydrocarbons, aromatic hydrocarbons, some alcohols and highly polar materials. Also, non-ionic surfactants should be avoided. Since these are present in some commercial fluxes and aqueous cleaners, formulated products should be evaluated carefully and suppliers' literature consulted before using such products.

Experience has shown Alpha Metals Inc. Type OA (organic acid) water fluxes are compatible with both PSF and PEI. Alpha types 709 and 2883 have produced excellent results at pot temperatures ranging from 460°F to 500°F, with line speeds ranging from 10 to 20 FPM. For applications requiring Freon post cleaning, Alpha Type 881 yielded comparable performance to the water soluble materials. Fully activated rosin fluxes (Type RA) are suitable; however, they tend to lack sufficient activity for soldering at slightly reduced pot temperatures and increased line speeds associated with the non-glass filled thermoplastic grades. Super activated rosin fluxes such as Alpha RSA 942 may be considered in certain applications.

In addition, experience has shown that adequate pre-heating is vital to assure complete removal of all flux vehicles prior to exposure in the molten solder. Odd shaped geometrics or large boards may require some degree of stiffening of support as part of the transport mechanism to avoid sag while passing over the wave.

Conclusion

Semi-additive thermoplastic circuits can offer performance advantages for a variety of product applications. These benefits become even more significant when economic factors are taken into consideration. Although the techniques for producing printed wiring boards on extruded or injection molded substrates is relatively new, the semi-additive technology is well established with over fifteen years of production history on unclad laminate base substrates.

The development of UDEL Polysulfone and ULTEM Polyether-imide materials with semi-additive circuit plating will result in a greater market penetration of fine line, high resolution circuit boards.

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TABLE I

THERMAL PROPERTIES OF PSF & PEI				
Property	PSF	Unreinforced PEI	20% G.R. PEI	FR-4
Heat Deflection (HDT) @ 264 psi	174°C	200°C	209°C	—
Glass Transistion (Tg)	190°C	217°C	217°C	120°C
U.L. Max. Temperature	150°C	170°C	170°C	125°C

TABLE II

COST COMPARISON (\$/FT²) for .060" MATERIAL	
Material	Cost
Epoxy-glass (1/1-FR-4)	\$2.40 (average)
Polysulfone (1/1-Udel)	\$14 to \$18
Polysulfone, UNCLAD	\$2.10 to \$3.40*
Polyetherimide, (1/1-Ultem)	\$16 to \$20 (est.)
Polyetherimide, UNCLAD	\$2.60 to \$4.00*
PTFE-Glass (1/1)	\$25 to \$35
*In medium volumes, Westlake Plastics	

Z-AXIS EXPANSION OF UNREINFORCED PSF AND PEI vs OTHER SUBSTRATES

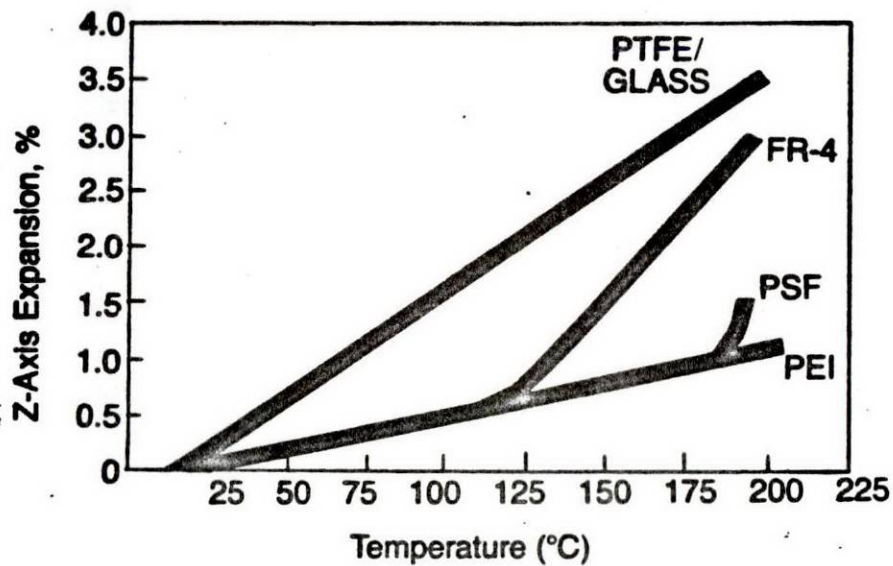


Figure A

ELECTRICAL INSULATION OF UNREINFORCED PSF/PEI vs OTHER SUBSTRATES

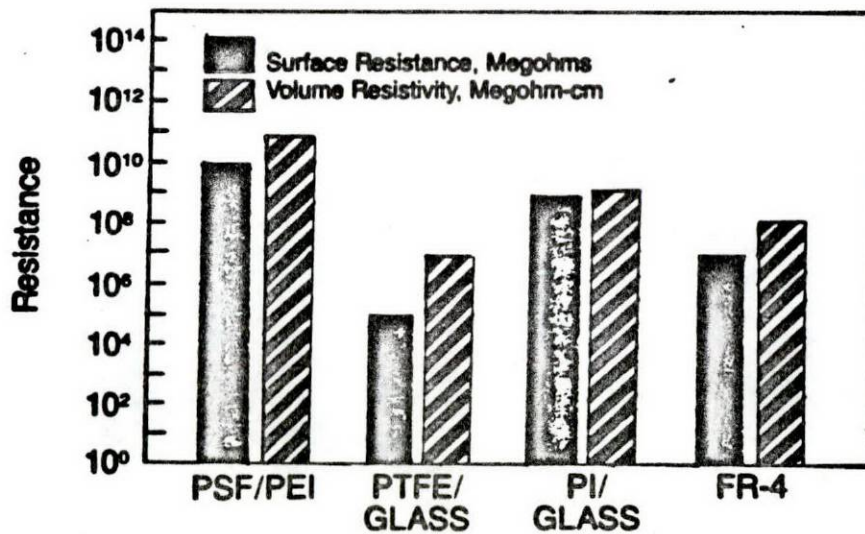


Figure B

**DIELECTRIC CONSTANT OF
UNREINFORCED PSF/PEI vs FREQUENCY, AT 50% RH**

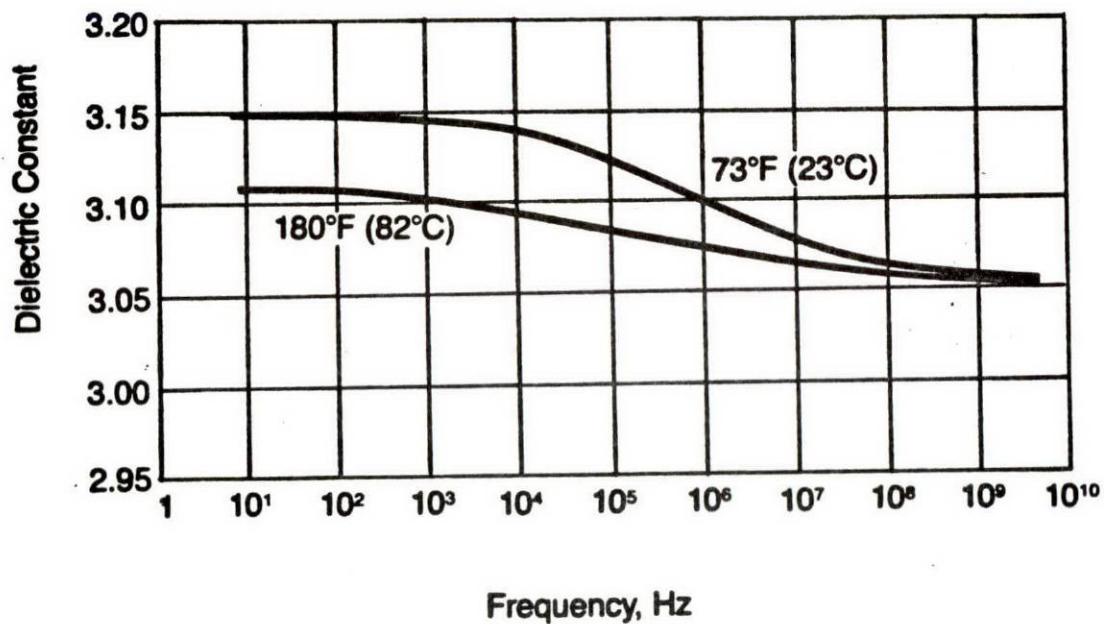


Figure C

**DISSIPATION FACTOR OF UNREINFORCED RESINS
vs FREQUENCY @ 73°F (23°C), 50% RH**

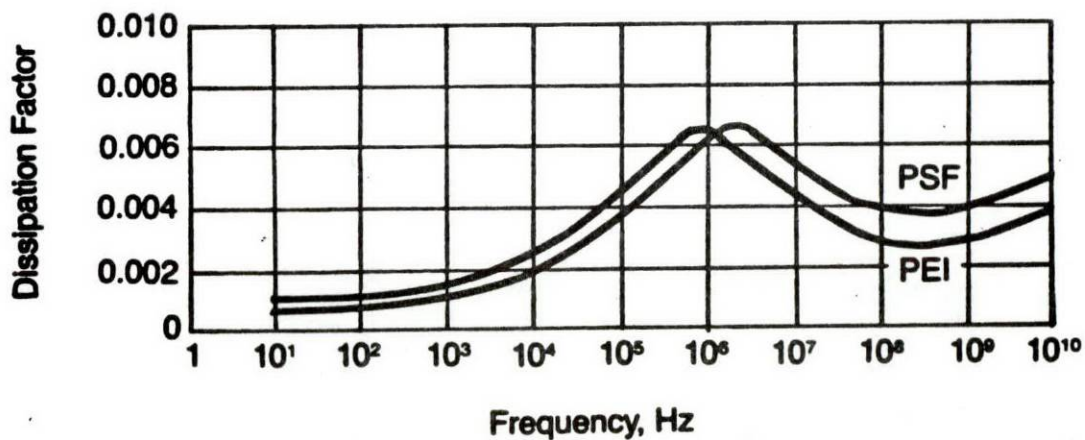


Figure D

Typical Sheet Extrusion Line

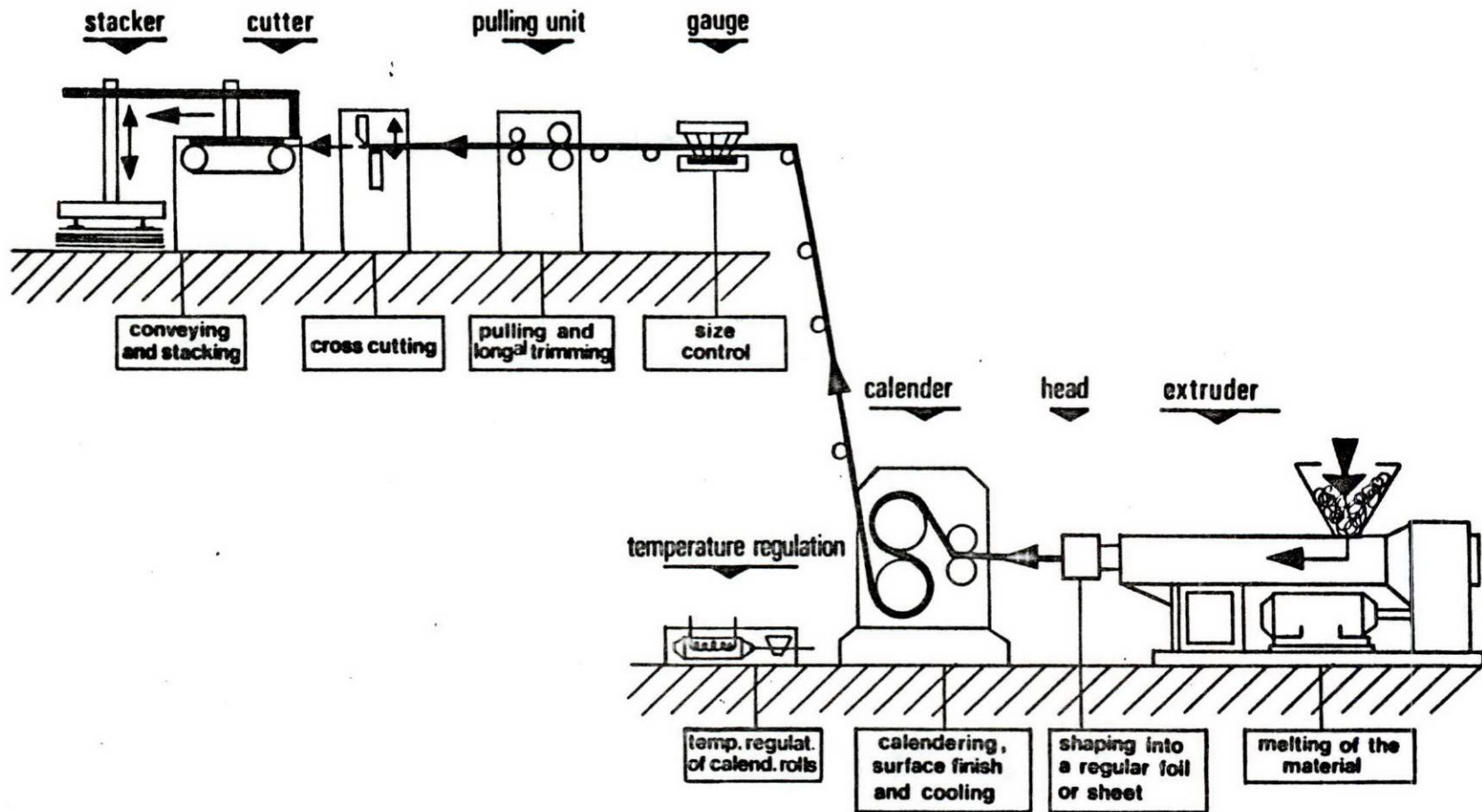


Figure E

**Drilled hole in UDEL[®]
polysulfone (50x, 30°)**

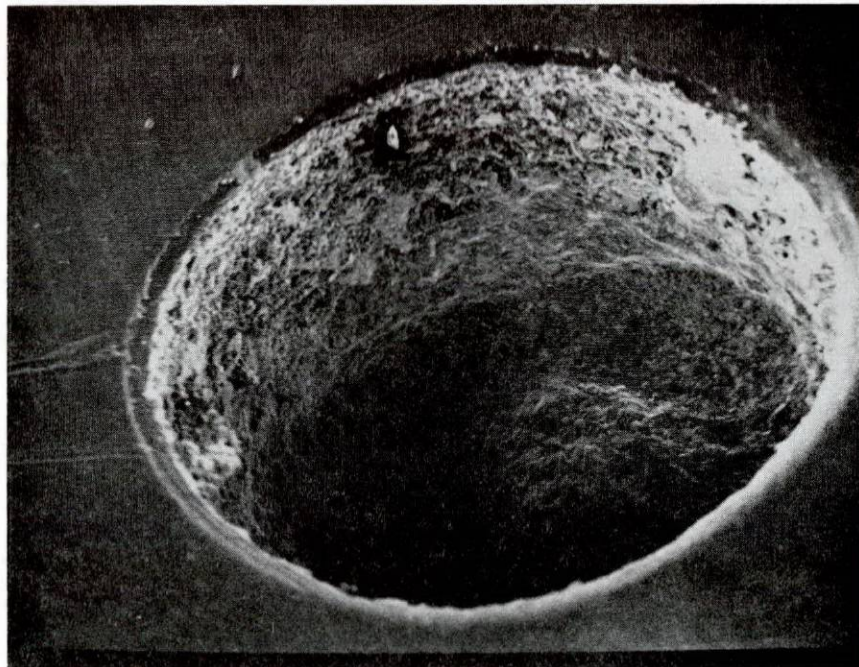


Figure F

Ultem 1000 Substrate
Over adhesion promotion at 200x, 30°

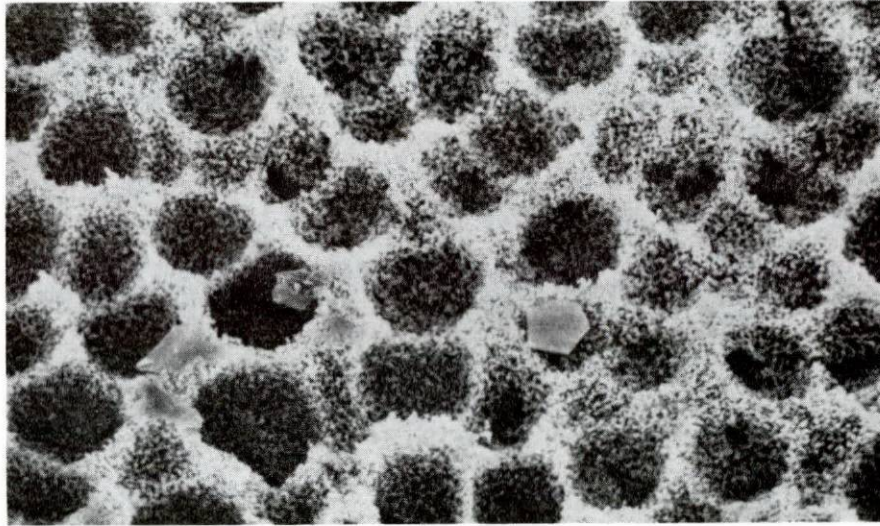


Figure G

Insufficient adhesion promotion
at 200x, 30°

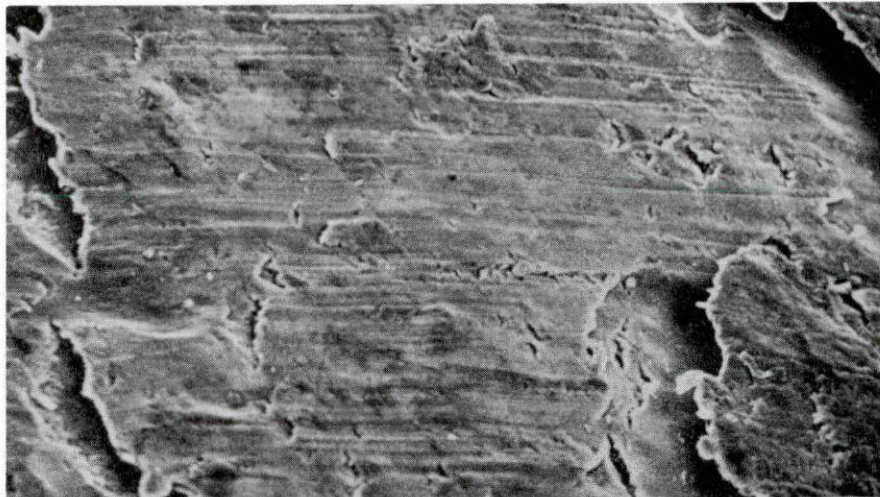


Figure H

Uitem 1000 Substrate
Proper adhesion promotion at 200x, 30°

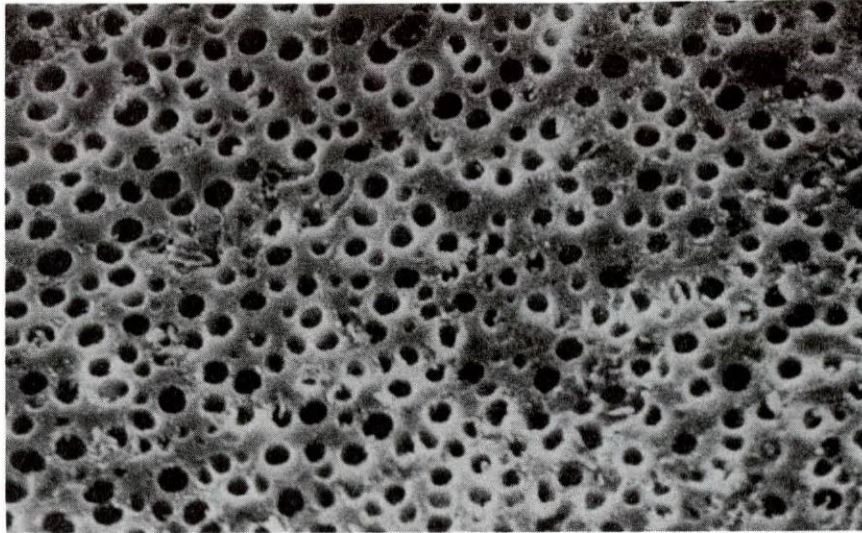
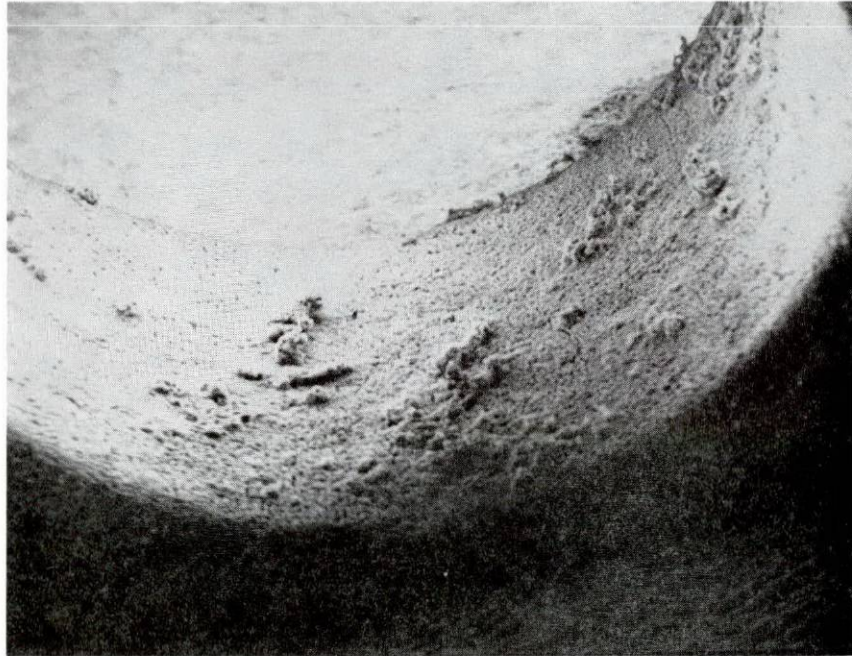


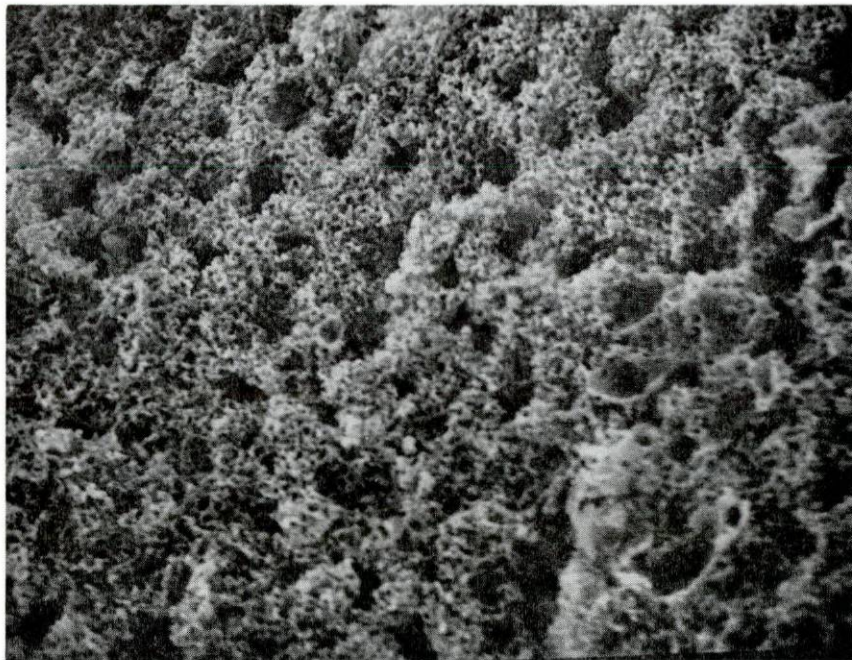
Figure I

**Adhesion promoted UDEL[®]
polysulfone**



(50x, 40°)

Figure J



(700x, 30°)

Figure K

P-t-h interconnection in UDEL[®] polysulfone

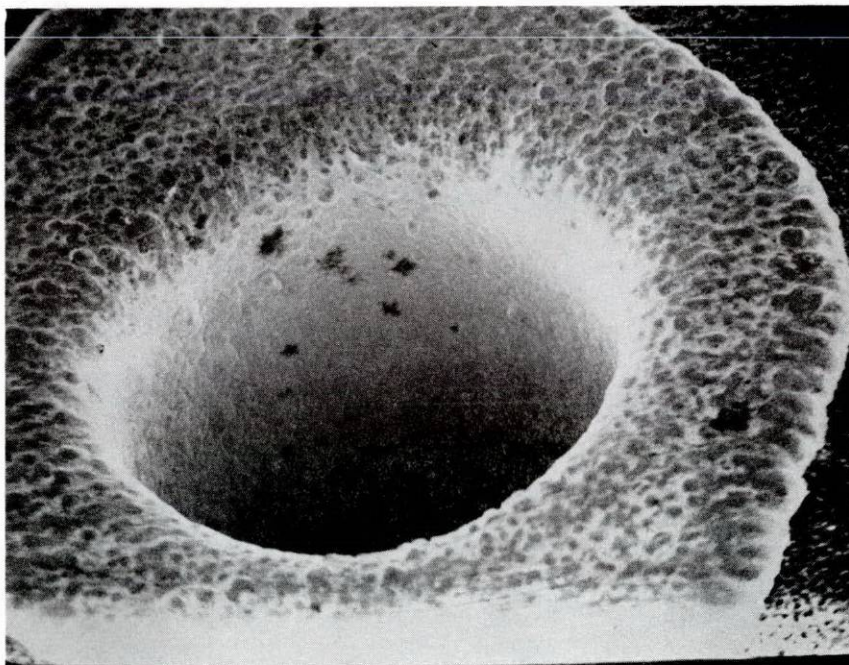


Figure L

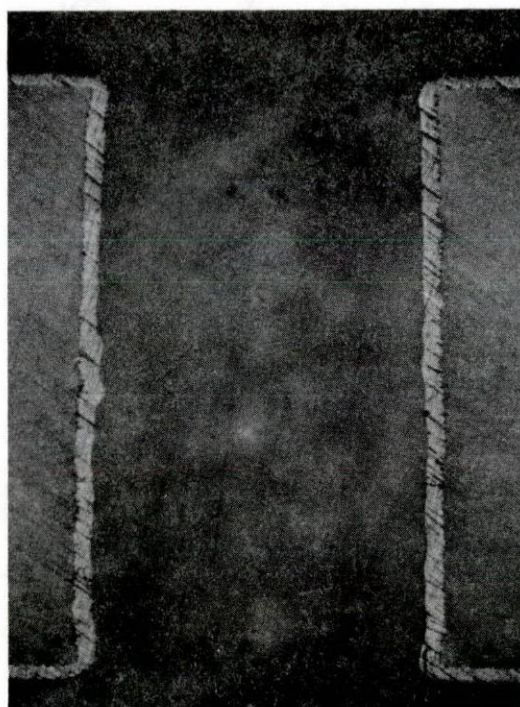


Figure M

Electronics I Session D

Tensile Testing of Printed Circuit Board Elements

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TENSILE TESTING OF PRINTED CIRCUIT BOARD ELEMENTS

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The integrity of electroless-copper deposits on printed-circuit boards depends on their mechanical properties. The determination of the mechanical properties presents problems, particularly the tensile-specimen configuration. IPC standards⁽¹⁾ specify specimen width of 1/2". Therefore for a typical foil thickness of 25 μm (1 mil), the width-to-thickness ratio is 500. ASTM Standard E8-77⁽²⁾ specifies a maximum width-to-thickness ratio of 8. On a typical printed-circuit board, the width-to-thickness ratio is about 50. For thin deposits, it is not possible to attain a ratio of 8. However, it would seem that the ratio in test specimens should be closer to 50 than to 500. As the gage length also has to be scaled, specimens with a width-to-thickness ratio of 50 are very small and difficult to test with conventional instrumentation. In order to investigate the mechanical properties of electrodeposits under AES Project 38, a tensile machine which can test very small specimens had to be designed and built.

This small, compact machine is shown in Figure 1. It is described in greater detail in a paper⁽³⁾ being presented at this conference in the Research Session. The purpose of this presentation is to demonstrate the applicability of the instrument in Figure 1 to the tensile testing of electroless copper for printed-circuit boards and to compare the results with those from another method.

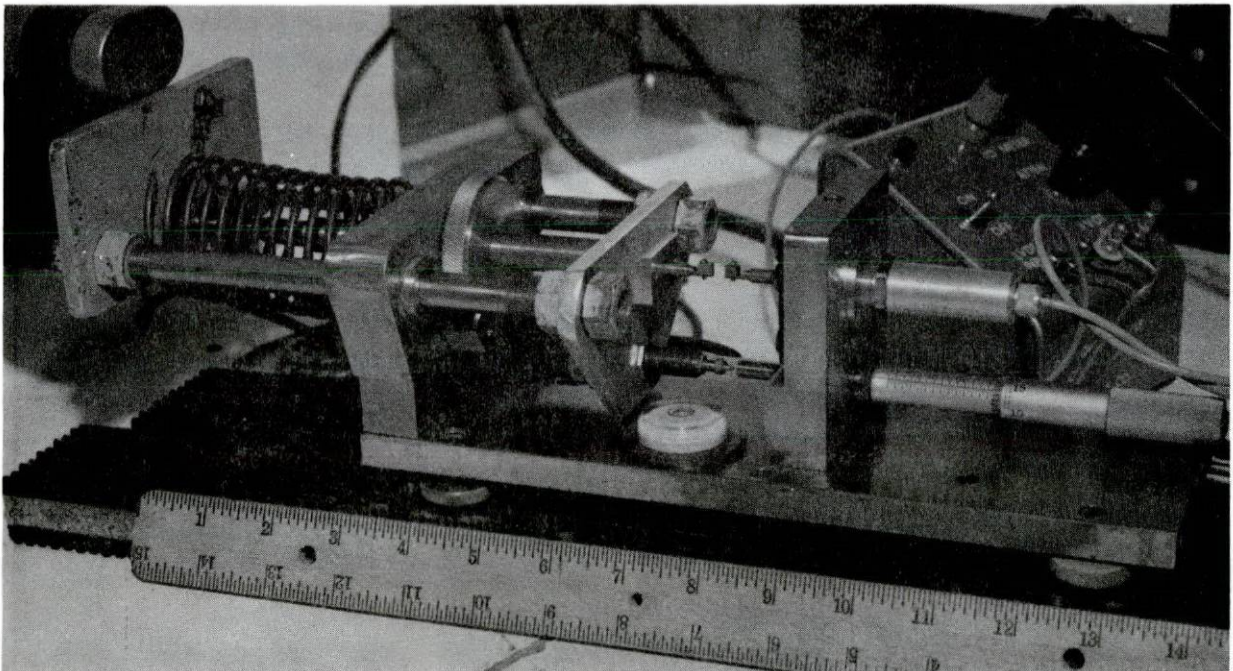


Figure 1.

Tensile Testing Machine

Electroless copper from a proprietary solution of the EDTA-formaldehyde type was plated onto epoxy-glass substrates in a way that the deposits could be readily stripped^(4,5) for subsequent testing. Such a stripping method is recommended in the IPC standards⁽¹⁾. The substrate was made catalytic by first coating it with adhesive to bind the subsequently laid-down layer. This layer, which was the catalytic one, was composed of a cured epoxy resin containing 20% TiO₂ pigment, phthalocyanine blue colorant and a 15% clay carrier containing the 0.1% palladium catalyst. By the use of photoresist and a mask having the shape of the tensile specimen and its supporting frame, electroless-copper deposits were plated which did not have to be cut to size or subsequently finished in any way. The tensile specimen and its supporting frame are shown in Figure 2. The purpose of the supporting frame, which is the stripe of deposit to the left of the dotted line in Figure 2, was to facilitate handling and mounting in the testing machine. This stripe was cut prior to testing after the tensile specimen had been mounted in the grips.

The results of tensile tests are presented in Table 1. It is evident that the reproducibility of the tensile strength for Samples 1-5 is very good. The reproducibility of the ductility, i.e., % elongation is also quite good for the type of material and specimen tested. A typical graph of applied load vs uncorrected gage-length change is shown in Figure 3. In the calculation of the strains, the gage-length changes had to be corrected for the stiffness of the machine. A rise is seen in Figure 3 to a maximum load, which divided by the original cross-sectional area is the tensile strength. After the maximum load, fracture begins and ends as indicated on Figure 3. The drop in the load beyond the maximum is due to a local decrease in the specimen thickness, i.e., necking, which preceded the beginning of fracture. In order to calculate the true stress, i.e., the load divided by the actual cross-sectional area, the minimum specimen thickness was measured by means of a scanning electron microscope. Assuming that the cross-sectional area at fracture was the minimum thickness times the original specimen width, the true stress was calculated to be 388 MPa (~54 Kpsi). The true stress at fracture was actually greater than 388 MPa because part of the specimen had already fractured so that the width and therefore the cross-sectional area was smaller than the one used in the calculation. The electroless-copper deposits were therefore stronger than their tensile strengths indicate. However, as discussed elsewhere⁽³⁾, the fracture stress of a deposit attached to the substrate lies between the tensile strength and the true fracture stress.

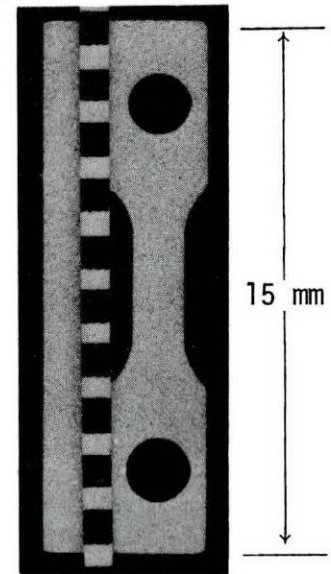


Figure 2
Tensile Specimen

An alternate method of measuring the mechanical properties which is not burdened with some of the problems of specimen size is bulge testing. Bulge tests⁽⁶⁾ were performed to compare their results with those obtained with the new machine. Samples 5.5 cm square were plated on the same substrates at the same time as the tensile specimens which were tested in the new

machine. The true stresses and strains were calculated using the equations (7):

$$\sigma_T = \frac{(P - P_0)a^2 \exp[-2\bar{\delta}]}{4ht_0}$$

$$\bar{\delta} = \frac{4h^2}{3a^2}$$

where σ_T is the true stress, P is the gas pressure to bulge the specimen, P_0 is the initial gas pressure, a is the specimen radius, $\bar{\delta}$ is the true significant strain and h is the bulge height. The results of these tests are listed in Table 1. Again the reproducibility is good. It is seen that the tensile strengths are significantly lower than those measured for the same material in the new machine. The lower strength can probably be attributed to the observation (7) in smaller samples that the strength increases as the cross-sectional area decreases. The reason why the ductility which was also somewhat lower when measured by the bulge tests was probably due to the fact that there was no necking. It can be seen from Table 1 that the values of the true strains at the maximum load, i.e., before necking occurred, and the true strains from the bulge test are about the same.

The results of this study show that consideration should be given to using tensile specimens of the same thicknesses and width as the elements on printed-circuit boards. The spin off from an AES Research Project is also illustrated. The new machine can also be used for the determination of the low-frequency fatigue properties of electroless copper by simply reversing the motor which turns the fine-threaded screw by which the load is applied.

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Acknowledgements

Mr. S. Delehanty prepared the substrates and Messrs. D. Karabag and L. Smith plated the samples. Mr. C. C. Nee performed the bulge testing. The support of the AES Research Board which led to the development of the new tensile machine is also acknowledged. Dr. Paunovic participated in this study as a member of the AES Project 38 Committee.

Electronics I Session D

Automatic PCB Plating Machinery

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In a matter of only a few years since their introduction to the industry, Automatic Tab Plating Machines have become a necessary piece of capital equipment for PCB/PWB manufacturer. Although relatively new to the industry, a multitude of field experience has been gained and many miles have been logged on the existing design machines. Sufficient time has elapsed to warrant a study being made of available machines and technology. The results of this study allows the "good features" of existing machines, field experience and new technology to be combined to enable one machine to be developed that will truly be a turn-key, state-of-the-art type machine. The following summarizes a study made of the existing machines and available technology and outlines the optimum methods that should be used to plate PCB tabs in an automatic machine.

Up until approximately 8-10 years ago, the manufacturing process of a PCB could have been described as closely fitting the shape of a venturi tube. That is, the capacity at the beginning of the process was large, got progressively smaller as it reached the nickel/gold tab plating step and again got progressively larger after nickel/gold tab plating. This was changed when an Automatic Printed Circuit Board Tab Plating Machine was developed and introduced to the Printed Circuit industry as a joint venture between a large chemical company and a small manufacturing concern. The first machine was slow, inaccurate, costly and in general had more than its share of problems. However, after being redesigned a number of times it was responsible for revolutionizing the technique of selectively plating tabs and over the years has evolved into a very necessary piece of capital equipment for the PC manufacturer. This was mainly due to the increased production capabilities of the machine and the gold cost savings. Since that time, two additional machines for the purpose of automatic tab plating have been introduced to the market place. Two of the three machines now available have been widely accepted in the industry for a various number of reasons. Both machines that have been accepted have their pros & cons and the decision as to which machine to purchase has been primarily a judgment call, usually by a capital equipment engineer. The following is how the optimum

automatic tab plating machine would be configured and the best approach, in the author's viewpoint, to the plating of fingers (tabs) on a printed circuit board on an in-line automatic continuous tab plating machine.

The process cycle that should be used is as follows:

Manual Load	D. I. Rinse
Reverse Current Strip	Soft Gold Strike
Rinse	Hard Gold Plate
Mechanical Scrub	Dragout/Reclaim Rinse
Rinse	Hot Rinse
Acid Activate	Blow-off/Dry
D. I. Rinse	Automatic Unload
Nickel Plate	

Before we get into each step in the process cycle, let's look at one of the most important and expensive steps in the preparation of the panel required to its being inserted into the machine. That being, first and foremost, with the machines available on the market today, the fact that the panel must be taped above the fingers to insure a good demarcation line, prevent contamination of plating baths and to prevent attack on other areas of the panel that are not being plated. The amount of tape required according to the machinery manufacturers varies from 3/4" to 1-1/2" wide. Although the necessity for fume tape is eliminated, this is still a considerable cost factor and a necessary evil with the machines presently on the market. It has been estimated, that taping a panel for gold tab plating can add as much as \$1.00 to the manufacturing cost of the PCB. A factor in the size of tape required is the accuracy of the shearing of the panel on the bottom edge. Since both machines available rely on the bottom edge of the panel for positioning during the loading process, the "line of plating" above the fingers will be directly parallel to the sheared edge of the panel. To exaggerate this point, if the panel were sheared at a 1° angle in relationship to the top of the fingers, it would result in a difference of .420" over the length of a 24" panel. Therefore, in this case, a minimum of .420" tape would be required just to insure a straight line on the top of the fingers and on top of this, you would have to add the minimum width of tape recommended by the machine manufacturers to prevent attack of areas not plated, contamination of baths, etc. It is not realistic to expect the PC manufacturer to hold the shearing of the bottom edge of the panel in relationship to the top of the fingers to within .010/.020". Therefore, the optimum here would be the ability to run without plating tape on a machine that would use some other part of the panel for reference for loading other than the bottom edge.

You will notice that manual loading was recommended in the process cycle, not automatic loading. This will be pursued

further towards the end of this discussion. The primary thing to be concerned with during the loading process is that the machine be capable of accepting boards loaded end to end (i.e. no gap between panels) to eliminate the high current density area on the leading and trailing edges of each panel. This in itself is a considerable cost savings if only the cost of the gold saved is taken into account. However, an additional factor to be considered is the increased production that can be realized by not having a space between each panel. For example, at 6'/min., based on an 8 hour day, a 3" gap between panels can mean a loss in production of approximately 576 twelve inch panels per day or approximately 1.6 million linear feet of material per year.

The stripping process should utilize a non-proprietary stripping solution such as a solution of 35% hydrochloric acid and water. To this can be added other chemicals to limit the attack of the copper and extend the life of the solution, although they are not necessary. The advantages of a non-proprietary stripping solution is the cost (approx. 65¢ to 70¢/gal, vs. \$7.00 to \$8.00/gal. for a proprietary stripper) and the fact that you minimize the undercutting that can take place with a proprietary chemical stripper. The amount of attack the copper can be controlled by varying the current density based on the thickness of SnPb being removed and the speed the machine is run at. The life of the solution can be extended and/or the strength increased by adding 1/4 - 1/2#/gallon of common table salt to the bath.

The rinse after stripping is required for the same reason every other rinse is required in a plating process. On occasion, a neutralizer is used here to de-activate the stripping solution; however, it is not required. Points to be concerned with about all the rinses are that they be at least 1/8" higher than the highest plating height and a sufficient amount of water necessary to properly rinse the panel is available. What is meant by this is that, spray rinses, although not required at every station should be used throughout the machine since overflow type rinses cannot compare with the effectiveness of a spray rinse. Since water is costly to bring into a plant and in some cases even more costly to dispose of, recirculating type rinses should be utilized throughout the machine. With recirculating type rinses, the water usage for the entire machine can be as low as 1/2 - 2 GPM.

The primary purpose of the mechanical scrubbing process is to brighten up the surface to be plated and secondarily to activate and clean the fingers. It should not be used for the purpose of leveling the copper, removing nodules, or to correct other prior defects in plating or manufacture. The brightening or polishing of the surface to be plated is important since the luster and brightness of the plated metal will only be as good

as the surface they are being plated onto. The activating and cleaning of the fingers is of secondary importance since activation will take place further down the line and if any solder is left on the panel when it reaches the scrubber, it will probably be smeared into the copper. The scrub brushes used should be a very fine or super fine silicone carbide, self-cleaning type brush. Very little pressure at approximately 800-1000 RPM should be used to prevent scratching or scoring of the tabs. Since scrub brushes are expensive, the design of the scrubber, should be such that a sufficient amount of adjustment is available to insure maximum feasible wear of the brush.

The rinse after scrub is used to remove any residue left from the brushes such as bristles or fibres.

The activator solution should be a non-proprietary solution of 20-25% sulfuric acid and water. The length of time in this cell is of primary importance since too long in this solution can cause attack of the copper fingers and dull the surface therefore affecting the appearance of the plated metals and defeating the main purpose of the scrubbing. Therefore, the length of this cell is of primary importance to the machine designer and must be sized based on the speed range of the machine.

This next rinse prior to nickel plating can be a tap water or D.I. water rinse depending on the purity of the water available to the machine. To be safe, a D.I. water rinse should be used.

Nickel plating is probably the single most troublesome step in the process to both machine manufacturers. To eliminate most of the problems normally experienced, soluble nickel anodes in the form of SD rounds or NI shot should be used here in conjunction with a sulfamate nickel bath. Without the use of soluble anodes, the control of the pH, specific gravity and metal concentration in the bath will be an on-going battle that the plater or chemist normally loses. Depending on the solution used and the machine cell design, the current density used in this step will vary from 200-800 ASF. The current density however, is not a key factor as many people feel. What is important, is the deposition rate of the metal and the sizing of the length of the cell based on the speed the machine is to be run at to yield a required thickness. This is important since the use of soluble nickel anodes will reduce the allowable current density and therefore the thickness that can be achieved at a given speed in a given length of cell. A machine originally designed to run with insoluble anodes cannot be converted to run with soluble anodes and yield the same thickness at a given speed as it was originally designed for. Of secondary importance is that the bath needs to be run at the saturation point with boric acid and the reservoir tank in the machine should be made with a compartment that will easily allow for the addition of boric acid when needed.

The rinse after nickel plate and prior to gold can be a tap water or D. I. water rinse again depending on the purity of the water available. However, again to be safe, a D. I. water rinse should be used.

You will notice that the recommended process cycle did not include an acid activator after nickel plate as is normally used in a hand line and some automatic machines. This step is not required since the speed an automatic machine is normally run at (from 1-12'/minute) does not allow the panel tabs time to become passive. What this additional step will do is provide for the very real possibility of dragging acid into the gold baths, add cost to the machine and provide another bath in the machine that must be maintained. It has been proven on many occasions with machines in the field that an acid activator is not required here and also that the machines with an acid activate after nickel are more trouble than they are worth.

The gold strike is used primarily to help prevent possible contamination of the gold plating bath and provide a good base needed for passing porosity tests. The need for this step to prevent contamination of the gold bath can be minimized with the proper utilization of squeegees or wipes at the exit end of the nickel cell and a good rinsing after nickel. Another point to be concerned with here is that the anodes should be a platinum clad material rather than plated. It has been proven that platinum clad anodes will last 4-5 times longer than plated anodes. Although initially more expensive, the minimizing of the down time involved in changing them when the platinum wears off and the rejects that can result in using an anode without platinum far exceeds the initial cost advantage. Another factor is that the machine be flexible enough to allow this cell to be used as a plating cell (by switching of valves, etc.) if a gold strike is not required and additional speed or gold thickness is desired. Depending on the solution used and the machine cell design, the current density this bath will be run at will vary from 5-20 ASF. High speed plating baths as marketed by most chemical suppliers can be utilized here and are normally run a 1/2 to 1 oz/gallon. Of course, being able to run this bath at the lower concentration of gold and still be able to achieve the desired results is preferred from an inventory standpoint.

The gold plating step is one of the most important processes in the machine. Points of concern based on the machines on the market today, are the appearance of the plated gold and the current density the gold is being deposited at. The appearance of the plated gold does not normally have any effect on the functioning of the PCB but does however, effect the esthetics of the part which could be of primary concern to a job shop plater. The appearance of the plated gold is a result of current density, agitation and/or the formulation of the bath. Most high speed plating baths can be used here and the current density

adjusted to accommodate the agitation in the cell of the machine purchased. The current density at which the tabs are being plated at is of concern since the gold is being "blasted" on at high current densities and could effect the deposition, grain structure, porosity and tolerance of the plated metal. A maximum tolerance of $\pm 5\%$ of the plated thickness measured anywhere on the panel is not unreasonable to expect on a standard panel with today's technology. The proper use of squeegees or wipes at the exit end of this cell is as important here as it is for the nickel cell to minimize the gold dragout. Platinum clad anodes should also be utilized here for the same reasons as stated for the gold strike cell. High speed plating baths as marketed by most chemical suppliers can be used here and are normally run at 1 to 2 oz/gallon. Of course, again, for economic reasons it is preferred to use a bath that requires only 1 oz/gallon and still yields the desired results. Depending on the solution used and the machine cell design, the current density this bath will be run at will vary from 60-300 ASF.

The dragout/reclaim rinse is a necessary part of the process cycle but again, with the proper utilization of squeegees and wipes at the exit end of the gold plating cell and a 1 oz/gallon gold solution, the importance of this station can be minimized although, still required. The dragout that can be expected from the machines on the market today will vary from 1/4 - 5 ml/ft² of plated material. With possible dragouts of this concentration, it is recommended that the solution be run through an electrolytic reclaim unit first, then a resin column recovery unit prior to being dumped down the drain. Running the solution through an electrolytic recovery unit gives the plater a much more accurate account of the amount of gold being sent to the reclaimers and can extract as much as 90-95% of the gold from the dragout solution. Most of the additional gold in the solution will be recovered by running it through the resin column unit 2-3 times. The dragout solution should be changed periodically after running it through the resin column to prevent possible staining of the gold plated fingers.

The rinse after the gold dragout is primarily for the purpose of removing any remaining solution that can cause staining on the gold fingers when dried. The necessity for this rinse can be minimized by periodically changing the dragout solution and again the proper utilization of squeegees or wipes at the exit end of the dragout cell. Instead of a cold water rinse as is normally used here, a hot water rinse should be used. This would assist in removing any residue on the gold plated fingers and aid in the drying process.

Drying should be accomplished by using a high pressure, oilless, warm air blow-off since the drying needs to be accomplished quickly and the water blown off the gold plated fingers

to prevent the possibility of water spotting. The optimum way of accomplishing this would be with an oilless blower furnished with the machine as standard equipment. This would prevent the possibility of oil from a plant air compressor getting on the plated fingers and staining them and at the same time not tax the plant air supply.

In the beginning of this discussion, manual load and automatic unload was recommended. The reason for this is that the automatic unload should be designed such that it will return the plated board to the operator at the load end of the machine for reinsertion into the machine so the second edge may be plated or stacked in the case of a completely plated or single edge panel. Depending on the speed the machine is being run at, the operator can also be taking measurements of the plated metal and removing any plating tape that may have been required during the process. Utilizing an automatic load and unload as is presently available on the market today requires an operator to load the loader so it can automatically load the machine and an operator to unload the unloader so it can automatically unload the machine. For example, running at 6'/minute with a 12' long panel and a tray that holds 50 panels would require both the automatic loader and unloader to be filled and emptied approximately every 8 minutes. Utilizing a system described above would virtually require only one operator.

There are other factors that have not been previously covered that must also be considered in the selection process of a machine. Other things that are recommended are: all digital meters on the rectifiers, a digital speedometer, liquid level sensors that are reliable and in-tank filter systems that enable the carbon treatment of the solution while the machine is still running. Lastly, there should be independent rectifiers for the front and back sides of the panels for both the nickel and gold plate sections to allow for better control of the plating thickness and a soft, dense brass brush should be used for making DC contact to the panels as they run thru the machine.

Do not underestimate your company's need for an automatic tab plating machine if you wish to remain competitive in the PC board market. If your competitor is plating his tabs on an automatic machine, he is probably plating them with more accuracy, more consistency and using less gold to do the same job as you and therefore, he has a more desirable product at a lower price. If your company uses as little as 25-35 oz. of gold/month, you can easily justify the purchase of an automatic tab plating machine.

Electronics I Session D

Gold Distribution on Printed Circuit Board Edge Connectors

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GOLD DISTRIBUTION ON PRINTED CIRCUIT BOARD EDGE CONNECTORS

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Abstract

A potential probe technique has been employed to monitor the variations in cathode potential across PCB edge connector contacts during gold plating using a bottom anode configuration, with the objective of improving the metal distribution. Distribution in both the horizontal and vertical directions has been considered. The effects of geometry, anode masks, current robbers and current density have been evaluated. Anode masking was found to be the most effective practical method of improving distribution and current robbers to overcome the end board problem with stacked boards. Potential variations are however independent of the gold electrolyte and depend only upon the cell and electrode geometries. The current efficiency versus current density relationship is the most important solution factor in minimising thickness variations and work is reported on the efficiency behaviour of a range of proprietary gold solutions and their effect on distribution.

Introduction

The gold plating of double-sided printed circuit board (PCB) edge connector contacts can be carried out in two basic modes, namely:-

1. Side anodes with the PCB situated centrally between the anodes. This can be operated in a manual, automatic or continuous linear mode.
2. A stacked arrangement of boards with a bottom horizontal anode configuration.

The achievement of a uniform distribution of current (and hence thickness) over the surface of an electrode is very difficult in practice, but minimising such variations is particularly important with gold on economic grounds.

The factors which affect metal distribution may be divided into two main categories, namely:-

1. Geometric factors which determine the primary current distribution. These include the shape and size of the electrodes and plating cell and their relative separations and orientation.
2. Electrochemical and electrical factors which determine the secondary

current distribution, having a positive or negative effect on the primary distribution.

- (a) Potential - current relationship
- (b) Solution conductivity
- (c) Current efficiency - current density relationship

and the factors which influence these parameters (composition, temperature, pH, specific gravity etc.). For a given electrolyte and plating conditions the metal distribution can be improved by optimising the geometry. In the case of side anodes, the anode width is typically $1/3$ to $1/4$ the width of the cathode (the actual width being dependent upon the anode-cathode separation). In the bottom anode configuration, where the anode is exposed to the edges of the work rather than the total area to be plated, a much more complex relationship holds. Shielding effects between the stacked boards also affect the distribution. However, as a rough guide the width of the anode should be approximately $1/4$ the width of the cathode and its length is usually $1/2$ to $2/3$ the distance between the outer boards (1,2).

The utilisation of a bottom anode configuration enables a high work load to be employed for a relatively small volume of solution. An initial assessment of a bottom anode arrangement showed large gold thickness variations in both horizontal directions, i.e. across a given board and also across the stack of boards. Thickness variations outside specification were also observed in the vertical direction along the length of the contact pads.

The present paper considers improvements in the gold distribution on PCB's in terms of geometric factors using a bottom anode arrangement. It is known that the size and positioning of the anode is very critical but changes in the anode size cannot be easily made for changes in board dimensions. Anode masks are normally employed which can be more readily changed than the anode. Therefore the role of anode masks and also current robbers have been considered. A potential probe technique to monitor potential variations over edge connectors during deposition was employed. Variations in potential were equated to variations in current density and with a knowledge of the current efficiency versus current density relationship of the electrolyte the thickness variations could be estimated. Later work studied the efficiency - current density relationship for a range of proprietary acid hard gold solutions and the influence on the thickness distribution. The probe technique can be used to rapidly assess the performance of different cell geometries without the need for carrying out complete plating runs. Off-line experiments can however only be used as guidelines for production, there being no substitute for carrying out the potential measurements under the actual production conditions.

Experimental

The simulated PCB plating cell ($2\frac{1}{2}$ l solution) is diagrammatically illustrated in Figure 1. Short samples of edge connectors (10.5cm wide with 20 pads on each side of 1.5×0.3 cm) were used as cathodes and a board separation of 2.5cm was used for the stacked board experiments (X3 boards). Rigid plastic

sheeting provided the anode masks, with variable openings, and were assessed at the two levels shown in Figure 1 and also when positioned directly on the anode. Current robbers in the form of copper strips or wire were positioned opposite the contact face of the outer boards of the stack and operated either in the same electrical circuit as the boards or in a separate circuit.

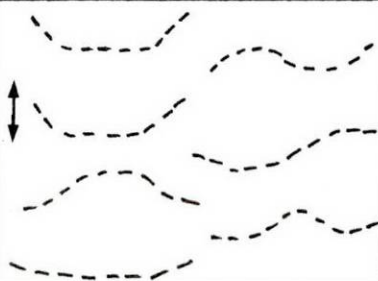
Cathode potentials were measured with respect to a calomel electrode positioned outside the plating cell and connected to the solution via a flexible remote junction probe (2mm diameter). The probe was filled with saturated KCl and fitted with a ceramic frit at the end. Potentials were measured close to the pads (1mm separation), in varying positions, and recorded on a high impedance voltmeter. The circuit diagram is shown in Figure 2. Potentials were equated to current density by monitoring potential variations along a Hull Cell panel at points of known current density. Potential variations are independent of the gold electrolyte but thickness variations are solution dependent, based upon different current efficiency characteristics. The current efficiency - current density relationships and actual thickness distributions were determined for a range of proprietary acid hard gold electrolytes (Co-Au and Ni-Au). Efficiency was determined by a weighing technique based on sheet cathodes centrally positioned between vertical anodes. Gold thickness was measured by a beta back-scatter method.

Results and Discussion

Single Boards.

Average values of potential variations in both the horizontal and vertical directions for a single board and the influence of various masks are presented in Table 1. In the case of the 2 x 4cm mask the board was positioned along the short length of the mask. A plating current density of 1A/dm² was used. The vertical variations represent potential differences between the bottom and top of the pads and those in the horizontal direction the difference between the maximum (board edge) and minimum (centre pads).

TABLE 1: POTENTIAL VARIATIONS OVER A DOUBLE-SIDED BOARD

Mask	Average potential variation mV		Potential profile across board
	Horizontal	Vertical	
None	22	69	
1 x 1cm., position 1	17	-	
1 x 1cm., position 2	16	-	
1 x 1cm., position 3	17	-	
2 x 4cm., position 1	18	42	
4 x 4cm., position 1	15	52	
4 x 4cm., position 2	11	57	
4 x 4cm., position 3	16	48	

In the absence of a mask the potential variation in the horizontal direction shows a typical U-shaped profile with most of the change occurring towards the ends of the board. All the masks studied reduced the horizontal variation, with the 4 x 4cm mask in position 2 giving the smallest change. Under ideal geometric conditions with parallel electrodes filling the cross-sectional area of the cell a uniform distribution would be expected. However, in normal practice with the electrodes not filling the cell section a build-up of deposit would occur at the edges (as observed). On the other hand a point anode close to the centre of a board would be expected to give a build-up on the centre pads rather than the ends. Therefore one would predict an optimum position for a given size anode or mask (the mask acting as the effective anode) to equalize the two effects and yield a uniform horizontal distribution. If one considers the schematic potential profiles across the boards (Table 1) the inversion in potential is apparent under some of the conditions, the closer the mask to the board the greater the effect. Differences in profiles between mask positions 1 and 2, which have a separation of only 2cm, suggests that the positioning of a mask is very critical. The profiles exhibiting a maximum and minimum reflect the importance of centrally positioning the cathode over the mask. The mask produced only small improvements in the vertical direction. Typical bottom to top variations (over 1.5cm length) of $\sim 50\text{mV}$ indicated that this distribution is more significant and also more difficult to influence than the horizontal direction. Again a flat profile was found over the central region of a pad, the minimum in potential in the centre reflecting the influence of the solution interface in concentrating the current. A semi-quantitative relationship between cathode potential and current density was obtained by plotting the potential at points of known current density on a Hull Cell panel. This gave a linear plot of potential against log current density with a slope of 160mV/decade , i.e. a 50mV change for a doubling of current density. Using this relationship the calculated thickness variations were found to be in general agreement with actual thickness values, confirming the validity of the technique. For example a typical across board variation of 20mV would predict a $3.25\mu\text{m}$ maximum on a $2.5\mu\text{m}$ minimum, while the use of a mask to halve the variation would reduce the maximum to $\sim 2.9\mu\text{m}$ (neglecting efficiency effects).

The observed vertical variation raises the question of if the current rail should be stopped-off. This is illustrated in Table 2, which shows that plating the rail significantly improves the pad distribution; the rail acts as a current robber, but is itself plated with excessive thicknesses. This gold can however be reclaimed. The efficacy of stopping-off needs to be equated with the improved pad distribution, reclamation costs and taping costs. Under optimum conditions it is normally found to be advantageous to stop-off.

Potential variations as a function of immersion depth show, Table 3, that increasing the depth of board immersion improves both the horizontal and vertical distributions, particularly across the board. This confirms that the solution interface acts effectively as a "mirror", concentrating the current flow. This improvement was shown not to be influenced by the minor changes in the anode-cathode separation.

TABLE 2: THE INFLUENCE OF THE PLATING RAIL ON POTENTIAL VARIATIONS

	Vertical Potential Variation, mV
Rail stopped-off	50 - 60
Rail plated	25 - 30
Rail plated	100 (pad top+rail)

TABLE 3: EFFECT OF IMMERSION DEPTH ON POTENTIAL VARIATIONS

Current density 0.75A/dm^2 No mask

Condition	Average potential variation, mV	
	Horizontal	Vertical
Solution level with pad top	20	70
Solution 0.5cm above pad top (standard)	10	65
Solution 1.5cm above pad	5	59

Table 4 shows that reducing the plating current density reduces the potential variation in the horizontal and vertical directions, in both cases a linear relationship is observed. However, any reduction in current density would have to be compatible with the subsequent increased plating time. Also efficiency effects may be more favourable at higher current densities for certain electrolytes (see current efficiency section).

TABLE 4: EFFECT OF CURRENT DENSITY ON POTENTIAL VARIATIONS

Current density, A/dm^2	Average potential variation, mV	
	Horizontal	Vertical
0.25	2	16
0.5	6	33
1.0	16	64
1.5	22	99
2.0	29	131

Stacked Boards.

In the case of the stacked boards (3 boards) the anode masks again influenced the potential variations (Table 5). The optimum mask size and position appeared to be different for 3 boards than for the single board experiments, the actual optimum size and position not being determined. The small 1 x 1cm mask in fact worsened the distribution. Again inversion of potential occurred with certain combinations. Column 3 of Table 5 (variation between boards) represents potential differences between pads at a given location on the 3 boards (e.g. all the 6 centre pads or 6 end pads) averaged between the various locations measured. In this series of experiments the horizontal variation through the stack was affected to a different extent to that in the across board horizontal direction, for a given mask condition.

TABLE 5: EFFECT OF ANODE MASKS ON POTENTIALS FOR STACKED BOARDS

Board separation 2.5cm. Current density 1A/dm²

Mask	Potential Variation, mV		
	Across board, average 6 sides	Average Variation between boards	Max. - Min.
No mask	22	56 (15)	73 (38)
1 x 1cm., position 1	31	74 (21)	93 (46)
2 x 4cm., position 1	12	59 (21)	68 (29)
4 x 4cm., position 1	28	53 (11)	77 (41)
4 x 4cm., position 2	19	61 (12)	73 (28)
The figures in brackets neglect the outer two faces			

The detailed potential measurements for the run without the mask (Table 5) are presented in Table 6. Even in the absence of a mask a slight inversion in potential is observed.

The data of Tables 5-6 show that the majority of the potential change occurs on the outer two faces of the stack. Therefore masks of the type considered will never significantly improve the distribution on the outer faces in relation to the inner layers. Further extensive potential profiling was carried out utilising vertical masking with and without the conventional horizontal masks. Detailed shaping of the masks enabled potential variations to be reduced in the vertical direction as well as horizontally. However, the complexity of the jigging arrangements and the effect of the masks on the solution flow pattern produced a non-viable production technique and further work was curtailed on this aspect.

Current robbers.

Table 5 demonstrated that with stacked boards the main problem on thickness distribution arises on the two outer faces. In practice the two end boards

are used as burners, with reclamation of the gold. This leads, in production (20 board stack), to a 10 per cent reduction in board throughput. Therefore consideration was made into the use of current robbers to overcome the end face problem. The robbers were placed parallel to the end contacts and extended the full length of the board. The effects of robber width, distance from the board and applied current density were studied and the results are summarised in Figures 3-6. With the robber at a fixed distance from the board and in the same circuit (Figure 3) the potential difference between the outer and inner faces of the end board decreases with increasing robber width, giving negative values (i.e. a higher potential on the inner face) at > 1.0 cm for a separation of 1.5 cm. Figure 4 shows the potential difference sensitivity for variations in separation for a given robber, indicating the need for accurate positioning. A more controllable process is obtained if the robbers are placed in a separate electrical circuit. Figure 5 shows that the current density required on the robbers to equalize the inner-outer face potentials decreases with increasing robber width, e.g. $7.5\text{A}/\text{dm}^2$ on the wire and $0.5\text{A}/\text{dm}^2$ on the 1 cm wide robber. The above current densities represent applied currents of 0.3A and 0.1A respectively and therefore the lower current on the larger robber would reduce the frequency of gold reclamation. For a given robber and separation a linear relationship is observed, Figure 6, between the applied current density on the robber and the potential difference. Adoption of robbers in production would give an increase in board throughput, but the probe technique would be necessary to establish the optimum geometry.

TABLE 6: POTENTIAL DATA ON STACKED BOARDS (NO MASK)

Position	Potential, mV				
	Pad 1	5	10/11	15	20
Board 1, right hand (outer face)	1241	1232	1226	1223	1233
Board 1, left hand	1210	1185	1175	1180	1195
Board 2, right hand	1196	1185	1181	1186	1204
Board 2, left hand	1205	1195	1190	1196	1210
Board 3, right hand	1213	1192	1184	1192	1204
Board 3, left hand (outer face)	1238	1236	1237	1246	1248

In the above work all the robbers were maintained in a constant vertical position, with the top of the robber being level with the top of the pads. In this situation no improvement in the outer face vertical potential difference was observed, typically $\sim 50 - 70\text{mV}$. The vertical variation could be reduced to 20-30 mV by positioning the robber towards the bottom of the pads. However, if the robber extends beyond the bottom of the board it will adversely affect the potentials on the inner faces. Therefore it is preferred to use a narrow robber (in a separate circuit), e.g. 1cm rather than 2cm, located towards the bottom of the pads but not extending beyond the bottom of the boards.

Current efficiency.

The potential probing work has demonstrated that electrode geometry is important in improving the deposit distribution. Another very important factor which is solution dependent is the relationship between current efficiency and current density. The efficiency versus current density ($0.2 - 4 \text{ A/dm}^2$) relationship for a range of proprietary cobalt and nickel hardened gold electrolytes is shown in Figure 7. The solutions were operated under the manufacturers recommended conditions of temperature and pH. Under the given experimental conditions all solutions show a decreasing efficiency characteristic above $1 - 1.5 \text{ A/dm}^2$, with varying rates of change. Below 1 A/dm^2 solutions A, C, E and G show an increase in efficiency with increasing current density, the first two solutions having steep initial slopes. On the other hand solutions B, D and F exhibit a decrease in efficiency over the whole current range. It may be concluded that the latter three solutions should be the most suitable for reducing gold thickness variations, particularly if it is required to operate below 1 A/dm^2 . The potential measurements showed that it was beneficial to reduce current density to improve the distribution. The maxima in the efficiency curves were found to be dependent upon the agitation rate, increased rates shifting the maxima to higher current densities. Higher agitation rates than used in the present experimental work would normally occur under production conditions. Changes in efficiency and the position of the maximum are illustrated in Table 7 under controlled agitation conditions, with rotation of a cylindrical cathode (low efficiency solution)(3). Similar effects have previously been reported in the literature (4).

The conclusion that can be drawn from the effects of agitation is that agitation should be maintained uniform over the cathode and that since current density varies over a component the agitation level should be in the region where the efficiency varies little or decreases with increasing current density.

TABLE 7: VARIATION OF EFFICIENCY WITH AGITATION AND CURRENT DENSITY

Agitation, r.p.m.	Current density, A/dm^2		
	0.25	0.75	1.2
	Current efficiency, %		
20	32.6	35.1	24.8
40	19.4	39.6	36.2
60	20.6	40.5	36.2
80	15.5	32.0	40.6
100	-	31.6	39.4

Care needs to be taken in interpreting efficiency curves since a sharp decrease in efficiency with current density often leads to an increase in poro-

sity levels. A more informative method of presenting the data is to plot current efficiency X current density (or plating rate) against current density, the flatter the curve the more uniform the metal distribution.

The thickness distribution on a PCB test piece (7 contacts on each side of 1.1 x 0.35 cm) was evaluated for some of the proprietary solutions at a current density of 1A/dm². The results (average of 3 readings) are presented in Table 8, the thicknesses being normalised to a minimum of 2.50 μ m.

TABLE 8: GOLD THICKNESS VARIATIONS IN DIFFERENT SOLUTIONS

1A/dm². Normalised to 2.50 μ m. 14 contacts.

No mask.

Solution	A		B		C		D		F		G	
Pad position	T	B	T	B	T	B	T	B	T	B	T	B
Thickness, μm	3.59	4.26	2.79	2.82	2.93	3.41	2.62	2.84	2.64	2.96	2.62	2.92
	2.83	3.22	2.60	2.78	2.70	2.97	2.57	2.78	2.55	2.80	2.57	2.91
	2.50	3.68	2.50	2.73	2.70	2.97	2.61	2.79	2.53	2.77	2.52	2.84
	2.54	3.38	2.50	2.79	2.50	3.12	2.50	2.82	2.62	2.78	2.52	2.85
	2.61	3.23	2.55	2.75	2.53	3.19	2.58	2.77	2.50	2.70	2.60	2.90
	3.08	3.61	2.66	2.76	2.59	3.31	2.54	2.77	2.63	2.78	2.64	2.80
	3.95	4.62	2.98	3.11	2.60	4.05	2.95	3.18	3.00	3.19	3.01	3.25
	3.37	3.95	2.73	2.73	3.27	4.07	2.63	2.91	2.62	2.87	2.75	2.99
	2.65	3.37	2.56	2.81	2.81	3.37	2.58	2.81	2.50	2.72	2.51	2.86
	2.65	2.88	2.60	2.79	2.72	3.12	2.53	2.80	2.53	2.79	2.50	2.83
	2.61	3.26	2.66	2.70	2.55	3.19	2.55	2.88	2.50	2.59	2.56	2.75
	2.77	3.35	2.55	2.75	2.67	3.09	2.56	2.85	2.51	2.70	2.57	3.01
	3.10	3.52	2.59	2.82	2.70	3.27	2.59	2.86	2.58	2.85	2.67	2.72
	3.95	4.19	3.07	3.00	3.02	3.44	3.04	3.22	2.79	3.07	3.25	3.38
$\bar{x}$, μm	3.31		2.74		3.07		2.75		2.72		2.80	
σ , μ	0.57		0.16		0.42		0.19		0.18		0.24	
max.-min., μm	2.12		0.61		1.57		0.72		0.69		0.88	
T = 2 mm from top of pad B = 2 mm from bottom of pad.												

The data of Table 8 show the superior distributions obtained with solutions B, D and F and to a lesser extent G, in both the horizontal and vertical directions. This is in agreement with the efficiency characteristics (Figure 7), solutions B, D and F operating on the decreasing portion of the curves and G in the flat plateau region. The other two solutions (A and C) were operated in the region of the efficiency maximum or even on the ascending part of the

curve. The former solutions show an average horizontal variation of $0.73\ \mu\text{m}$ compared to an average of $1.85\ \mu\text{m}$ for the latter two solutions.

These results illustrate the importance of selecting the correct electrolyte to obtain the minimum thickness variation. For example changing from solution A to solution D would provide gold savings of ~ 20 per cent, under the given set of experimental conditions. On the other hand the earlier work demonstrated that the use of anode masks and/or current robbers could reduce the thickness variations and thereby reduce cost savings in changing the plating solution.

The effects of gold concentration, agitation rate, nickel or cobalt content, pH, temperature and specific gravity have not been considered in the present work. Preliminary investigations have shown that all the above parameters influence the gold distribution and need to be taken into account before the optimum electrolyte can be selected. The question of deposit porosity and brightness in relation to all the parameter combinations also needs to be considered.

Conclusions

The potential probe technique is a convenient method for designing electrode geometries and optimising the size and positioning of anode masks and current robbers. Horizontal masks are effective in reducing potential variations and hence thickness variations across the contacts of a PCB using a stacked arrangement of boards with a bottom anode configuration. The optimum geometry is very critical for the bottom anode mode of operation. Masks are not effective in influencing vertical distributions. Reductions in current density and increasing the depth of board immersion in the solution improve the potential variations in all directions. With stacked boards the major potential increase occurs on the outer faces of the stack. Conventional masks cannot overcome this adverse distribution. An alternative approach to the use of anode masks would be to utilise anodes constructed from thin strips of material, which are mutually insulated. Switching the appropriate segments could then cope with a range of cathode sizes.

Current robbers are an effective means of overcoming the end face problem. The optimum size, position and applied current density have been derived to equalize the outer-inner face potentials.

The shape of the variation of current efficiency with current density curve of the electrolyte is another important factor having a major influence on distribution. The efficiency characteristics of a range of proprietary gold solutions have been determined and shown to exhibit significant differences. A decreasing efficiency over the plating current density range is the most desirable, such that the plating rate varies little with current density. Thickness variations are in general agreement with the efficiency data, and gold savings of up to 20 per cent can be achieved between different electrolytes.

Acknowledgement

The author is indebted to the Directors of the Plessey Company for permission to publish this work.

References

- (1) J.S. Stevenson, Engelhard Industries - private communication.
- (2) "Technology of Electrodeposition", A.T. Vagramyan and Z.A. Solov'eva, R. Draper Ltd., 1961, pp.308.
- (3) Plessey Telecommunications Ltd. - private communication.
- (4) E.D. Winters, Plating, 1982, 59 213.

FIG.1 SIMULATED PCB PLATING FACILITY

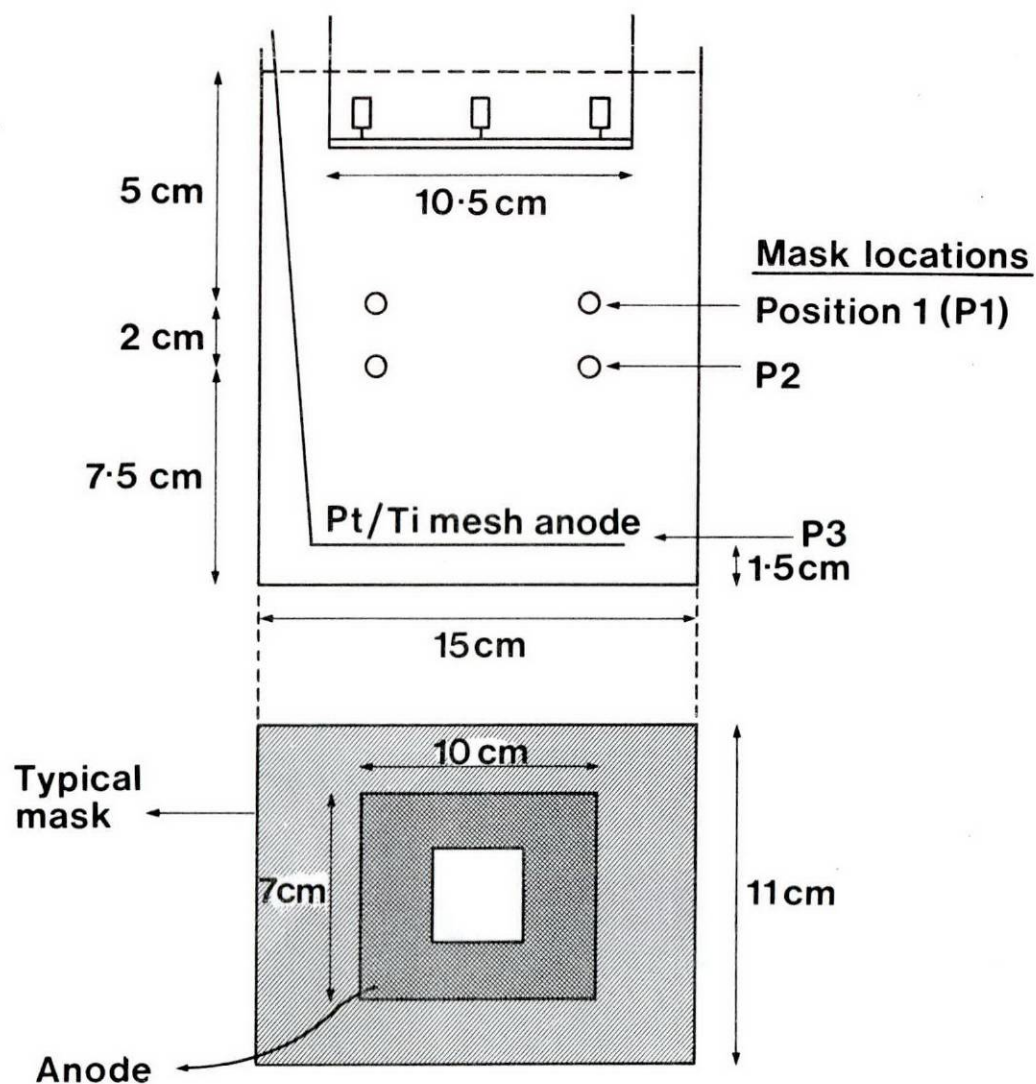


FIG. 2 CIRCUIT DIAGRAM FOR POTENTIAL MEASUREMENTS

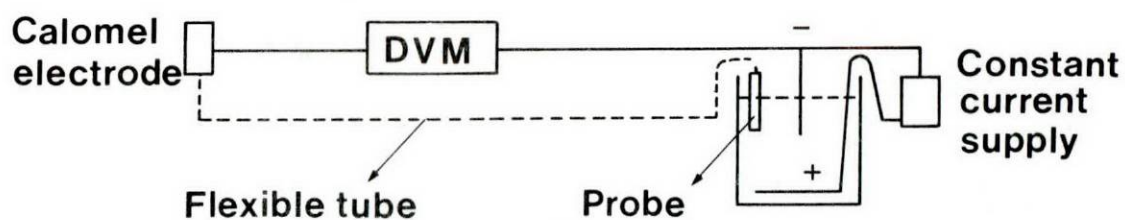


FIG. 3 EFFECT OF ROBBER WIDTH ON POTENTIALS - Same circuit

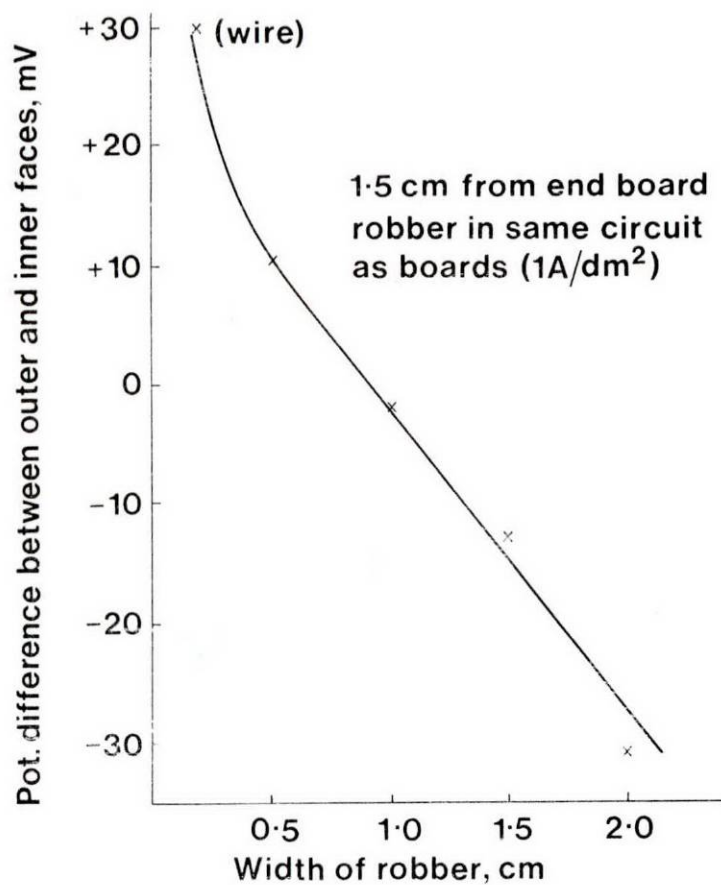


FIG. 4 EFFECT OF ROBBER-BOARD SEPARATION ON POTENTIALS
- same circuit

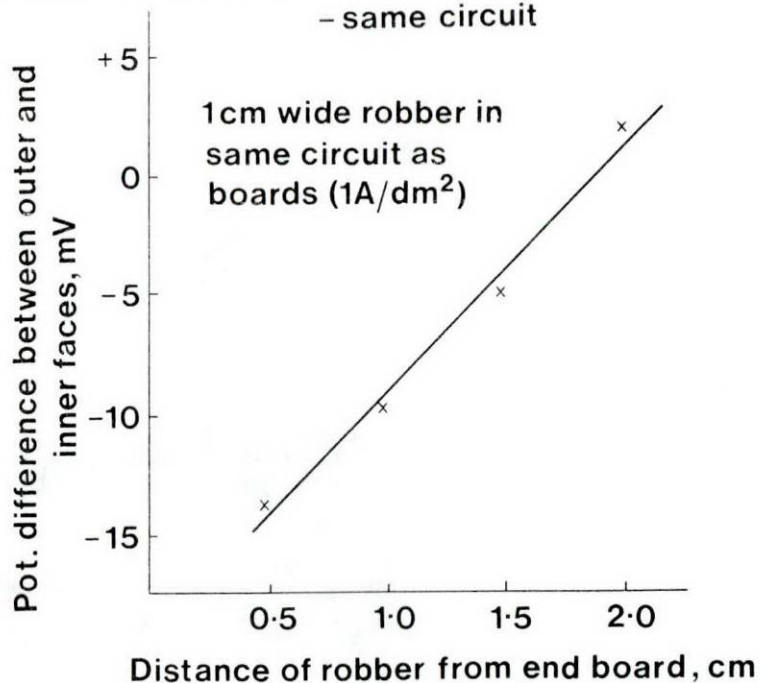


FIG. 5 APPLIED CURRENT DENSITIES TO EQUALISE POTENTIALS
AS A FUNCTION OF ROBBER WIDTH. Separate circuit.

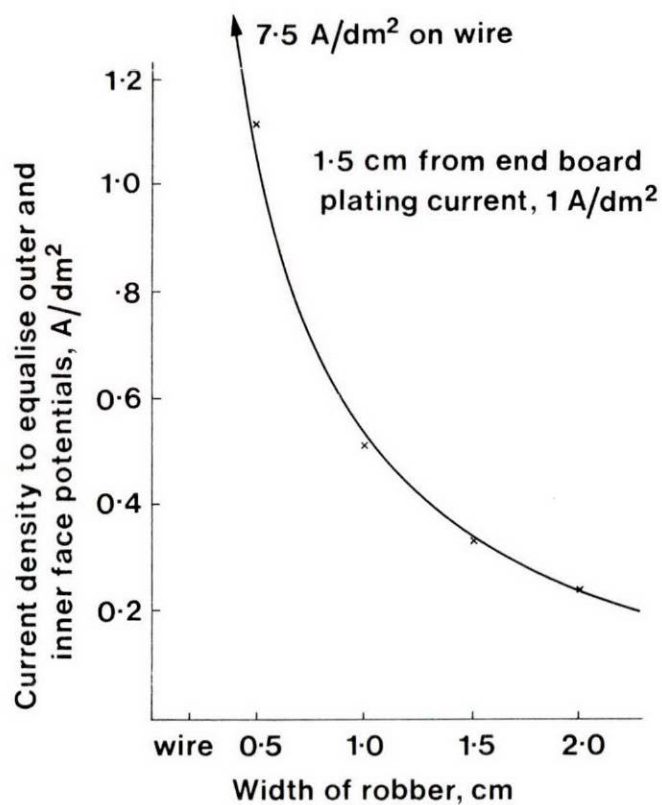


FIG. 6 EFFECT OF APPLIED CURRENT DENSITY ON POTENTIALS.
Separate circuit.

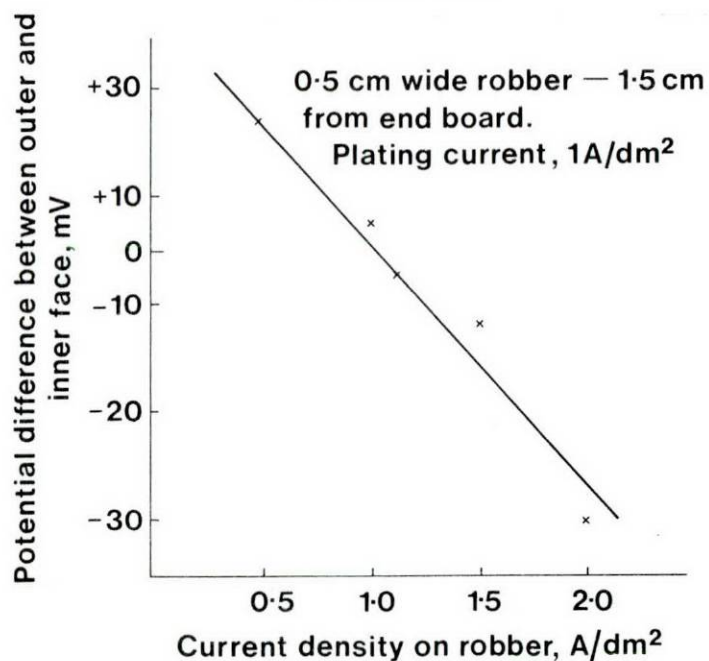
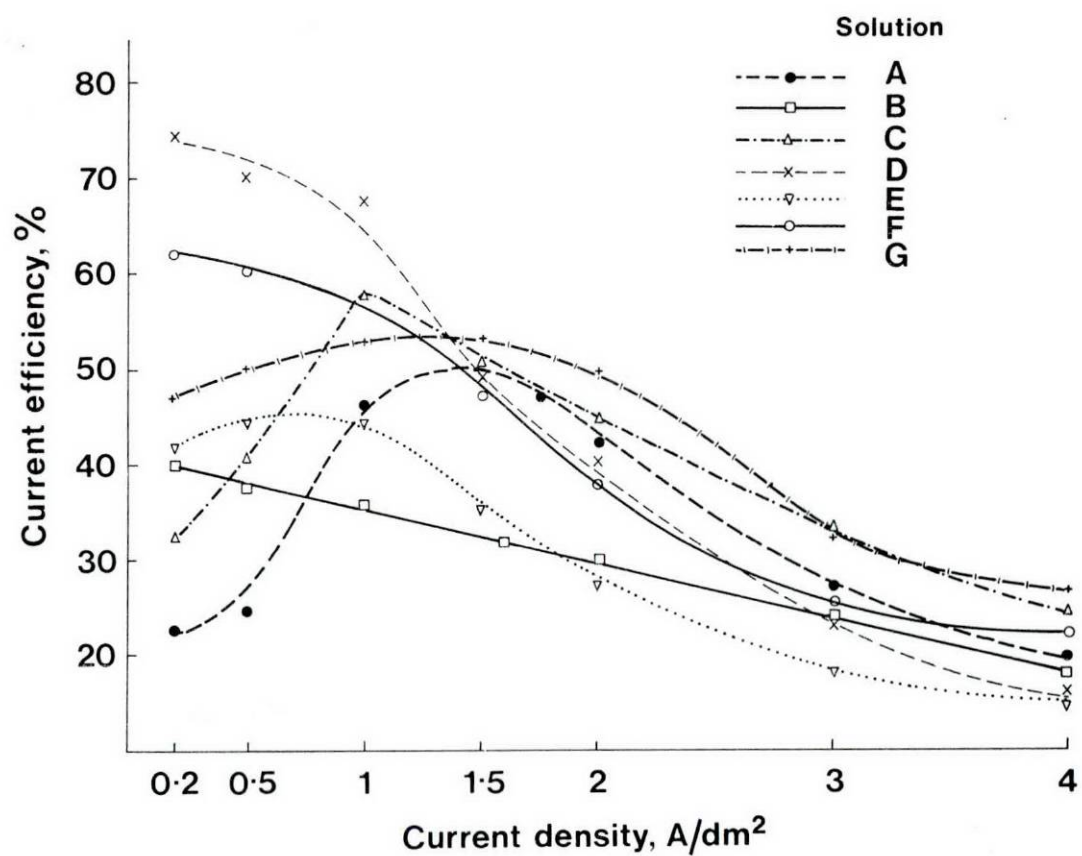


FIG.7 CURRENT EFFICIENCY vs CURRENT DENSITY RELATIONSHIP FOR A RANGE OF PROPRIETARY GOLD ELECTROLYTES



Electronics I Session D

New Procedures for Predicting Solderability Performance of Electroplated Tin Deposits

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NEW PROCEDURES FOR PREDICTING SOLDERABILITY PERFORMANCE OF ELECTROPLATED TIN DEPOSITS

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Historical Background

The "Wren Tin,"¹ acid matt tin plating process was developed at the Naval Avionics Center in 1968 and 1969, when bright acid tin plate outgassed during soldering leaving a very porous and cratered deposit at the end of the meltzone. This outgassing caused by volatilization of entrapped organics, could potentially promote electrolytic corrosion of the electronic lead material. The effect of these organics on the solderability of plated tin leads was not known. The matt tin produced by the Naval Avionics Center process adequately resolved the outgassing problem. Over the years since, when long term solderability has been a prime requirement, many manufacturers have adopted a modified version of this tin process successfully.

Matt Tin Advantage: Solderability

One of the key attributes of the matt tin process is excellent solderability after extensive burn-in. (Reference '82 Hom Study, Highlights from Hom/Hobson talk - AES second annual Golden West Regional Conference).

In this study, both bright tin and matt tin solderability on cerdip devices over various temperature and time intervals to simulate device burn-in conditions were evaluated. The solderability testing was done in compliance with MIL-STD-883B, Method 2003.2 using a rosin flux. The criteria for acceptance was 95% solder coverage of the dipped lead below the seating plane. The solderability results were plotted on semilog graph paper, with temperature along the vertical axis in °C and time to first failure in hours along the horizontal axis (see Illustration I). The graphs empirically show that at every temperature interval from 125°C to 200°C matt tin is functionally superior to bright by a factor of almost 10. The graphs (see Illustration I) also show that an accelerated manufacturing solderability test at 10 hours/200°C, 20 hours/175°C or 48 hours/150°C should ensure solderability at 125°C/168 hours (a standard military burn-in).

To delineate the solderability failure mechanism unsoldered units at time of solderability failure (for bright tin at 10 hours/175°C and for matt tin at 188 hours/175°C) were cross-sectioned and evaluated. The leads on both sides of the failed devices were cross-sectioned lengthwise, (see Photograph I). Photomicrographs were taken at 480X and 1200X at the midsection of the leads (see Illustration II).

¹ U. S. Patent 3,585,114 is available from the Office of Naval Research as a royalty free non-exclusive license.

ILLUSTRATION 1.

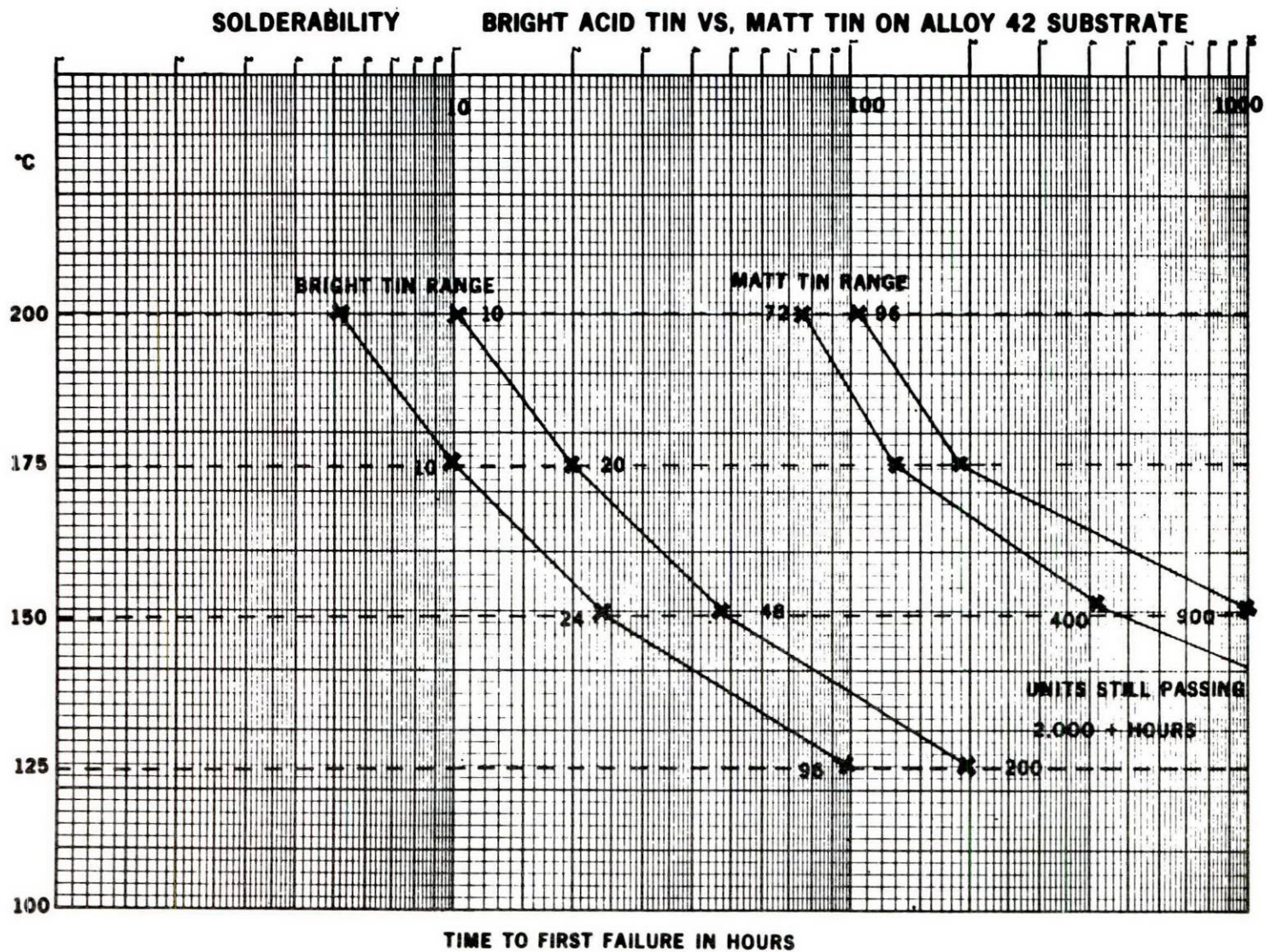
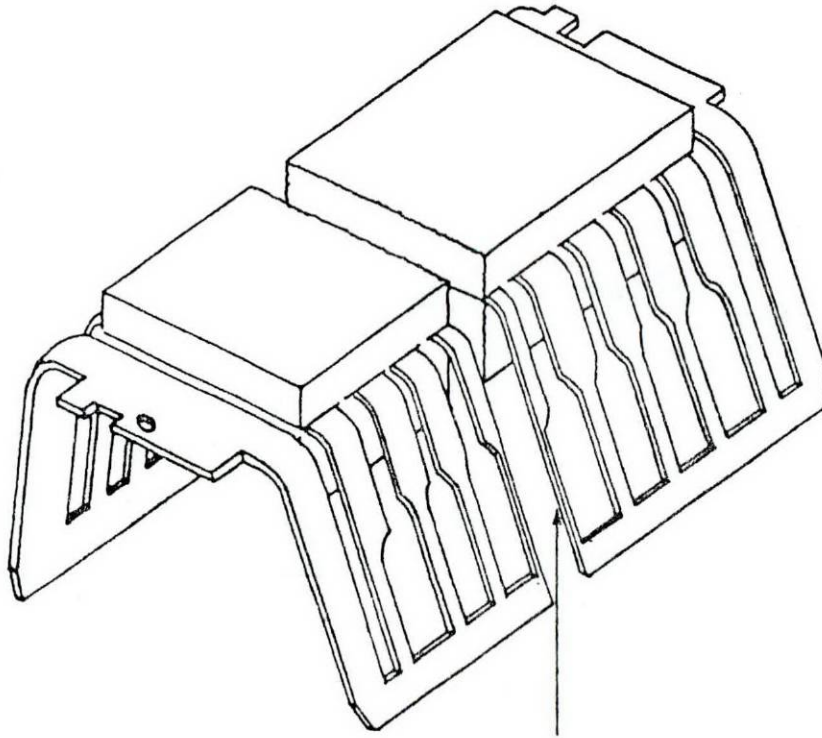
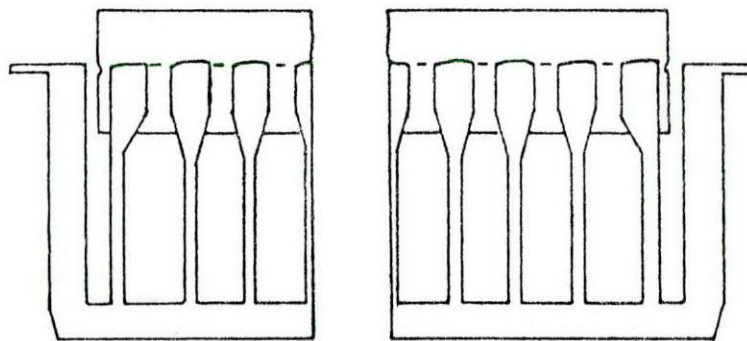


Illustration II

POINT OF CROSS-SECTION



Cross-sectioning site



The bright tin deposit micrographs (see Photograph I) show numerous voids in the tin plate where entrapped organics volatilized during high temperature exposure, resulting in solder joint defects due to outgassing. The tin thickness was measured at 350 microinches. The tin/alloy 42 interface is noticeably contaminated with carbon residues and devoid of intermetallic formation. The solderability failure mechanism for bright tin is, therefore, a function of brightener co-deposition and occlusion, coupled with elevated temperature exposure resulting in organic vaporization within the tin deposit.

On the matt tin deposit micrograph (see Photograph I), a continuous layer of tin-nickel intermetallic (Ni_3Sn_4) can be seen along the entire lead at the tin and alloy 42 interface. A weak nital etch was used to enhance the grain and phase boundaries. These intermetallic compounds form at the interface between coating and base metal throughout the lifetime of a tin plated component by solid/solid diffusion processes.² On the top surface of the plating, a tenacious tin oxide layer exists, consuming a minor portion of the free tin. Voids were not noted in microsection views of the matt tin deposit, indicating negligible organic co-deposition and occlusion.

Shorter time to failure of bright tin deposits compared to generic matt tin deposits is attributed to a greater amount of co-deposited and occluded organic compounds in bright tin electrodeposits. A comparison was made by determination of carbon using a standard pyrolysis method for carbon in metals. (See Table I Percent Carbon Found In Electrodeposited Tin).

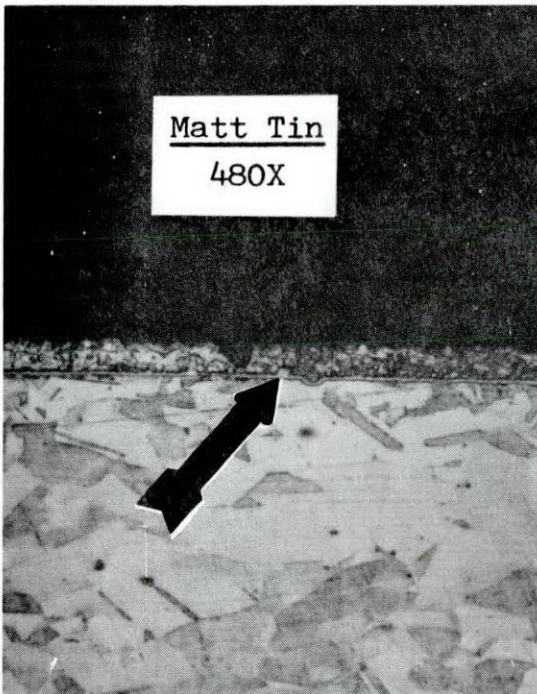
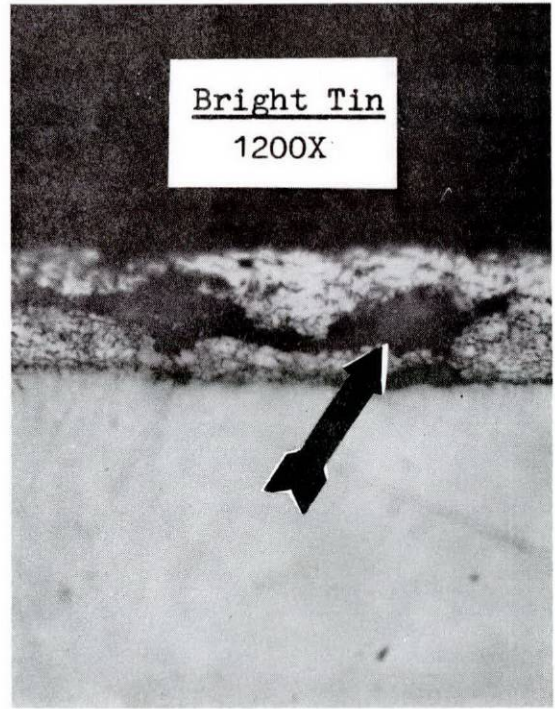
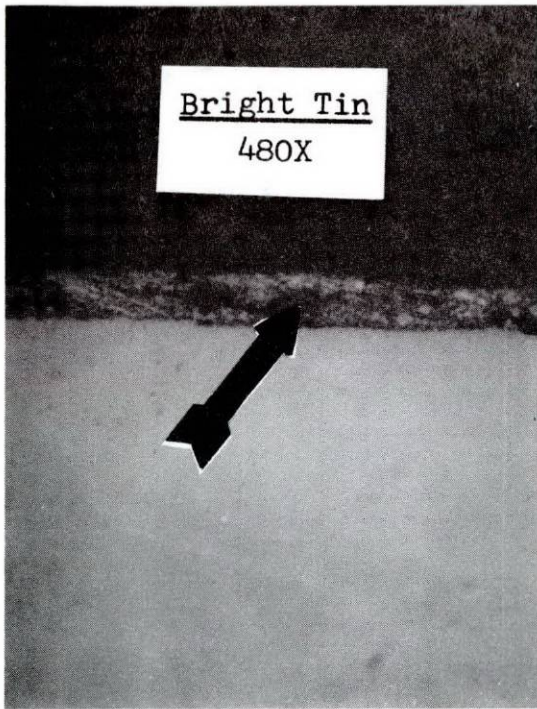
Generic matt tin electrodeposits exhibit lower carbon contents and outgas less than bright tin electrodeposits when exposed to elevated temperatures. The predominant solderability failure mechanism of generic matt electroplated tin exposed to elevated temperatures is formation of tin-nickel intermetallic compound by solid state diffusion. Bright electroplated tin deposits, however, become unsolderable quickly at elevated temperatures by the mechanism of co-deposited and occluded organic compounds decomposing and outgassing. When bright electroplated tin deposits are microsectioned at the time of first solderability, failure there has not been enough time at temperature to form an appreciable amount of intermetallic compound. Lower organic containing generic matt tin electrodeposits also exhibit less blue tin propensity and fewer adhesion failures than bright acid tin electrodeposits which characteristically contain greater amounts of codeposited and occluded organic compounds.

TABLE I
PERCENT CARBON FOUND IN ELECTROPLATED TIN DEPOSITS

<u>Process</u>	<u>Sample #1</u>	<u>Sample #2</u>
Matt Tin	.032	.039
Bright Tin	0.16	0.17

² "The Growth Of Intermetallic Compound On Common Basis Materials Coated With Tin and Tin-Lead Alloy", P. J. Kay and C. A. McKay, Transactions of Institute of Metal Finishing, Volume 54, 1976.

Photo I
SOLDERABILITY FAILURE MECHANISM



Development of Outgassing Tests

Background:

Because of prior solderability problems associated with bright acid tin plated finishes, MIL-M-38510E, 1 December 1981, (Microcircuits, general specification for), prohibits use of bright acid tin plate as a finish for microcircuit leads. Familiarity with the bright acid tin plating process allows adjustment of the plating parameters of a bright acid tin plating bath to produce a matt tin deposit. Such matt tin deposits, however, are subject to the solderability problems characteristic of bright acid tin deposits.

The Naval Avionics Center's Materials Laboratory thought it expedient to investigate methods for detection of outgassing in electroplated tin deposits. The outgassing characteristics of matt deposits from generic bright acid tin baths which are operated to produce matt deposits are very similar to the outgassing characteristics of bright acid tin. Methods were then proposed to differentiate between generic matt tin and a matt tin finish produced by a generic bright acid tin bath.

Procedure:

Fourteen different lots of evaluation packages plated by outside vendors and the Naval Avionics Center were used for development of five test methods. All finishes had been applied to Alloy 42 leads of 14/16 lead ceramic dual inline packages. The fourteen lots of evaluation packages consisted of the following:

- a. eight unique lots of bright acid tin plated leads
- b. four unique lots of matt acid tin plated leads
- c. one lot of furnace reflowed matt acid tin plated leads
- d. one lot of hot solder dipped matt acid tin plated leads

Each lot was assigned a code number as received and the typical thickness of the lead finish was determined by metallographic sectioning.

Documentation:

Since development of these outgassing test procedures is documented in NAC TR-2330 "Detection of Outgassing in Electroplated Tin Deposits", available from the U.S. Naval Avionics Center, 6000 East 21st Street, Indianapolis, IN 46218, only a short synopsis of the developed test methods will be detailed. Those interested in evaluating any of these test methods should request NAC TR-2330 on your company letterhead.

Testing:

All of the test methods which have been optimized or shown to be feasible share one common limitation -- they are only applicable to electroplated tin deposits which have not been melted (reflowed). The base premise is that co-deposited or occluded organics will, when heated to soldering temperature, outgas. The "Hot Iron Test" and the "Hot Oil Test" each provide static documental evidence that outgassing has occurred.

The "High Vacuum Melt Pressure Test" measures the amount of gas that is evolved at soldering temperatures. The "Mass Spectrometry Test" identifies and quantifies the gases evolved at soldering temperatures. The "Carbon Determination Test" measures the amount of free and combined carbon that has been co-deposited or occluded in the electrodeposited tin. A carbon determination is not an outgassing test, because the organics have been pyrolyzed in an excess of oxygen; however, outgassing test results are predicatable from the carbon determination test results.

Hot Iron Test

The "Hot Iron Test" (see Photograph II) consists of heating the tin plated lead until the electroplated tin melts. The end of the melt zone (melt area adjacent to the unmelted electroplated tin finish) is sliced with a very sharp knife or scalpel and the cut area is examined at 30 diameters for gas porosity (spherical voids).

Hot Oil Test

The "Hot Oil Test" (see Photograph III) is similar to the "Hot Iron Test", with the electrodeposited tin being partially reflowed by immersion in peanut oil that is somewhat hotter than the melting point of tin. The end of the meltzone is examined as in the "Hot Iron Test". The "Hot Oil Test" will detect smaller amounts of outgassing (an indication of the amount of co-deposited or occluded organics) than the "Hot Iron Test" (see Photographs IV, V, and VI).

High Vacuum Melt Test

The "High Vacuum Melt Test" (see Photograph VII) is performed by resistance melting a clean electroplated tin depoist on an alloy 42 lead at a very low pressure. The pressure rise of the system is used to calculate the percentage increase in pressure which is proportional to the volume of gas evolved by the melted electrodeposited tin.

Mass Spectrometry Test

The "Mass Spectrometry Test" is an analysis of the evolved gases from an electroplated tin deposit that has been subjected to 650°F for five minutes. The assay of the evolved gas is usually reported as micrograms of each gas per gram of electrodeposited tin. Using the ideal gas laws, it is possible to calculate the total volume of gases evolved at Standard Temperature and Pressure.

Carbon Determination Test

The "Carbon Determination Test" (see Photograph VIII) is based on the pyrolysis of a metal with an excess of oxygen in an isolatable sytem. The calculation of carbon by measuring the amount of carbon dioxide generated is a reliable method for determining the carbon content of a ferrous metal. In this test method, the percentage carbon found in stripped alloy 42 must be used in calculating the percentage carbon in the electrodeposited tin finish.

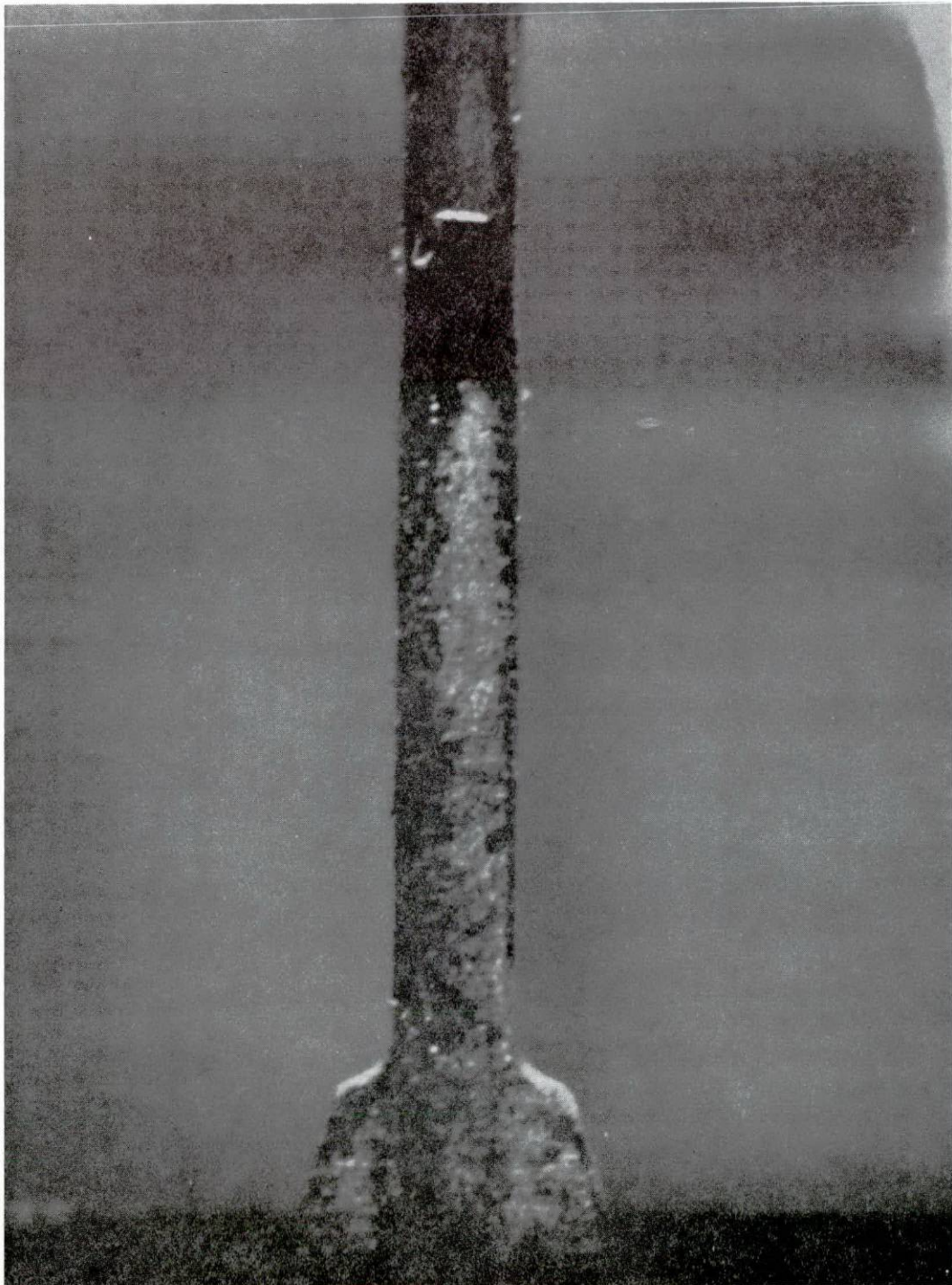
Photograph II



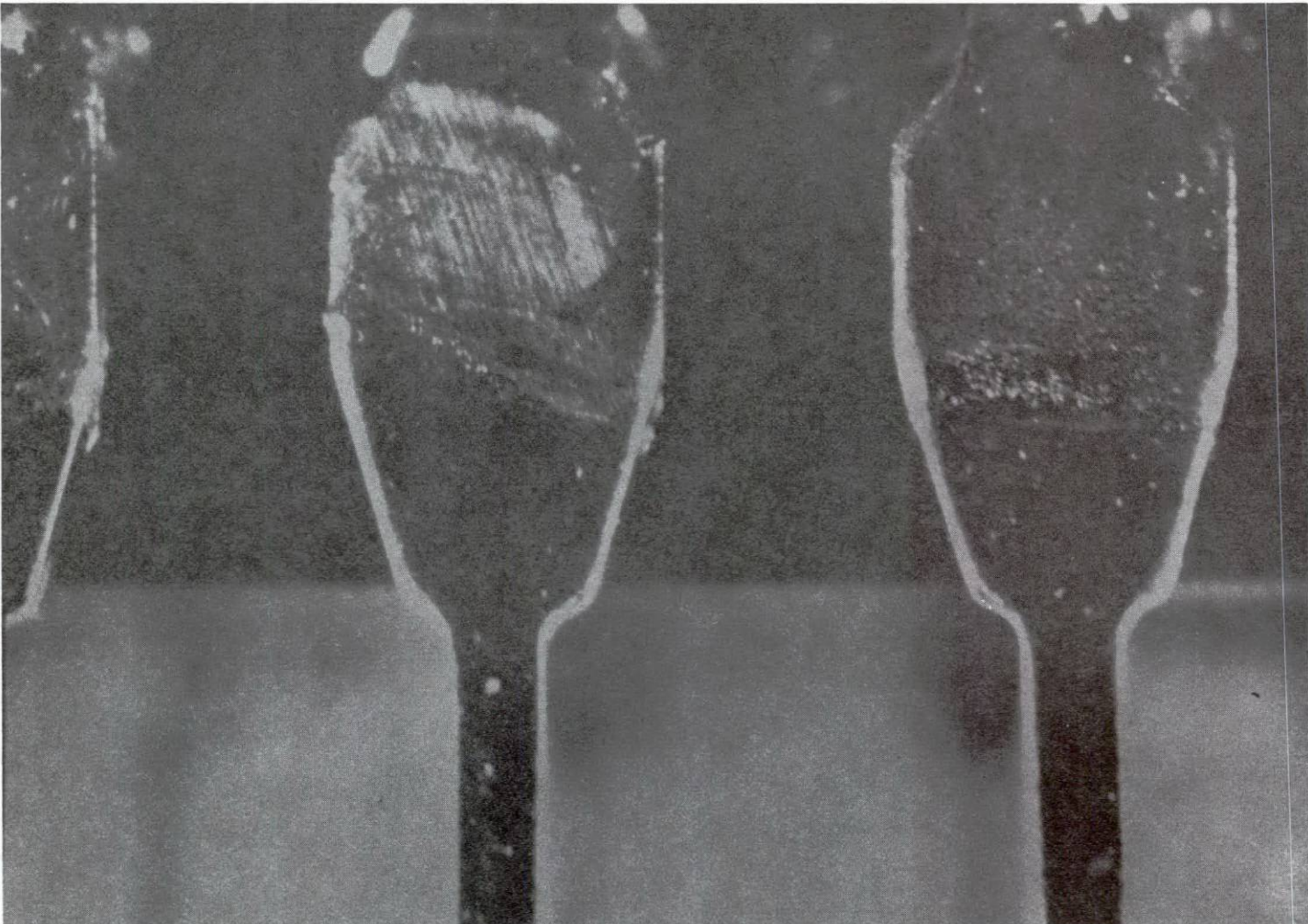
Photograph III



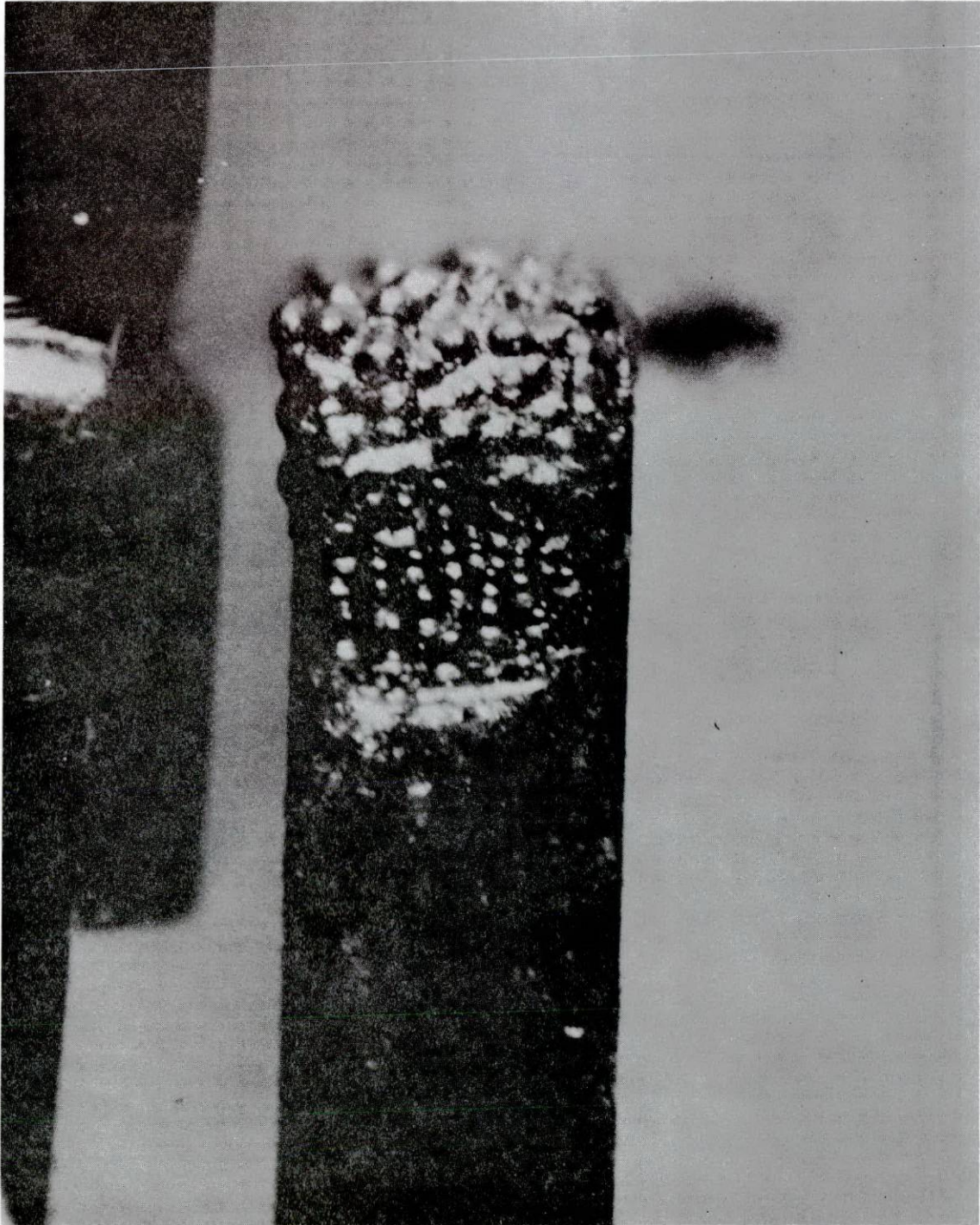
Photograph IV



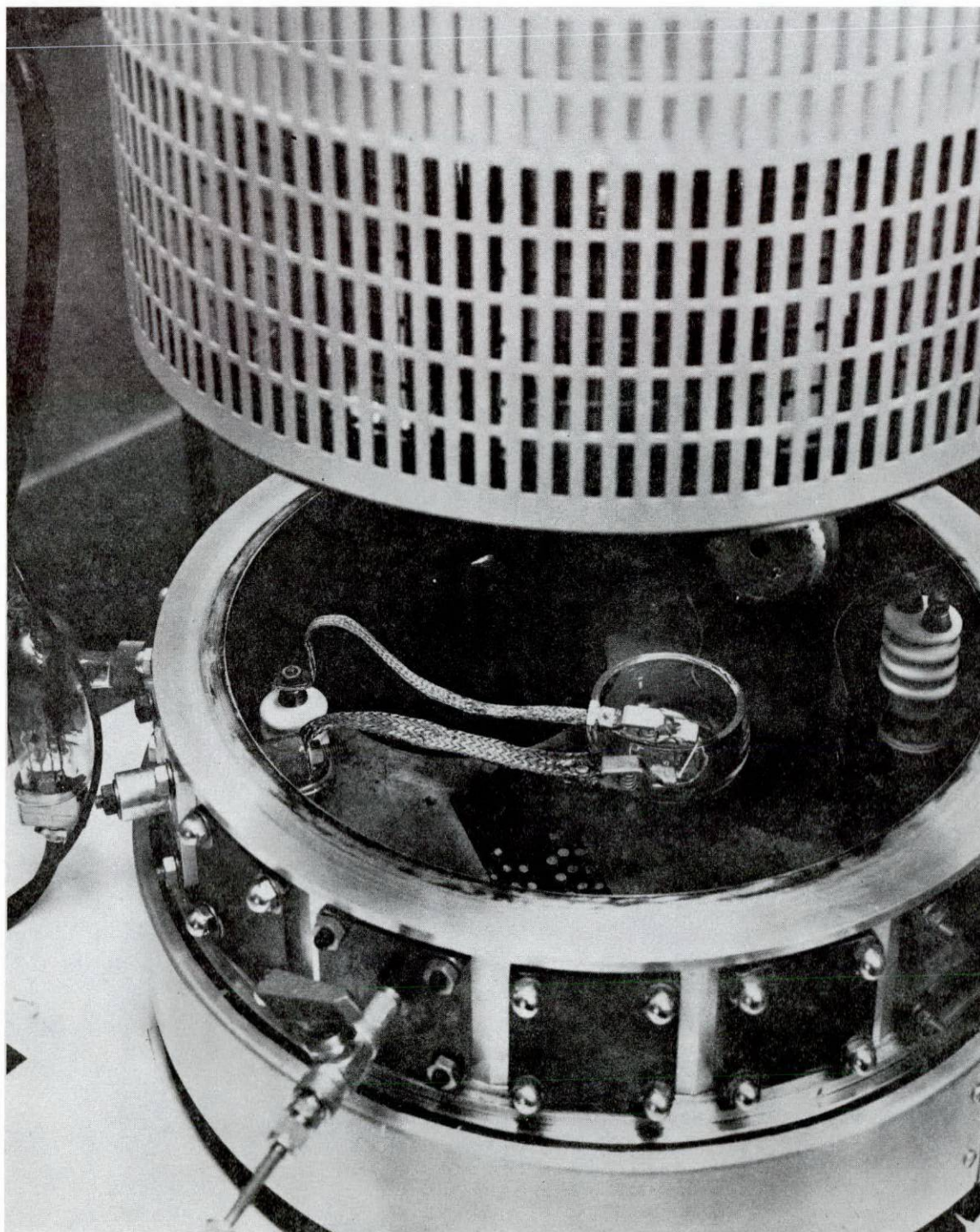
Photograph V



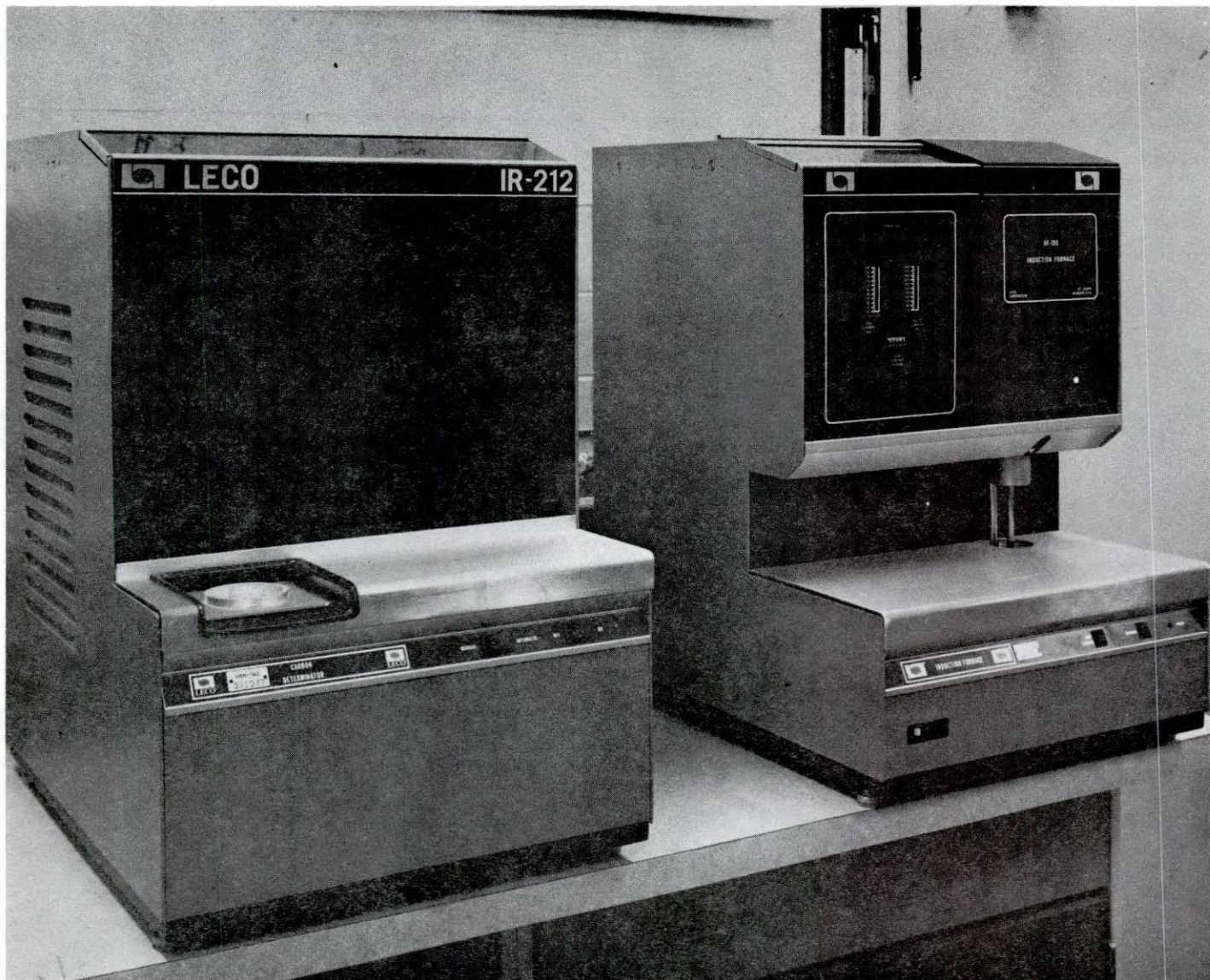
Photograph VI



Photograph VII



Photograph VIII



Results:

Data generated in the NAC TR-2330 Study and the RADC Correlation Study on Lead Finishes substantiate that the "Hot Iron Test", the "Hot Oil Test", and the "Carbon Determination Test" all exhibit precision, but the "High Vacuum Melt Test" and the "Mass Spectrometry Test", although feasible, have not as yet been used enough to validly demonstrate the same precision.

Data from two sub-matrixes (solderability and organic content testing) of the RADC Study revealed some significant correlations. Outgassing and organic content results from the five test methods were found to track very accurately to actual device solderability. In addition, empirical results from the test methods can be easily used to identify and distinguish generic matt tins with negligible organics from the higher organic deposits derived from bright tin or certain tin-lead plates.

The experimental devices were 16 lead cerflats assembled by a major integrated circuit manufacturer. The devices were subdivided into four plating lots and each lot was plated with a different deposit within the 300-500 micro-inch thickness range. A fused version of two deposits was also evaluated.

The solderability evaluation was done in compliance to the current revision of MIL-STD-883B, Method 2003.2. Units were baked at $165^{\circ}\text{C} + 5^{\circ}\text{C}$ and tested at predetermined time intervals until failure occurred. Results for solderability and organic level testing are tabulated in Table II.

The solderability performance spread between the higher organic finishes (A & B) and the lower organic finishes (C & D) tracked consistently with the order of magnitude spread in percent carbon contents of the deposits. The tin/lead plate had extremely poor solderability in relationship to comparable percent carbon in bright tin. This correlation indicates that another mechanism such as lead segregation during temperature burn-in may also be contributing to failure.

The fused version of the bright tin finish showed slight improvement of solderability performance in comparison to the non-fused finish. In high organic finishes, however, some benefit appears to be derived by subjecting the deposit to elevated temperatures (above 232°C). The contrary was found to be the case in lower organic matt finishes. The fused (reflowed) version of the proprietary matt tin finish showed degradation of solderability by a factor of six in comparison to the non-fused finish (see Table II).

TABLE II

<u>Lead Finish</u>	<u>Solderability Results Hours To First Failure</u>	<u>Outgassing Results Leads Outgassing/ Leads Tested</u>	<u>% Carbon In Plated Deposit</u>
A. Tin/Lead Plate	24	80/80	0.1366
B. Bright Tin (as plated)	168	80/80	0.157
*Fused Version	192	N/A	N/A
C. Proprietary Matt (New bath - 3 months)	1000+	12/80	0.0125
*Fused Version	180	N/A	N/A
D. Generic Matt (old bath - 2 yrs.)	1000+	16/70	0.0177

Summary:

Basic Precept:

- * Electrolytic tin plating processes have been developed which yield deposits of low outgassing levels.

Developmental Principles:

- * Generic matt electroplated tins remain solderable ten times longer than generic bright electroplated tins when stressed at the same elevated temperature.
- * Intermetallic compound formation, occluded carbon concentration and, to a minor extent, oxide growth interact together to degrade solderability.
- * The solderability failure mechanism for generic matt tin was found to be mainly intermetallic formation at the base interface with, to a minor extent, surface oxide growth as a co-contributor.
- * The solderability failure mechanism for generic bright tin was found to be co-deposited organic compounds which volatilize during high temperature exposures.
- * Deposit analyses show four to five times higher carbon in generic bright tin versus generic matt tin.

- * Tests have been developed which are capable of determining conformance to requirements for low outgassing electrolytic tin lead finishes.
- * An accelerated manufacturing solderability test at 10 hours/200°C, 20 hours/175°C, or 48 hours/150°C should ensure solderability at 168 hours/125°C (a standard military burn-in).

Conclusions:

- * Fusing before burn-in affects solderability time in two ways:
 1. Degrades generic matt tins
 2. Improves generic bright tins somewhat
- * The most eloquent statement of the validity of this investigation is the correlation of test results in Table III.

NOTICE

Publication of this report does not constitute approval by the U.S. Navy of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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TABLE III CORRELATION OF TEST RESULTS

STUDY IDENTITY AND AS PLATED LEAD FINISH	SOLDERABILITY RESULTS HRS. TO FIRST FAILURE AT 165° ± 5°C	PERCENT CARBON IN PLATED FINISH	OUTGASSING RESULTS		HIGH VACUUM MELT TEST PERCENT PRESSURE INCREASE	MASS SPECTROMETRY 650°F FOR FIVE MIN.		
			LEADS OUTGASSING/ LEADS TESTED	HOT IRON HOT OIL		μg/ g	cm/ ³ g	VOL. OUT GASSING/ VOL. TIN
AES *G MATT TIN	220	0.036	-	-	-	-	-	-
AES **P BRIGHT TIN	13	0.165	-	-	-	-	-	-
2330 G MATT TIN	-	-	2/80	63/80	-	20.5	0.23	0.8
2330 G MATT TIN	-	-	10/80	64/80	-	34.0	0.34	1.2
2330 P MATT TIN	-	-	0/80	26/48	31	-	-	-
2330 P BRIGHT TIN	-	-	73/80	80/80	-	-	-	-
2330 P BRIGHT TIN	-	0.124	80/80	80/80	224	201	1.60	5.7
2330 P BRIGHT TIN	-	0.041	61/80	73/80	71	52.3	0.40	1.4
RADC P TIN-LEAD	24	0.137	-	80/80	-	-	-	-
RADC P BRIGHT TIN	168	0.157	-	80/80	-	-	-	-
ABOVE FUSED	192	N/A	-	N/A	-	-	-	-
RADC P MATT TIN	1000+	0.013	-	12/80	-	-	-	-
ABOVE FUSED	180	N/A	-	N/A	-	-	-	-
RADC G MATT TIN	1000+	0.018	-	16/70	-	-	-	-

*G = GENERIC; **P = PROPRIETARY

