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Session G: Electronics III

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Electronics III
Session G

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Electronics III
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CYCLIC VOLTAMMETRIC STRIPPING ANALYSIS FOR USE IN THE PCB INDUSTRY

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Abstract

The Cyclic Voltammetric Stripping (CVS) analysis technique has become an important analytical tool for the control of various plating baths used in the PCB industry. This paper presents procedures and concrete examples along with some DO's and DON'Ts for the control of copper, solder and nickel baths. An emphasis will be placed on the role which CVS can play as an effective method for the early detection and prevention of potential problems and a useful troubleshooting tool.

Introduction

The plating of quality PCB's requires that many distinct yet interrelated factors be closely monitored. The Cyclic Voltammetric Stripping (CVS) technique [1] has emerged as an accurate and efficient method for the control of the effective additive concentration, degree of organic contamination and overall bath performance, in various stages of the plating process. The plating of acid copper will be used as an example with additional references to solder and nickel baths.

Principles of CVS Technique

The analysis of an organic species is accomplished by examining their effect on the deposition rate of the metal (Cu, Ni,....) onto a platinum rotating electrode. The potential of the electrode is cycled so that the metal in solution is alternately plated onto the platinum surface and then stripped back into solution. The charge required to strip the metal off the platinum surface is measured, and called the Area Rotating (A_R) value. It is this parameter which is then related to the effective additive concentration and the performance of the bath. The relationship between the A_R value and additive concentration can be seen by analyzing several graphs shown in Figures 1-3.

The calibration curve, Fig. 1 is generated by plotting the A_R values as a function of additive concentration. This yields an overall qualitative description of the behavior of the additive. This curve, generated for SAS-type additives shows two distinct regions - one at a low additive concentration where the A_R values are sharply decreasing, and a second portion where

the A_R values are gradually increasing. The first region is due to the small concentration of wetting agents which cause a polarization of the copper plating. The A_R values decrease as the "suppressors" are added until saturation has occurred. The second region is caused by the brightener component of the additive. Since the suppressors and brighteners are active at distinctly different concentrations, they can be analyzed independently.

A technique called Dilution Titration [2] is used for wetter analysis and the Linear Approximation Technique (LAT) [3] for brightener analysis. These techniques have been reviewed in earlier papers [4-5].

Let us now discuss a few stages in the plating process where CVS is used with great success. These processes are the analysis of incoming batches of additives, control of additives during the plating process and the monitoring of contamination and carbon treatment process.

1. Using CVS to analyze incoming additives

One of the first important factors to be considered is the activity of the additive. Earlier studies have shown large discrepancies in the Cyclic Voltammetric Stripping behavior of various additive batches (Fig.4). In addition, organic additives deteriorate at various rates while on the shelf and thus lose their effectiveness. Furthermore, entire batches of additives may become contaminated during manufacturing, testing or packaging. Therefore, in order to avoid possible problems, it is a good practice to verify the quality and integrity of the additive prior to its use in the plating bath. This can be accomplished quickly and accurately using the CVS technique. Manufacturers, in an effort to reduce batch-to-batch variations have been using the CVS technique as their quality control tool and the results have been promising.

A calibration curve (Fig. 1-2) is a graphic representation the relationship between the active additive concentration and the rate of metal deposition on the platinum surface. The curve generated is dependent on the ratio of components of the additive and their relative activities. The additive sample can be analyzed as the shape of this curve should be predictable and reproducible, both from run to run and from one additive batch to another. In their strive for perfection, manufacturers are, from time to time, changing and improving their additives or their components, thus creating a "family" of additives, each with different composition and behavior. The CVS calibration curve can be used to distinguish between the activities of modified additives, and help the user to maintain a properly functioning bath.

As mentioned earlier, the dilution titration method (Fig. 3) is used to determine the activity of the wetting agent component of the additive. Diluted additive is added to pure stock solution and its concentration corresponding to a 50% decrease in the initial A_R value is measured. This concentration, called a 'z' value, is a function of the wetting agent activity and should again be reproducible both from run to run and one batch to another. The lower the 'z' value, the more active are the wetting agents in this batch of additive.

From the above descriptions, it is clear that the notion of an additive standard deserves some mention. For analytical purposes, a single, synthetic compound generating a highly reproducible CVS response would be ideal. However, a more realistic alternative would be a proprietary standard supplied by each manufacturer. Cooperation among major additive manufacturers, instrumentation manufacturers and users is needed in order to establish the practice of supplying either synthetic or proprietary additive standards. Currently, several manufacturers supply standards to select customers and this procedure should be adopted by all. For the analysis of wetting agents, one plausible standard which has been used with success in the past [4] is Polyethylene Glycol (PEG) polymer of a specified molecular weight. Without standards for additive components, it is pointless to compare CVS results obtained using different additives. To perform such a comparison, one needs a standard for the analysis and another standards as far as the quality criteria are concerned.

It is a good laboratory practice to store for future reference a few additive batches for which CVS and quality responses are known. These samples should be used whenever questions about the performance of the instrument or bath arise.

Furthermore, an accurate record-keeping system of batch numbers, z-values and subsequent quality performance will aid in the detection of unacceptable additive lots and will eliminate the deteriorated or contaminated incoming additive as a possible source of plating problems.

2. Control of additive during actual plating process

Before the effect of the additive on the actual plating process can be examined, it is essential that the concentrations of metal, acid and chloride be determined and held constant. It seems rather senseless to be concerned about monitoring the additive use when more fundamental variables are not controlled.

The most fundamental point in the control of plating baths is the correlation between the quality of plating and additive

activity. The actual idea of 'quality' must be defined by the user and varies greatly from user to user. Is visual inspection enough of a quality check or does quality imply passing such tests as solder flow, cross section and tensile strength or elongation? As the demands on the plating quality increase, the acceptable additive activity range becomes much narrower and thus more attention must be paid to the selection of the additive, its concentration and its control.

The achievement of an optimum additive range and its subsequent maintenance requires the cooperation of the user, the additive manufacturer and the manufacturer of the analytical instrumentation. In the past, this cooperation has resulted in modifications to both the additive manufacturer's recommendations as far as bath maintenance is concerned as well as to the CVS technique. Through this cooperation, the user is able to obtain more accurate and reproducible results on a particular type of additive chemistry, leading to better quality and lower down-time.

It is advisable to build a bath history by keeping record of the volume of additive consumed, CVS results, manufacturer's recommendation and plating quality. Using the manufacturer's recommended additive concentration range as a starting point, the addition rate of the additive should be modified as needed to achieve the desired plating quality. Once this is obtained, the activity can be maintained using CVS analysis. The actual addition rate arrived upon can be higher or lower than the recommended start-up amount.

One such case is a facility in New Jersey (Fig. 5-7) [6] which was experiencing plating quality problems. CVS results indicated severe additive overdosing of the plating bath. By working with the additive manufacturer, the brightener addition rate was decreased by a factor of 4 from the recommended starting amount. This resulted in a decrease in the rejection rate from 3% to less than .25% while achieving optimum plating quality. The actual additive concentration needed is facility-dependent and depends on such factors as agitation, current-density, type of boards and anodes, temperature and anode/cathode ratio. It is therefore necessary to experiment with addition rates (starting with the recommended values) and optimize them for given conditions.

Brightener concentration is usually mentioned as the major cause of plating problems. The CVS technique can eliminate incorrect additive use as a source of problems and thus takes away the guess work out of maintaining a proper level of additive in the bath at all times. This enables the plater to concentrate on eliminating other sources of problems.

3. CVS and the Carbon Treatment process

The last step in assuring plating quality is bath maintenance and carbon treatment. Since the CVS technique is sensitive to oxidizable contamination, the CVS readings correlated to a bath history provide an accurate measure on which to base the frequency of carbon treatment. The ability to efficiently schedule the carbon treatment process minimizes bath downtime and reduces loss. Previous work [8] has shown that the use of CVS in determining proper carbon treatment intervals resulted in a three-fold decrease in the contaminant levels. Besides serving as a scheduling aid, the CVS technique can evaluate the success or failure of the treatment. A properly treated bath should yield similar CVS results to those of a virgin stock solution. If these readings do not agree, the process was not effective and the source of the problem should be investigated.

A question can be asked at this point: Why should I worry about removing every single drop of additive if I have to put it right back in?

The answer is simple. Since CVS is so highly sensitive to additives, we can use them as an indicator of complete carbon treatment. If all of the additives were not removed, what else was left in the solution? Field experiences have shown that contaminants decrease the activity of brighteners, thus requiring increased addition rates of additive. This results in increased manufacturing costs as well as further increasing the contamination level while decreasing the overall plating quality.

Several cases outlining problems which can be detected by CVS were previously described in literature [7]. In one case, high contamination levels were detected in a bath after treatment. Re-filtering using a fresh cartridge produced the same, or worse, CVS results. The source of the problem turned out to be that the filter supplier had switched manufacturers and contaminants were leaching from the new filters into the solution during the filtration process. In another case [8], contamination has been traced to carbon, which was not of sufficiently high quality, causing leach-out of contaminants. Anodes of different grain sizes, photoresists, inefficient rinsing process and other problems can also cause contamination of plating baths.

In all cases, CVS results were instrumental in detecting the problem and locating the source.

4. Further Applications of CVS technology

Although CVS was originally used to analyze copper pyrophosphate baths, procedures have been developed for applications to other plating baths, such as acid copper, tin, solder and nickel. Several manufacturers have made available CVS procedures for additives in fluoroborate and non-fluoroborate solder baths [9], and an increasing number of CVS users are presently adding the solder bath monitoring to required procedures. CVS procedures have also been published for determination of Class 1 brighteners (e.g. Saccharin) in Nickel baths (Fig. 8) [10], and for additives in Tin plating baths (Fig. 9) [5].

So extensive has been the progress in CVS application to plating bath control that work has started at some facilities to include CVS in closed-loop, "hands-off" manufacturing processes. For laboratory applications, a semi-automated system is now available to increase the through-put of the lab and decrease guesswork.

Conclusion

The CVS technique has become a important method for plating bath control due to its wide range of analytical applications and direct correlation of results to additive activity in solution. The ability of CVS to detect plating problems early on and help prevent their reoccurrence make it a valuable tool for the PCB industry where tight control is essential, resulting in monetary savings and increased quality.

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9. J. McCaskie, "Electroanalytical Methods for Process Control of Printed Circuit Plating: Copper and Solder", Proceedings of 74th AESF Technical Conference, Sur/Fin, July 1987, Chicago, IL.

10. P. Bratin, D. Cupolo and W. Ward, "Application of CVS to the Analysis of Organic Additives in Nickel Plating Baths", Proceedings of the 72nd AES Technical Conference, Sur/Fin, June 1985, Detroit, MI.

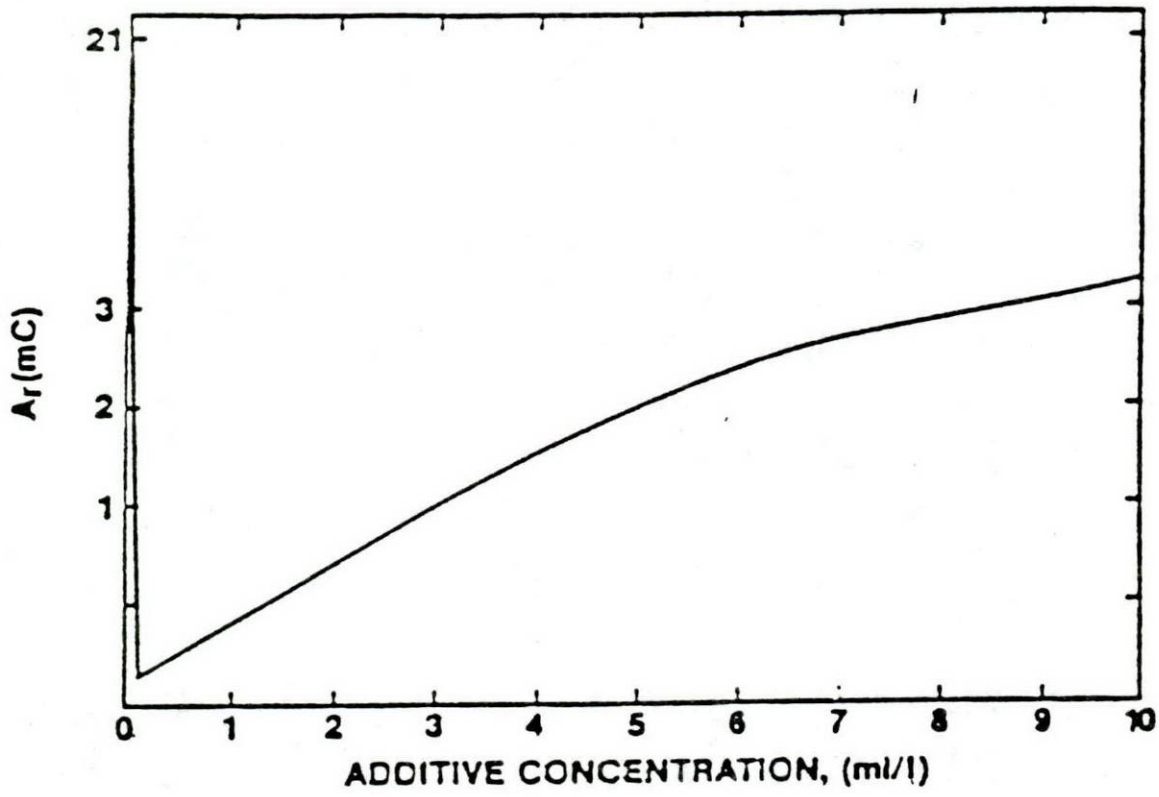

Fig. 1 Typical CVS calibration curve for SAS-type additives in acid copper plating bath (scan rate = 100mV/S, rotation rate = 500RPM, scan limits = -0.2 to 1.6V).

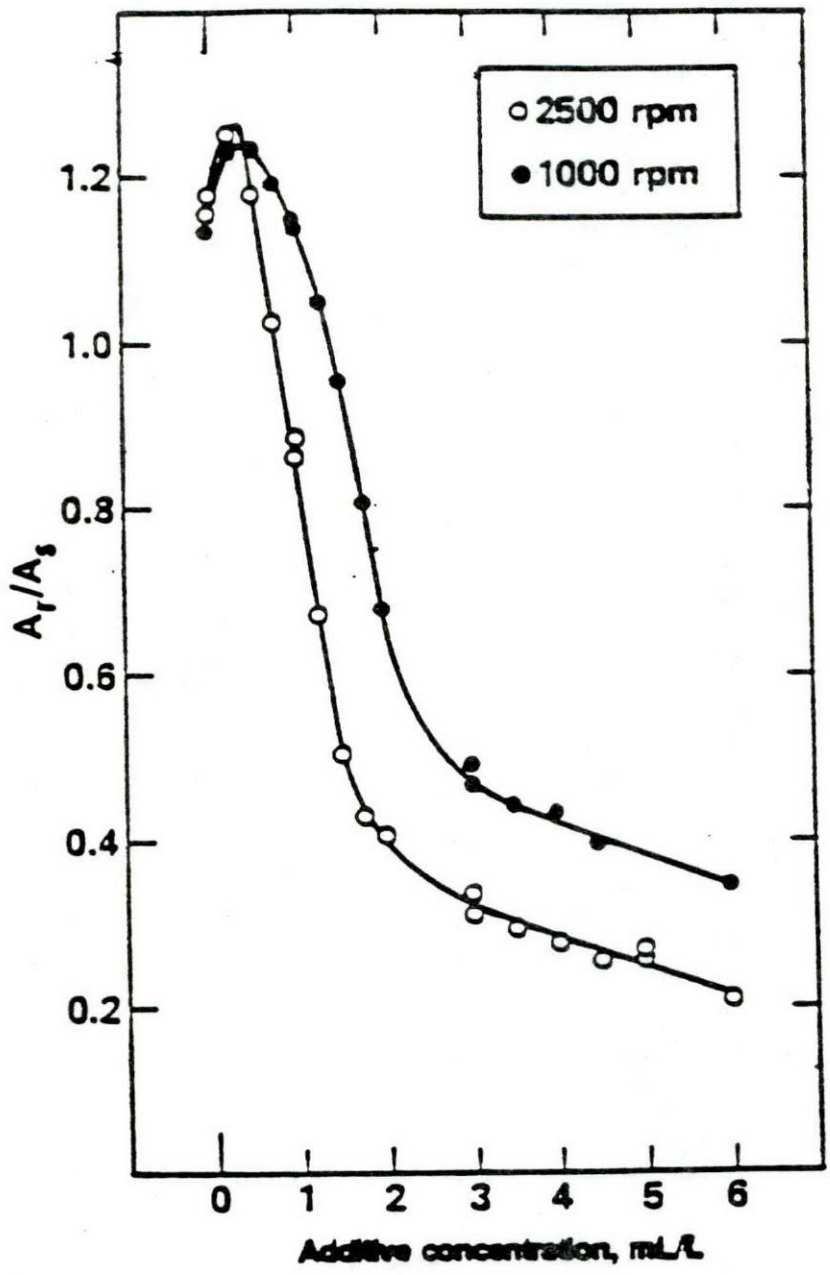

Fig. 2 Typical calibration curve for PES-type additives in acid copper sulfate plating bath (scan rate = 100mV/S, scan limits = -0.15 to 1.9V).

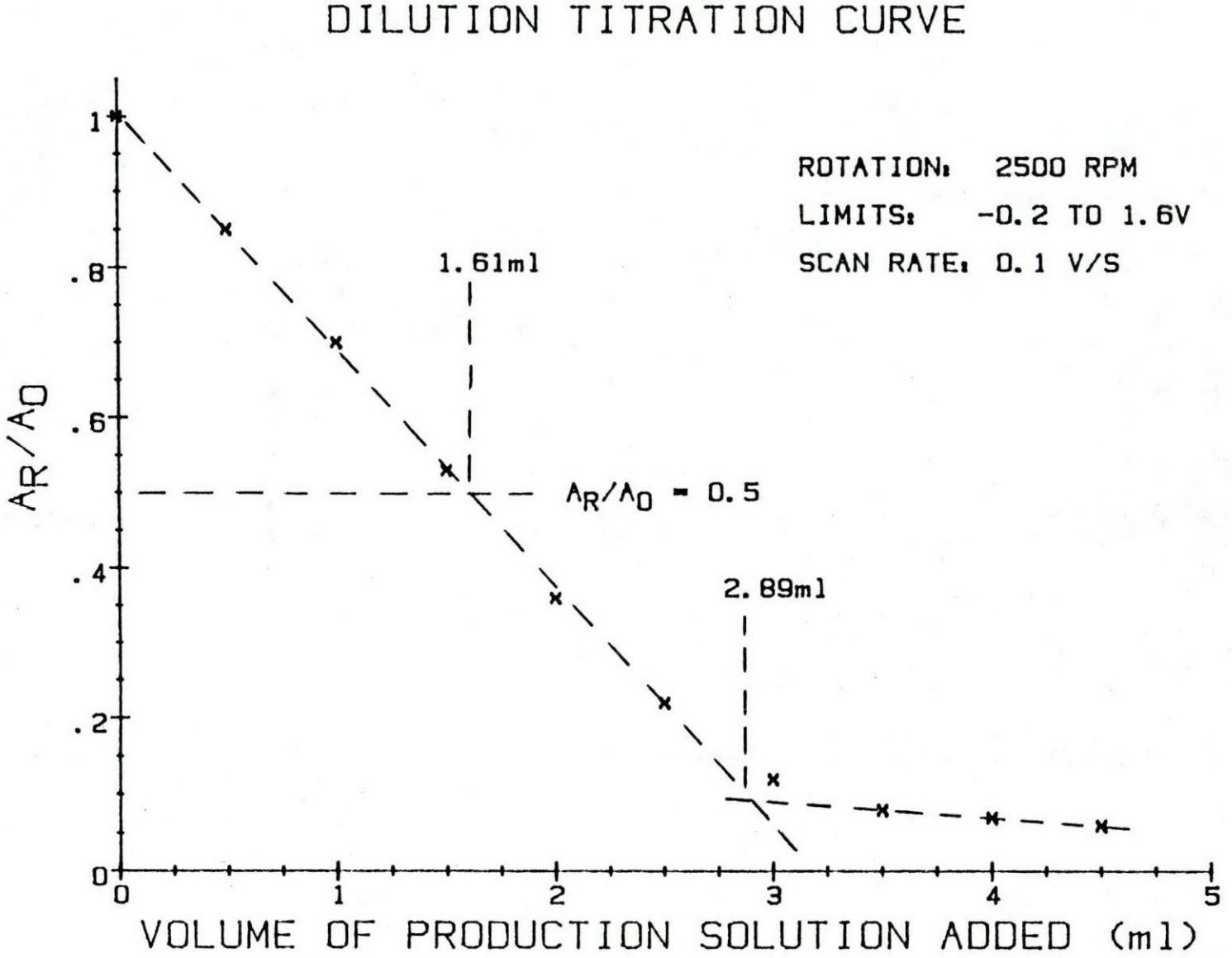
DILUTION TITRATION CURVE
ROTATION: 2500 RPM
LIMITS: -0.2 TO 1.6V
SCAN RATE: 0.1 V/S
1.61ml
2.89ml
$A_R/A_O = 0.5$
A_R/A_O
VOLUME OF PRODUCTION SOLUTION ADDED (ml)
0
.2
.4
.6
.8
1
0
1
2
3
4
5

Fig. 3

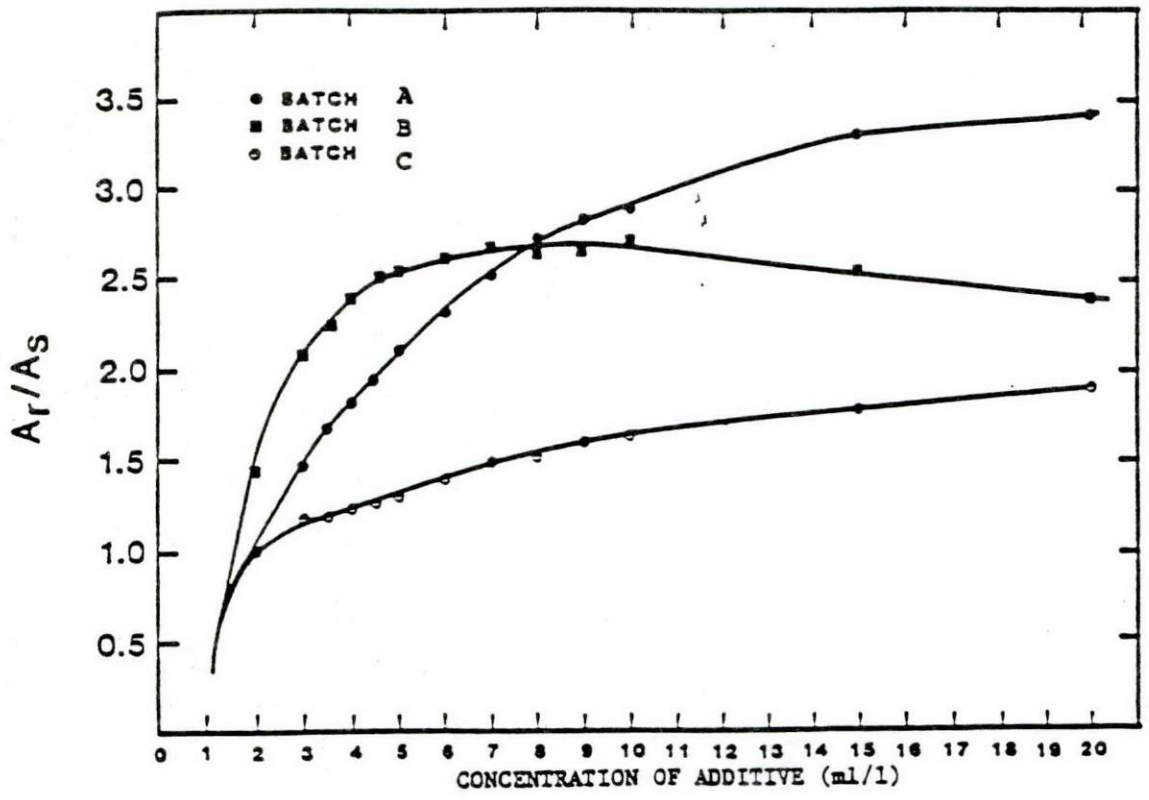

Fig. 4 Voltammetric comparison of three batches of acid copper sulfate proprietary additive, showing large variations in activity.

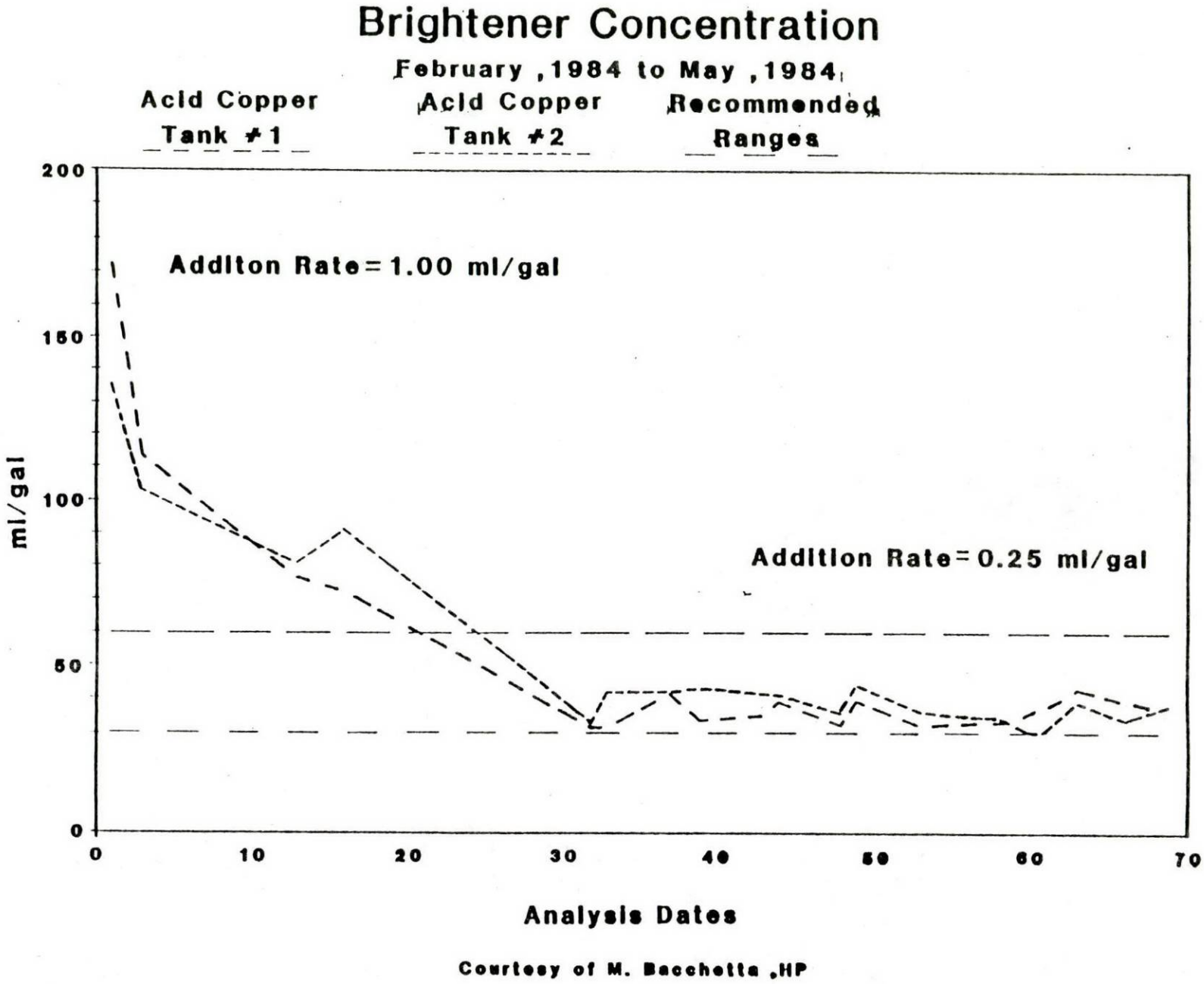
Brightener Concentration
February ,1984 to May ,1984
Acid Copper Tank #1
Acid Copper Tank #2
Recommended Ranges
Addiion Rate=1.00 ml/gal
Addition Rate=0.25 ml/gal
ml/gal
200
150
100
50
0
0
10
20
30
40
50
60
70
Analysis Dates
Courtesy of M. Bacchetta ,HP

Fig. 5

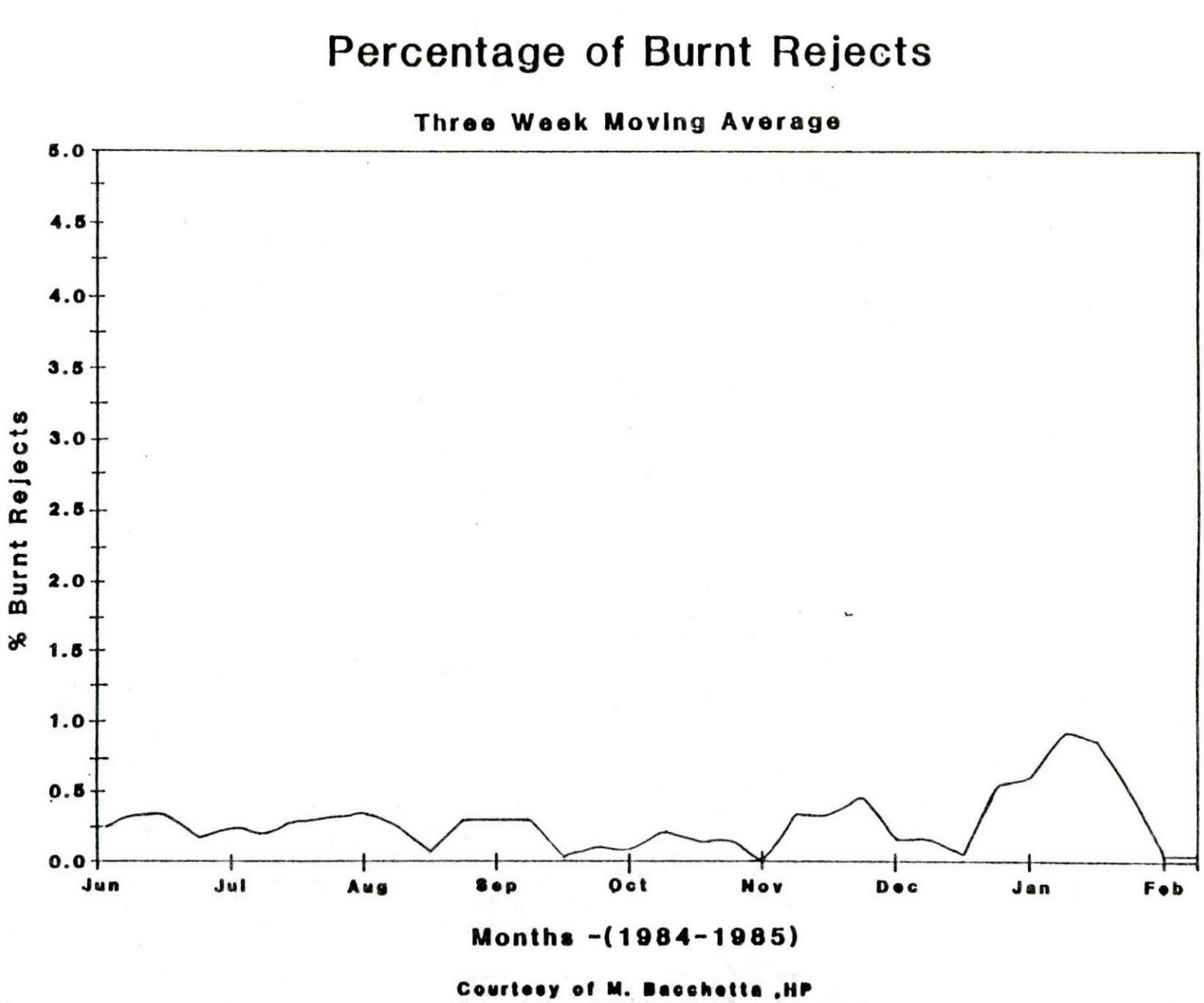
Percentage of Burnt Rejects
Three Week Moving Average
% Burnt Rejects
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Jan
Feb
Months -(1984-1985)
Courtesy of M. Bacchetta ,HP

Fig. 6

Percentage of Burnt Rejects

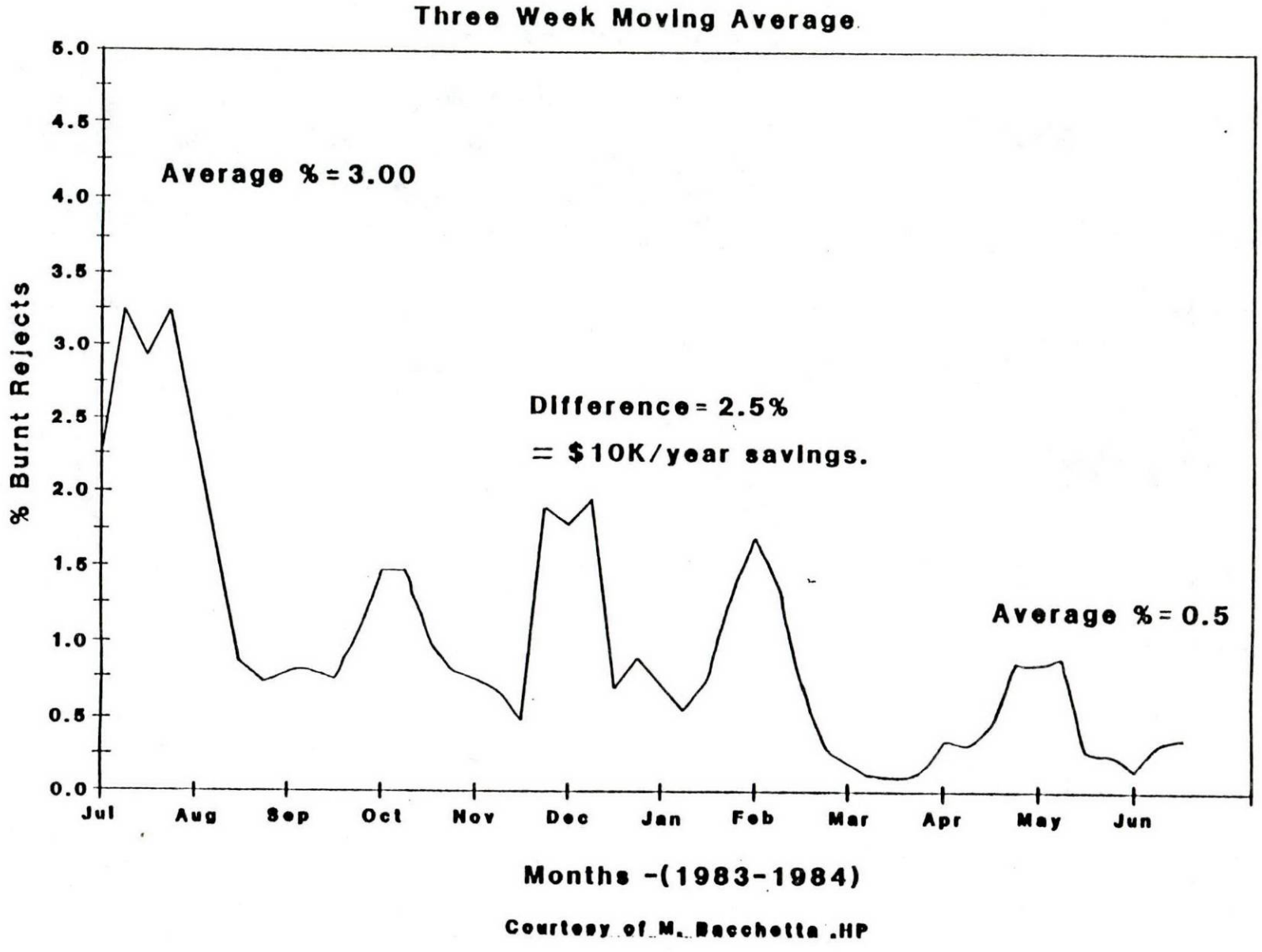

Fig. 7

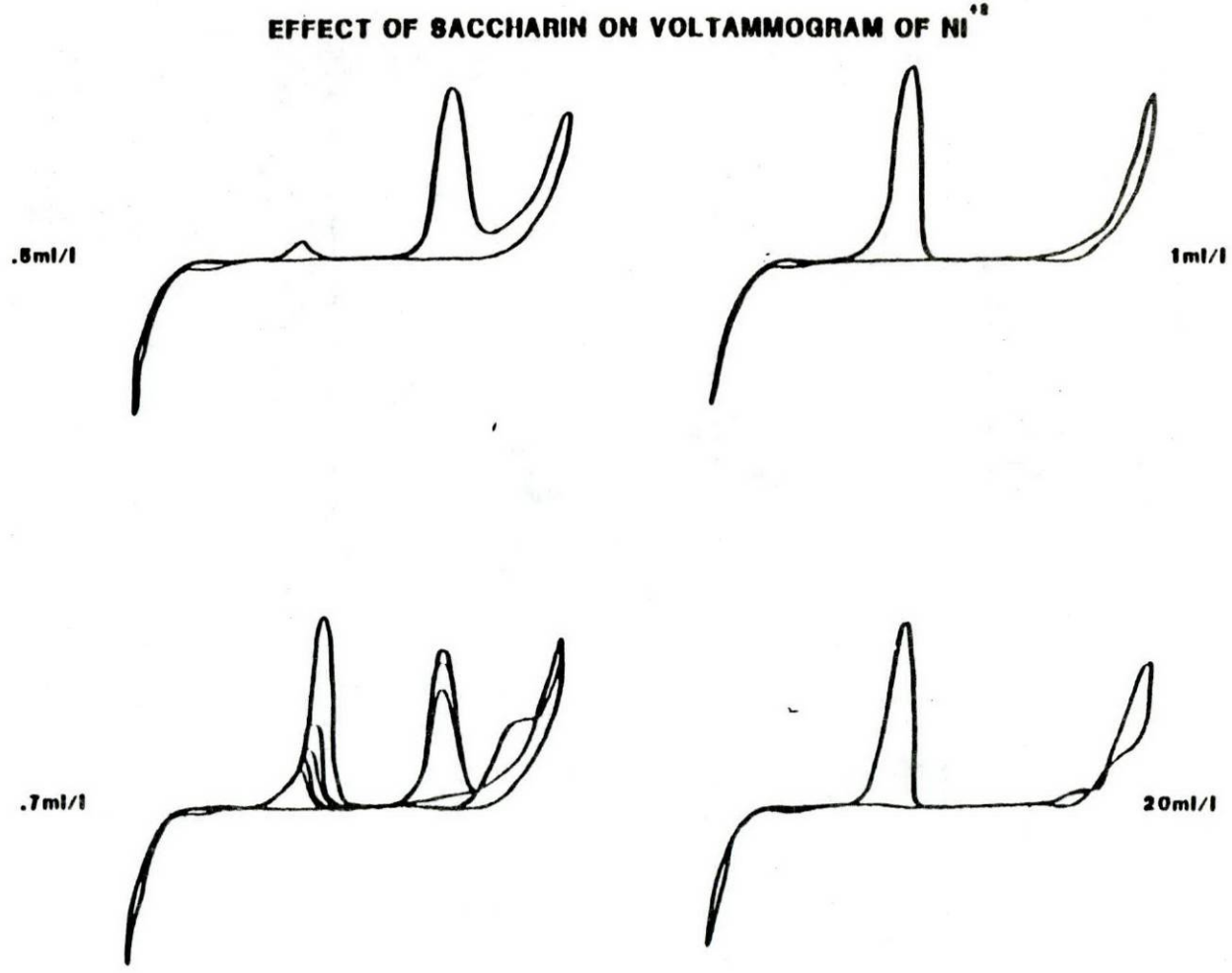

Fig. 8 Effect of saccharin-containing additive on the voltammogram of Watt's nickel plating bath (Pt rotating electrode, scan limits = -1.20 to 1.75V vs SCE, scan rate = 100mV/S, rotation rate = 2500RPM).

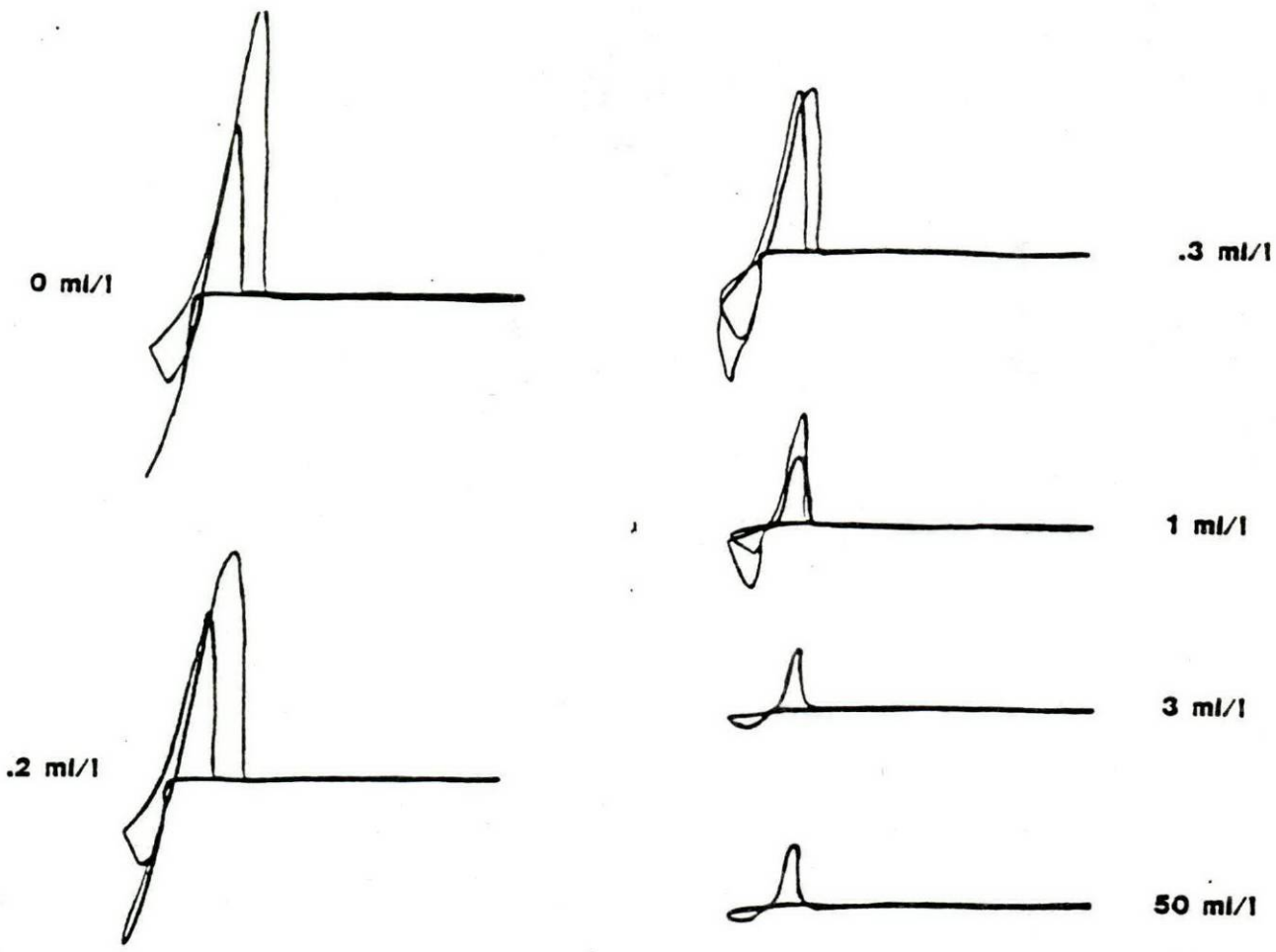

Fig. 9 Effect of the make-up component of the proprietary additive on the voltammogram of the acid tin sulfate bath (Pt electrode) scan limits = -0.55 to 0.2V vs SCE, scan rate = 100mV/S, rotation rate = 2500RPM

G-2

Electronics III
Session G

Multi-Layer Processing: Oxide Control

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MULTI-LAYER PROCESSING: OXIDE CONTROL

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Introduction:

During the infancy of multi-layer technology, the engineers attempted to laminate bare copper to a glass weave material that is impregnated with a partially cured resin. The adhesion of bare copper to "B-STAGE PREPREG" was extremely poor, yielding peel strength tests less than 2# per inch.

Subsequently, the engineers felt that by changing the surface topography of the smooth copper surface to a mechanically or chemically roughened surface that peel strength test results would increase. As expected, peel strengths did increase, but only slightly. The copper surface was roughened, but still not ideal for copper-prepreg adhesion.

What was needed was a unique approach to roughening the copper surface. Rather than just mechanically and/or chemically roughening the copper surface, chemically changing the copper surface to a form that would have better adhesive qualities toward prepreg was attempted.

The technology for this first attempt to chemically change the topography of the copper surface was borrowed from the Metal Finishing industry. For many years the Metal Finishing industry employed an oxidizing process to produce a functional/ decorative finish for copper and brass. This black oxidizing process was applied to the innerlayers of the multilayer booklet. The results were quite favorable, hence, the surface topography was better suited for copper-prepreg adhesion. After years of modifications, present day black oxide processes produce peel strengths upwards of 6# per inch.

As the multilayer segment of the PC industry developed, the black oxide process became the center of attention. Two new requirements were placed upon the oxidizing process. First, the black oxide process needed to be modified to obtain higher peel strengths for FR-4 material. Secondly, and more importantly, the oxidizing process needed to have the ability to bond successfully to dielectric materials other than epoxy.

Research and development chemists and engineers discovered that by refining the black oxide formula, both of these requirements could be met. This chemical re-formulation produced an oxide coating different than the velvety black coating that was characteristic of the black oxide bath. This new oxide was bronze

to dark brown in color, and is referred to as "BROWN" oxide. This brown oxide coating produced peel strengths in the range of 9# to 12# per inch for epoxy dielectric materials and 2# to 4# per inch for polyimide dielectric materials. Refer to Table #1 for a comparison between bonding techniques and peel strengths for FR-4 and polyimide dielectric materials. Therefore, due to the ingenuity of the early multilayer engineers and the increased requirements placed upon the oxide process, the trend towards miniaturization via multilayer printed wiring boards has become feasible. The multilayer manufacturers have obtained their goal to produce a strong, heat-resistant bond between copper circuitry and B-STAGE prepreg.

Oxide coatings also have other advantages besides producing a strong, heat resistant bond between copper circuitry and B-STAGE prepreg.[1] A second advantage is the passivation of the copper surface.[1] The oxide process produces a fully oxidized surface of cupric oxide (CuO). Therefore, during the lamination process the copper is not available to react under the heat and pressure cycling to produce disadvantageous gases. Trapped gases, including water vapor, would deter adhesion of the copper circuitry to the prepreg resulting in delamination. Finally, the other advantage is that the oxide coating is easily applied. Although the oxide line may be lengthy, it does not require expensive, specialized equipment nor specialized personnel to produce properly coated innerlayers.

Basic Oxide Process:

A typical oxide line appears as Figure #1. The requirements for this line are as follows:

1. Alkaline Cleaner

This step is designed to remove heavy soils and dirt from the innerlayers. It should also remove residual resist debris that may still be present on the innerlayers after resist stripping.

2. Acid Cleaner/Neutralizer

This step is designed to remove light soils and dirt while neutralizing any residual alkaline cleaner still present on the innerlayers by the previous rinse step. This step should leave the innerlayers very clean so that the following micro-etch step will uniformly etch the copper surface.

3. Micro-Etch

This step is critical for producing a perfectly clean copper surface. It is recommended to micro-etch 50 - 75 microinches from the copper surface to insure residue-free surfaces (no residues from cleaners, adhesion promoters from photoresists, etc.). The

type of etchant is not important, but the innerlayer must be perfectly clean and oxidation-free. Refer to Table #2 for a comparison between micro-etch type and peel strength test results.

4. Pre-Dip

This step is the final preparatory step prior to the oxide bath. It is designed to permit optimal performance of the oxide coating. Presently, the industry uses either an acid or alkaline pre-dip.

A. A 10% by volume HCl solution is used to produce an oxidation-free surface, since pre-oxidation deters uniform oxide coatings. If an acid pre-dip is used, then a subsequent rinse must be employed to minimize neutralization of the alkaline oxide bath by acidic H^+ ions from this type of pre-dip.

B. An alkaline pre-dip (a dilute amount of the alkaline component of the oxide bath or dilute NaOH) is preferred. This pre-dip prevents neutralization of the oxide bath, allows direct immersion into the oxide bath, and increases the speed of the formation of the crystalline oxide coating. The temperature of this bath should be approximately $70^{\circ}F$ and the immersion time should be relatively short to prevent pre-oxidation before entering the oxide bath.

5. Oxide Bath

This bath is formulated as an alkaline oxidizing solution. Upon bath make-up the source of alkalinity normally comes from two sources NaOH (sodium hydroxide) and a buffering agent for highly alkaline solutions. Following use, a third source of alkalinity becomes evident by the reaction of NaOH and CO_2 (carbon dioxide) from the air, i.e. Na_2CO_3 (sodium carbonate).

The basic chemical reaction when an oxide coating is formed on a copper surface is as follows:

$$Cu + NaClO_2 + H_2O \rightarrow 2\ Cu(OH)_2 + NaCl$$

$$2Cu(OH)_2 \rightarrow 2CuO + H_2O$$

$$2\ NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

6. Dry

The final drying step is mandatory to prevent moisture entrapped in the oxide crystal lattice from being introduced into the multilayer booklet.[2] This drying step can be accomplished by a one hour bake at $110^{\circ}C$.

Oxide Processing Considerations:

Although the quality of rinsing in many chemical processes may not be considered critical, proper rinsing between all major process steps in the oxide line is essential to obtain optimum performance of the process. For example, the quality of rinsing between the cleaners, micro-etch, and oxide bath can determine the uniformity of the oxide coating. The quality of rinsing after the oxide bath can influence the adhesive nature of the oxide surface. Failure to remove the alkaline oxide solution from the innerlayers increases the possibility of ionic contamination and subsequent delamination. The final rinse is recommended to be between pH 5 and pH 7 with a temperature of 120° - 130°F. This hot, slightly acidic final rinse neutralizes any alkaline surface condition that may still remain on the innerlayers along with aiding in the drying step.

The control of the oxide bath is similar to other chemical processes. The critical parameter for oxide control are immersion time, bath temperature, and chemical concentration. These three parameters are strongly related to oxide performance and must be scrutinized when optimizing the oxide bath. By varying these parameters, the spectrum of oxide colors and crystalline topography can be generated. Some of the relationships between these parameters and oxide performance will be discussed in the following paragraphs.

A visual comparison of brown and black oxide crystalline topography appears as Figure #2. Brown oxide appears as a short, fine-grained crystal with a larger surface area in comparison to the long, needle-like crystal of black oxide. The brown oxide crystal structure produces superior peel strengths in comparison to the fragile and less thermally-stable black oxide crystal structure. This fact is attributed to the fact that the bonding mechanism of oxide to pre-preg is primarily mechanical in nature, not chemical.[3] Thus, brown oxide is better suited for polyimide dielectrics which receive higher thermal and mechanical (pressure) stresses in lamination and in final board operation.

Brown oxide baths are formulated to operate between 140° to 200°F. Black oxide baths generally operate at approximately 200° F, although low temperature black oxide baths are being developed. For oxide baths, temperature directly influences the rate of crystal formation. The higher the temperature, the less time required to generate a certain weight of cupric oxide.

The relationship between chemical concentration, temperature, and oxide color can be determined from Figures #3 through Figure #6.[4] From these figures, one can also notice that black oxide baths are more alkaline than brown oxide baths.

To optimize the amount of the oxide coating present, a weight

gain experiment is generally performed. Here, a dry oxide coated panel of known dimensions is weighed, the oxide is removed in H^+ (acid), dried, and then reweighed. The weight difference is generally tabulated in grams per ft^2, refer to Table #3. These weight gain values are optimized with respect to prepreg material, exact oxide process employed, lamination cycle, and post-bake cycle. If this procedure is followed, the adhesion of copper oxide to prepreg is maximized (optimized). The effect of the method of oxide application, oxide color, and post-bake cycle versus peel strength tests are tabulated as Tables #4, #5 and #6 respectively. From Table #4 one can notice that the oxide formed from either spray or immersion systems are identical within experimental limitations. Table #5 shows that a brown to dark brown oxide color produces the highest peel strength values. Table #6 shows the importance of optimizing post-bake cycles for FR-4 and polyimide dielectric multilayer booklets.

Conclusions:

Production of good-quality multilayer printed wiring boards can be achieved by:

-producing a fine-grained, non-porous oxide coating that is thermally stable

-employing a proper innerlayer treatment process prior to lamination

-having careful quality control on incoming raw materials (chemicals, pre-preg, etc.)

-determining the optimum lamination and post-bake cycles for the dielectric material used for the booklet

Optimization of the oxidizing process is required to enhance the reliability and performance of multilayer printed wiring boards.

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TABLE #1

COMPARISON OF BONDING TECHNIQUES TO PEEL STRENGTH TESTS

BONDING TECHNIQUE	INNER LAYER DIELECTRIC MATERIAL	
	FR-4	POLYIMIDE
	PEEL STRENGTH (#/INCH)	PEEL STRENGTH (#/INCH)
SMOOTH COPPER	LESS THAN 2	0
CHEMICALLY/MECHANICALLY ROUGHENED COPPER	LESS THAN 3	0
BLACK OXIDE	4 - 6	LESS THAN 1
BROWN OXIDE	9 - 12	2 - 4

TABLE #2

PEEL STRENGTH
EFFECT OF PRECLEANING

TYPE OF MICRO-ETCH	PEEL STRENGTH (#/INCH)	
	FR-4	POLYIMIDE
SULFURIC-PEROXIDE	8.7	4.8
CUPRIC CHLORIDE	8.8	4.6
SODIUM PERSULFATE	8.7	4.8

TABLE #3

IMMERSION TIME (MINUTE)	BROWN OXIDE WEIGHT IN GRAMS/FT^2 OF AREA	BLACK OXIDE WEIGHT IN GRAMS/FT^2 OF AREA
2	0.058	0.44
4	0.08	0.95
8	0.16	1.17
16	0.16	1.35
32	0.16	1.35

TABLE #4

EFFECT OF APPLICATION METHOD ON PEEL STRENGTH

	BROWN OXIDE PEEL STRENGTHS (#/INCH)	
METHOD OF APPLICATION	FR-4	POLYIMIDE
SPRAY	8.7	4.9
IMMERSION	8.8	4.8

TABLE #5

EFFECT OF COLOR ON PEEL STRENGTHS

	PEEL STRENGTH (#/INCH)	
OXIDE COLOR	FR-4	POLYIMIDE
BRONZE	7.1	3.4
BROWN	8.7	4.9
DARK BROWN	8.8	4.8
BLACK	3.2	0.3

TABLE #6

POST BAKE EFFECT ON PEEL STRENGTHS

POST BAKE TIME (MINUTES)	BROWN OXIDE PEEL STRENGTHS (#/INCH) FR-4 300°F	FR-4 350°F	POLYIMIDE 425°F
0	6.0	6.0	0.6
1	6.3	6.5	1.0
2	7.0	6.5	4.0
3	6.6	6.3	4.4
4	6.0	4.8	3.6
5	5.7	5.2	2.4
6	5.0	5.0	2.6

FIGURE #1

TYPICAL OXIDE LINE

ALKALINE CLEAN

RINSE

ACID NEUTRALIZE/CLEAN

RINSE

MICRO-ETCH

RINSE

PREDIP

RINSE (OPTIONAL)

OXIDE

RINSE

RINSE

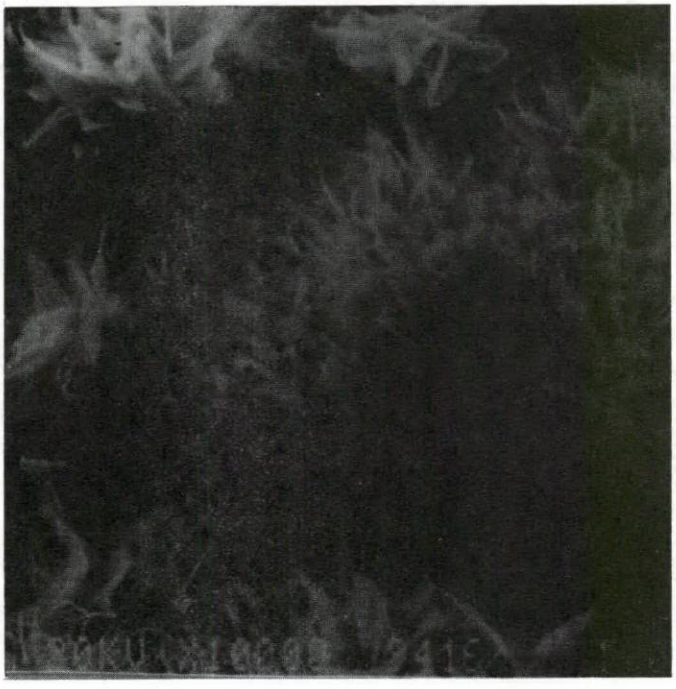
DRY

FIGURE #2

CRYSTAL STRUCTURE COMPARISON BETWEEN
BROWN AND BLACK OXIDE



BROWN OXIDE
CRYSTAL STRUCTURE

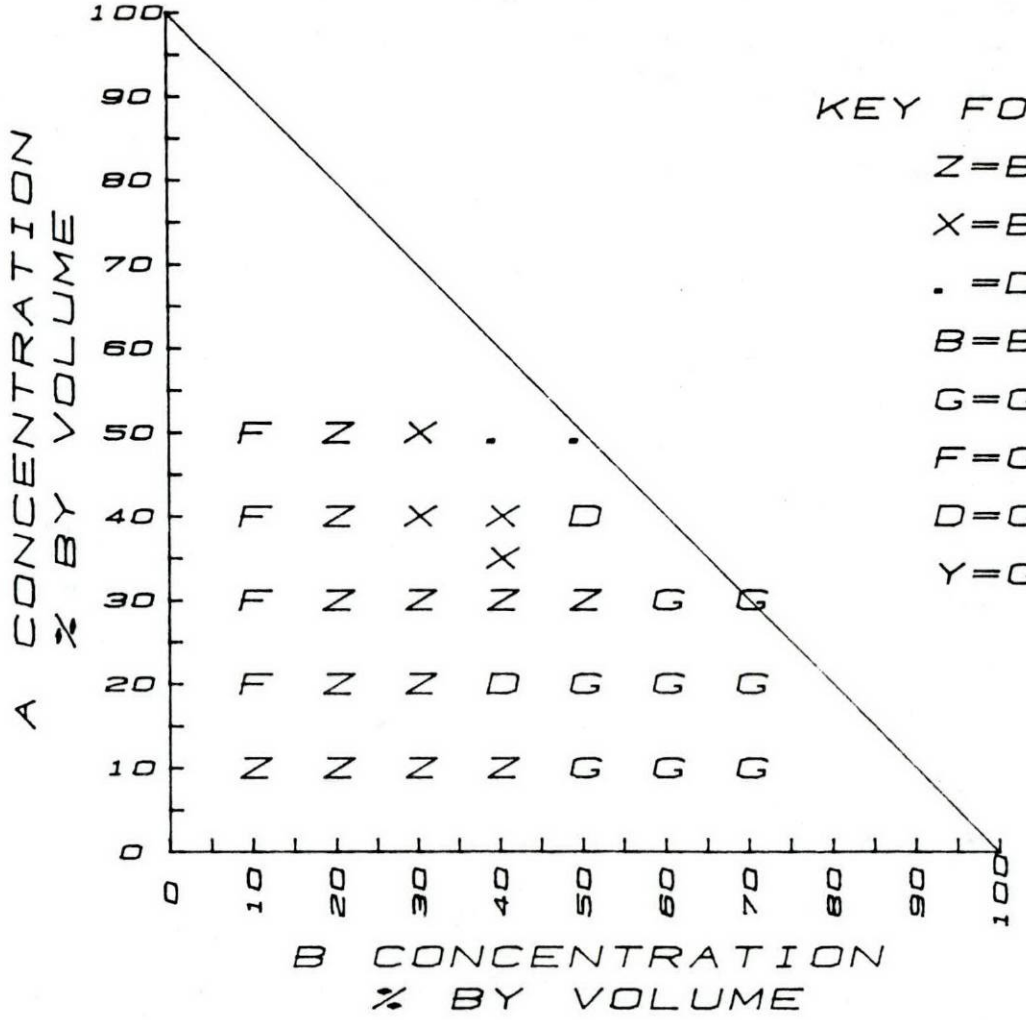


BLACK OXIDE
CRYSTAL STRUCTURE

*SCANNING ELECTRON MICROGRAPHS
AT 10,000 MAGNIFICATION

OXIDE COLOR

TEMPERATURE= 140 F TIME= 3 MINUTES



KEY FOR COATING COLOR

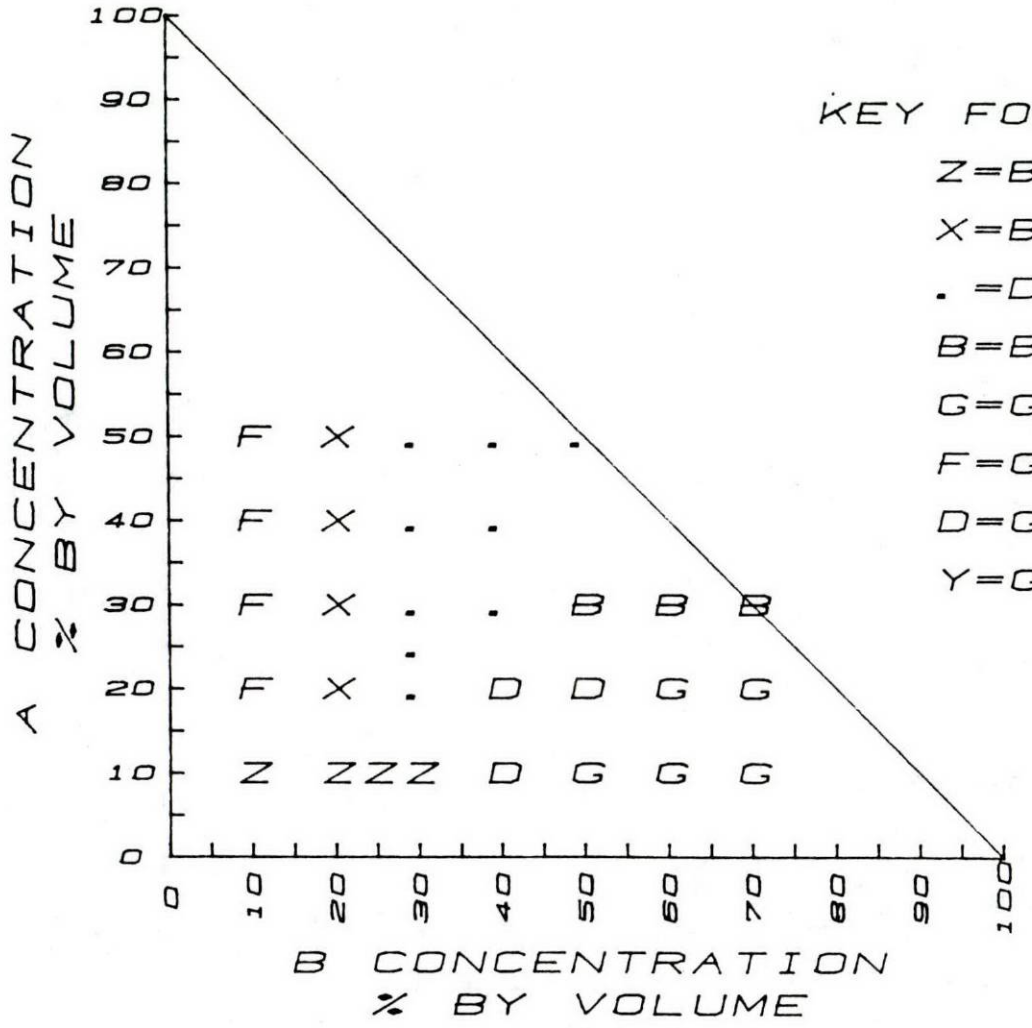
Z=BRONZE
X=BROWN
. =DARK BROWN
B=BLACK
G=GREY
F=GREY/BRONZE
D=GREY/BROWN
Y=GREY/BLACK

A=OXIDIZER
B=ALKALINE

FIGURE #3

OXIDE COLOR

TEMPERATURE= 160 F TIME= 3 MINUTES



KEY FOR COATING COLOR

Z=BRONZE

X=BROWN

. =DARK BROWN

B=BLACK

G=GREY

F=GREY/BRONZE

D=GREY/BROWN

Y=GREY/BLACK

A=OXIDIZER

B=ALKALINE

FIGURE #4

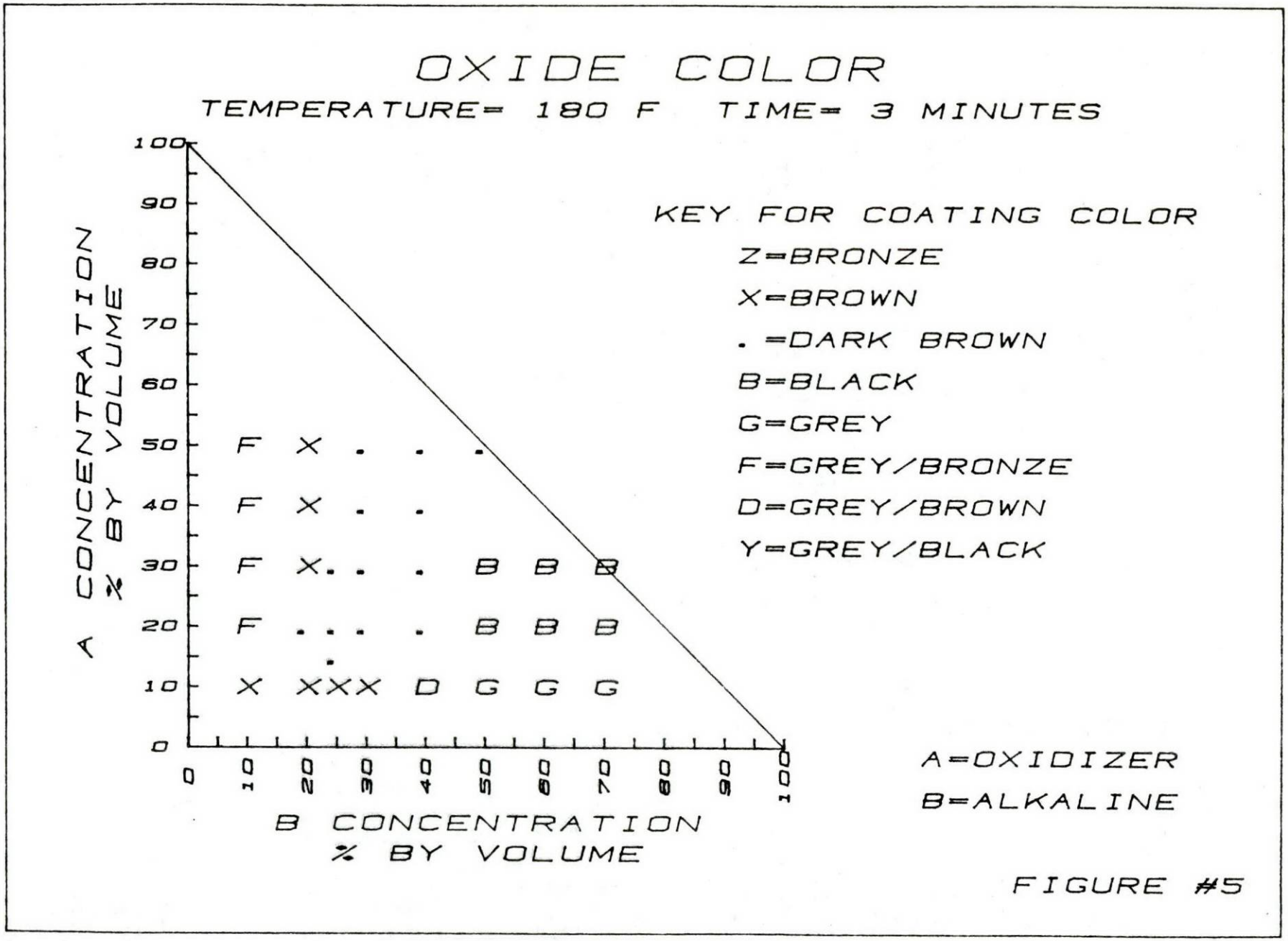
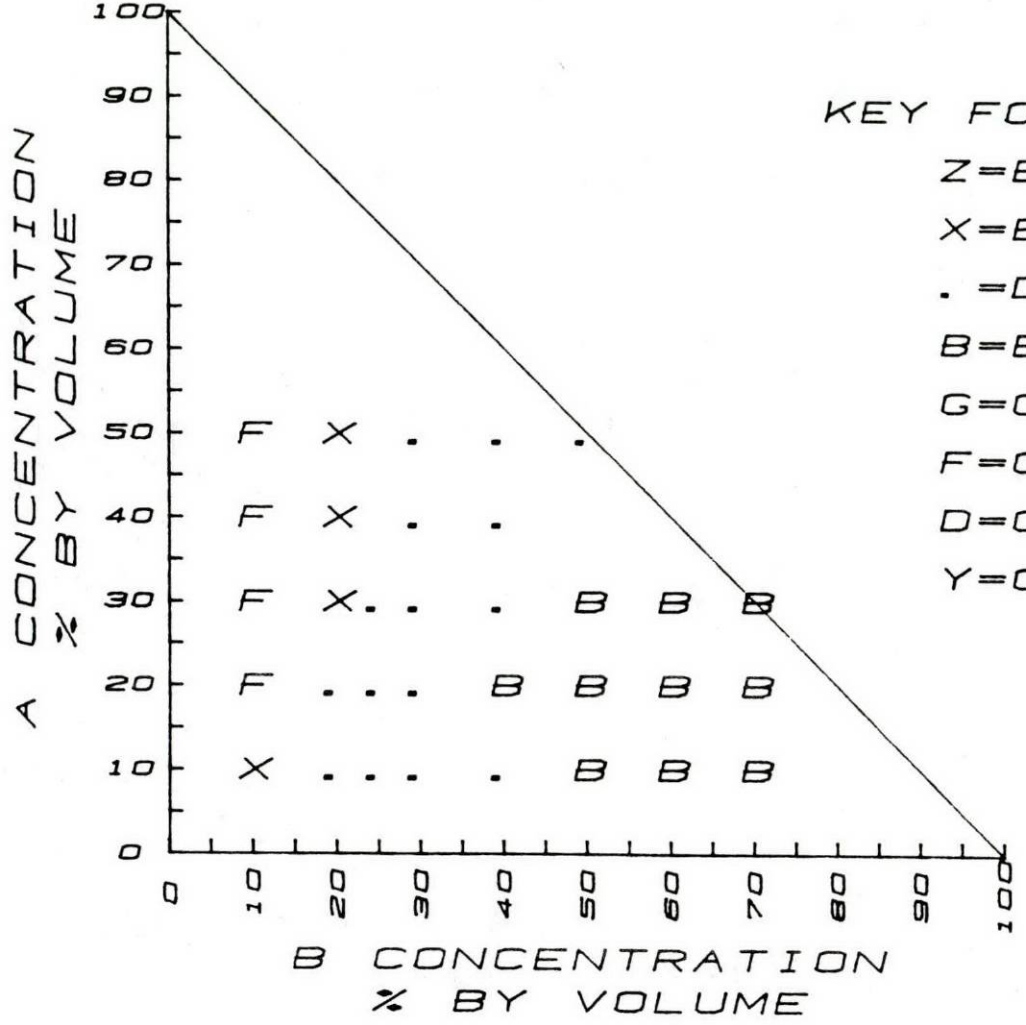

OXIDE COLOR
TEMPERATURE= 180 F TIME= 3 MINUTES
A CONCENTRATION
% BY VOLUME
B CONCENTRATION
% BY VOLUME
0
10
20
30
40
50
60
70
80
90
100
F X . . .
F X . .
F X. . . B B B
F . . . . B B B
.
X XXX D G G G
KEY FOR COATING COLOR
Z=BRONZE
X=BROWN
. =DARK BROWN
B=BLACK
G=GREY
F=GREY/BRONZE
D=GREY/BROWN
Y=GREY/BLACK
A=OXIDIZER
B=ALKALINE

FIGURE #5

OXIDE COLOR

TEMPERATURE= 200 F TIME= 3 MINUTES



KEY FOR COATING COLOR

Z=BRONZE

X=BROWN

. =DARK BROWN

B=BLACK

G=GREY

F=GREY/BRONZE

D=GREY/BROWN

Y=GREY/BLACK

A=OXIDIZER

B=ALKALINE

FIGURE #6

G-3

Electronics III
Session G

Plating-Thru Holes in Printed Wiring Boards Which are Restrained in the X/Y Direction During Thermal Excursions

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PLATING-THRU HOLES IN PRINTED WIRING BOARDS WHICH ARE RESTRAINED IN THE X/Y DIRECTION DURING THERMAL EXCURSIONS

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Hinton "PWB" Engineering
Tucson, AZ

Abstract: Printed wiring boards which contain materials which restrain the planar expansion or shrinkage during deviations from ambient temperature create some unique processing requirements. The restraining material which include Invar planes or quartz and aramid fibers produce construction requirements and a hole-wall structure which make necessary a different set of parameters for processing internal layers and preplate hole preparation for the electroless and electrolytic plating systems. Despite these difficulties, the process systems can be modified so that acceptable registration, interconnects and hole-wall plating can be effected.

INTRODUCTION

Multilayer printed circuit boards which are designed so that their planar coefficient of thermal expansion (CTE) closely matches the coefficient of thermal expansion of surface mounted devices require some different processing techniques than are used in the conventional lead-in-hole printed boards. The most common of the materials employed in the industry to achieve a controlled thermal expansion are; quartz fibers, aramid fibers and copper-clad Invar planes. These materials are used in combination with epoxy resins, polyimide resins and resin impregnated glass cloths. The current methods of; (1) imaging, (2) laminating, (3) drilling, (4) hole prep and desmear, and (5) plating-thru must be modified in order to fabricate acceptable products when these non-conventional materials become a functional part of the board or circuitry. The conditions noted in the following paper were experienced during the manufacture of 6 and 8 layer multilayer boards using 0.013 to 0.020 inch dia. plated-thru via holes and represent several constructions. Figures shown are of Invar type boards only; photomicrographs of sections containing quartz and aramid are usually indistinquishable from the common epoxy glass sections.

IMAGING and ETCHING

The materials from which the cured laminate is made must be the first consideration when implementing the imaging and etching plan. The multilayer construction is determined by the position and pattern density of the copper layers on the panel.

Quartz and Aramid: Both of these fiber composite materials have a lower CTE in their planar direction than the copper foil which is applied to both sides at the laminate supplier. When

the supplied clad laminate is at to room ambient conditions, the double clad laminate is relatively flat and amenable to imaging. However, if the imaging and etching process removes the surface copper so that the remainimg cladding is unbalanced from side to side then the nicely imaged and etched interal layer detail will emerge from the etcher in a tightly rolled tube; if it emerges at all and does not entangle in the etcher. Additionally, even if the copper image is balanced on both sides the residual stress relief when the copper is removed causes the internal layers to shrink in the planar direction. Usually more in the warp direction than in the fill direction dependent upon thickness of the dielectric layer.

A solution to the rolled-up interal layer is to make it with balanced metal layers. This can be partially accomplished by adding more copper to the lowest circuit pattern side of the internal layer. More difficult to balance is the externals and the first buried layers; therefore, it is more desirable to make the first buried layer a part of one of the internal layer details and apply the externals as cap-foil.

Pattern shrinkage of the interal layers after etching is a less easily solved problem since it is not predictable for each construction and is controlled by the amount of retained copper. However, if a similar border copper pattern is used for each interal layer, an artwork compensation is usually acceptable. The use of a thinner copper layer (1/2 ounce) imparts less residual stress and final dimensional change in the etched internal layer. A post bake at as high a temperature possible after making the laminate or prior to starting fabrication will decrease some of the post etch shrinkage.

Invar: Copper-clad Invar is a relatively stable material during imaging and etching and the conventional methods are utilized with either ferric or cupric chloride etchants. The galvanic differences between Invar and copper do cause undercutting of one or the other; use of the higher metal concentrations in the etchants reduce this effect but will slow etching time. The thickness of the material (0.005 to 0.010 inch) makes the relative time to etch the pattern in the Invar planes quite long. A dimensional change is experienced in the planar directions after laminating and requires artwork compensation as is discussed in the next section.

LAMINATING

The three types of materials act quite differently during multilayer lamination and usually must have some compensation programmed into the artwork for boards with high density and small tolerance to pattern shift.

Quartz: The quartz fiber materials are most stable with some

shrinkage seen in the multilayer boards after laminating; the initial change after etching is of a larger magnitude. Boards made from quartz fibers systems usually require little or no artwork compensation if all internal layers are balanced and external copper is applied by the cap-foil method. Quartz fiber multilayer boards also will have less shift during laminating if a kiss cycle of about 25 PSI is applied and the temperature rate of rise is near 15 degrees F. per minute.

Aramid: The aramid fiber materials when used in the printed boards also exhibit shrinkage after laminating which often approaches 0.001 of an inch per inch. The shrinkage is increased by a large amount of retained copper pattern which seems to produce the destabilizing effect. The high amount of dimensional change seen during lamination of aramid boards almost always requires an artwork compensation in the initial patterning if hole pattern and registration limits are tight.

Invar: The laminated epoxy-glass boards with restraining Invar planes indicate that there is a pattern shrinkage in the Invar layers and a growth of the images previously generated on the epoxy-glass internal layers. For polyimide resin systems the difference in the growth and shrinkage is slightly greater than for epoxy-glass systems. The mismatch between the internal copper layers and the Invar layers after lamination is found to be from 0.0007 to 0.0012 inch per inch. This high mismatch condition is determined to be caused by the wide CTE difference between the copper/resin-glass laminate and the Invar material; at laminating temperatures the expanded planar images are quite divergent. At the temperature at which the Invar and glass-resin material are laminated together the image/pattern relative positions are frozen-in, when the panel is returned to room temperature the Invar layers are in compression and the copper/resin-glass layers are in tension. The stronger material will cause the other material to conform and cause a drill pattern misfit. Higher initial clamping pressures, 300 PSI, proposed to cause the resin-glass material to move with the Invar layers only caused an asymmetric pattern shift which seemed to start at one corner of the panel instead of being the perferred equidistant from the center; the B-stage when it melts seemed to act as a lubricant which allows nearly free expansion of the internal layer up to the Tg or softening point temperature of the resin binder. A lower laminating temperatures at 290 degrees F. for and initial resin hardening helps to decrease the mismatch for polyimide materials. After determining initial pattern shifts in the Invar and the resin-glass internals, a compensated artwork for one or the other of the materials is necessary.

DRILLING

The drilling is again uniquely different for the three types of materials. Quartz systems with its harder reinforcement exhibits the greater difficulty and is the least manageable while the

other two offer problems, but conventional solutions are more available.

Quartz: The quartz reinforcement wears out carbide drills at a very rapid rate; about fifty hits between drill changes being about the best achieved with conventional feeds, speeds and drills. Drill wear is improved by using the lower speeds (35000 rpm) and lower feeds (0.001 inch per rpm) than are normally used with the glass reinforcements. Some improvement of drill life is seen with the diamond impregnated drills, 1000 to 2000 hits with quite good hole quality. Drill cost with the diamond drill is between 10 and 20 cents a hole or about 100 times the cost per hole with carbide drills and epoxy-glass multilayers.

Aramid: The aramid fiber reinforcement does not drill so that the hole quality is as acceptable as with the glass reinforced materials. Among the problems are high amount of fiberous residue in the hole; a tendancy for the drill to drift and a loading of the drill with the laminate materials. A method of drilling the hole in two steps will generally aid in all of these conditions if a good vacuum scavenging around the drill is maintained. The high fibrous residue remaining in the holes must be cleared at a later desmearing step, namely plasma.

Invar: Copper-clad Invar in the panel drills like a heavy layer of 3 to 7 ounces of copper foil. The drills load and the Invar extrudes and spreads at the hole-wall interface. A good vacuum vacuum scavenging and sharp drills are very important. Drill feeds should be 0.001 inch per rpm chip load with a speed of 50,000 rpm. Two step drilling shows some improvement in decreasing drill loading. Nail heading as measured will often be a high number but is very seldom a problem if a percentage of foil thickness is used for acceptablity criteria.

HOLE WALL PREPARATION AND DESMEAR

At least one of the methods of hole-wall preparation is acceptable for each of the restained boards.

Quartz: The quartz fiber/resin systems are very similar to their equivalents in the glass system. Etch-back of the quartz fiber with the acid-fluorides compounds is somewhat slower than on the E-glass, perhaps due to a normally larger fiber size. Plasma, sulfuric acid, chromic acid and alkaline permanganates are used on epoxies while the polyimide systems are best desmeared with plasma and alkaline permangnates. Grit blasting the holes with one of the several machines on the market also decreases residual debris.

Aramid: Some reactions are seen with all of the desmearing agents on the aramid fibers but to reduce the high fiber residue in the holes and prevent the resulting roughness the plasma method is by far the most satisfactory. An oxygen burn out cycle

at the end of the regular plasma cycle aids in coverage by the electroless copper.

Invar: Copper-clad Invar due to high galvanic activty between the dissimilar metals creates several conditions which must be avoided or considered in the overall hole-wall preparation. Plasma being non-aqueous is very sucessesful for both epoxy and polimide systems when combined with Invar. A commonly used post-plasma clean with an alkaline permanganate may cause deep etchback in the Invar layers if chlorite compounds are used for permanganate regeneration (See figure 1); additionally, sulfuric acid or sulfuric acid and hydroxyl-amine sulfate solutions used to neutralize the permanganate will quickly pick up copper ions and deposit copper on the Invar layers as an immersion coating which must be removed prior to electroless coating. Concentrated sulfuric acid will also perform satisfactorly as an epoxy smear removal if kept fresh with very little water or copper ion contamination. Chromic acid also may be used on epoxy systems. The alkaline permanganates if used following plasma must be handled with care and any permanganate regenerative compound must not be reduced to a chloride or a large amount of Invar erosion will result.

ELECTROLESS COPPER

The quartz and aramid systems can be electrolessly copper coated by the conventional methods, but the Invar system exhibits a more troublesome operation due to the dissimilar metal couple of the copper and Invar.

Invar: A micro-etch in the form of sulfuric-peroxide or acidified persulfate may be used to prepare the surface copper cladding and the copper foil interface for electroless copper; however, the dwell time must be short since a reaction occurs at the copper-Invar diffusion layer in less than thirty seconds and a "V" shaped etchout appears at this place. The micro-etch also deposits immersion copper on the Invar which must be removed or the hole-wall to Invar bond is weak and may show pullaway at microsection examination. (See figure 2).

A second microetch is necesssary to slightly etch the Invar and strip any immersion copper which may have be deposited on the Invar at the desmear neutralization step or the at the first microetch. For this second microetch either a cupric or a ferric chloride solution is used. Again a short dwell is necessary because both of these solutions will more quickly etch the copper cladding on the Invar faster than the Invar itself. An etchout of the copper cladding on the Invar 0.001 to 0.003 inch deep will result. The larger the the ratio of Invar to copper the faster the etchout. (See figure 3).

When using the conventional tin-palladium catalyst systems, the

catalyst predip and the palladium-tin catalytic system should not be a very low acid solution or poor Invar to electroless bond will result. Additionally, with the tin-palladium catalyst the accelerator should be the fluoroboric type in order to avoid a poor adhesion to the Invar. An electroless system which uses an alkaline catalyst and does not contain tin has been found to work very well with the Invar systems; however, the ferric or cupric pre-etch must also be used.

Electroless coppers plate onto the activated hole wall at a different rate on the Invar surfaces than on the copper surfaces or on the polymer. The higher deposition rate is often noted on the Invar when a bath is is on the high side of its activity. Copper whiskers up to 0.015 inch long by 0.0001 inch in diameter will sometime grow from the Invar; the whiskers plate up in the electrolytic bath and cause nodules which will almost clog the hole. (See figure 4).

ELECTROLYTIC PLATING

With quartz and aramid fiber the plating process after the electroless may follow the conventional practices used for the glass fiber materials. With the Invar the extreme activity of the two dissimilar metals create some odd conditions which are not experienced with the single-metal board. If an electrolessly coated board is immersed in the acid-copper electrolytic solution without a voltage exceeding the couple voltage (about 0.55 volts) for as little as 30 seconds, a rapid undercutting of the Invar layers result. The undercutting can be up to 0.010 inch within about 5 minutes. (See figure 5). No such undercutting was found when the same conditions were presented to a panel in pyrophosphate-copper elelectrolyte.

Several reports have been circulated in the industry for the past few years in which boards with restrained growth/shrinkage in the x/y planes have had a reduced ability to withstand long term thermal cycling from -55 to +125 degrees celcius. Additional testing has confirmed these reports, but it is also been found that electrodeposits from acid-copper with low codeposited additive and pyrophosphate-copper from a non-additive bath will withstand may thousands of thermal cycles without barrel cracking or interconnect failure.

SUMMARY

The processing of plated-thru hole multilayer boards which contain materials to restrain the thermal expansion or shrinkage in the planar directions is more difficult and costly than the FR-4 multilayer boards. However, within the present printed wiring board industry the methods, tools and chemistry are used and available to all fabricators and they can produce excellent results. (See figure 6).

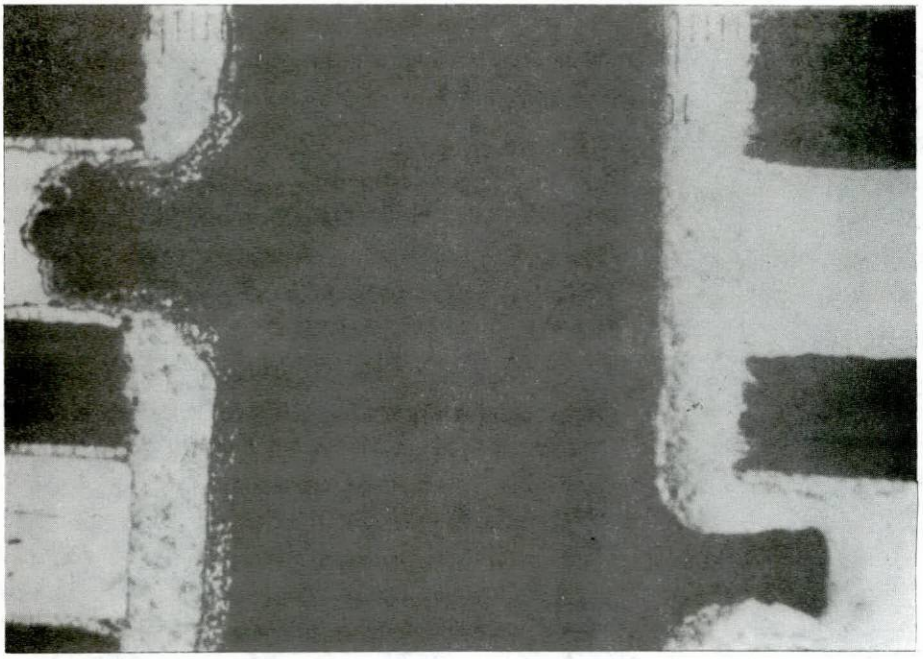

FIG. 1. HOLES ETCHED IN THE INVAR IN THE PERMANGANATE DESMEAR

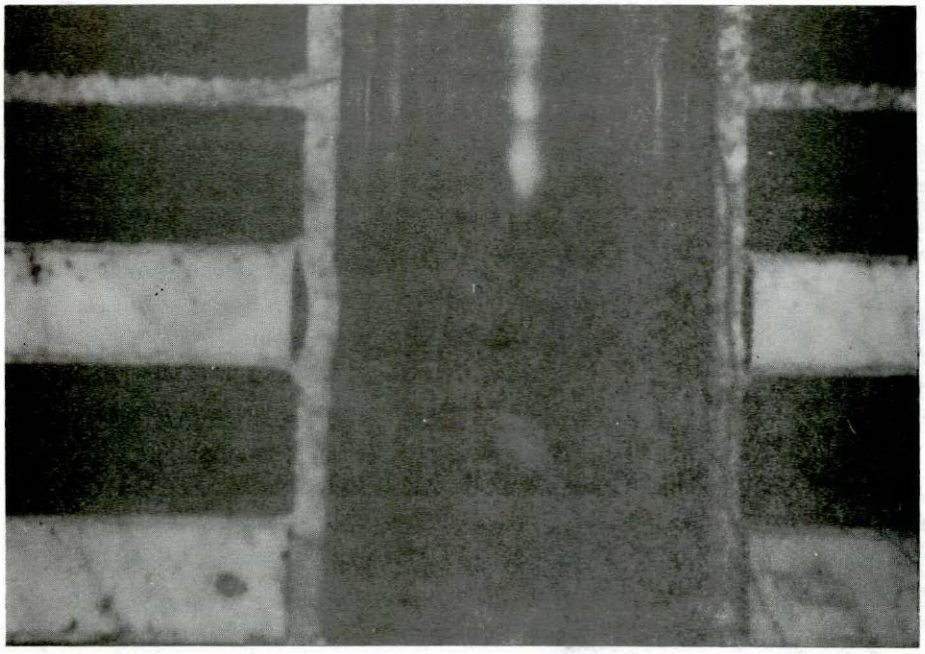

FIG. 2. SEPARATION OF THE COPPER PLATING FROM THE INVAR

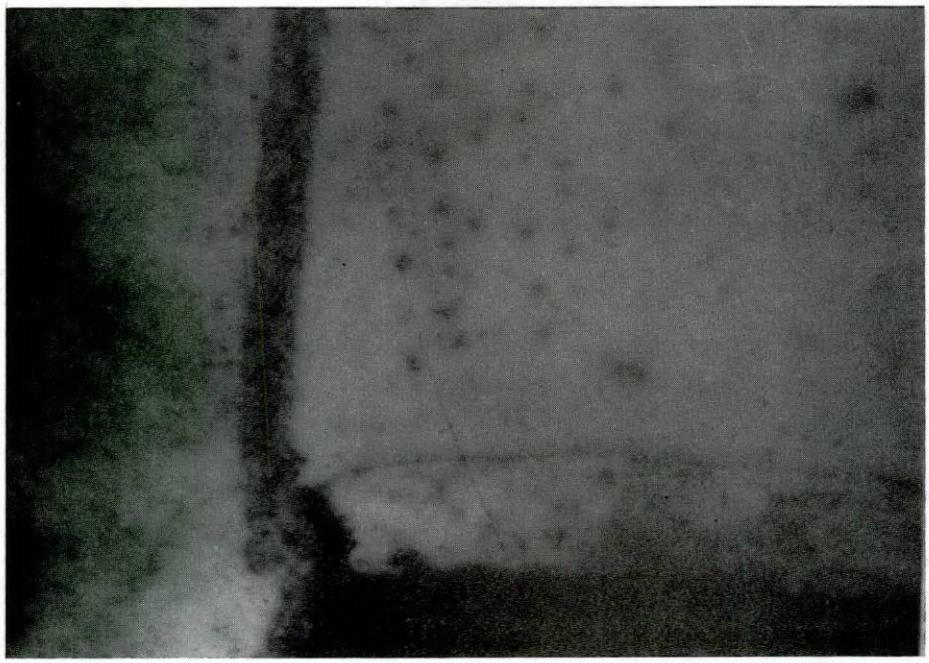

FIG. 3. ETCHBACK OF THE COPPER CLADDING ON THE INVAR IN CUPRIC CHLORIDE

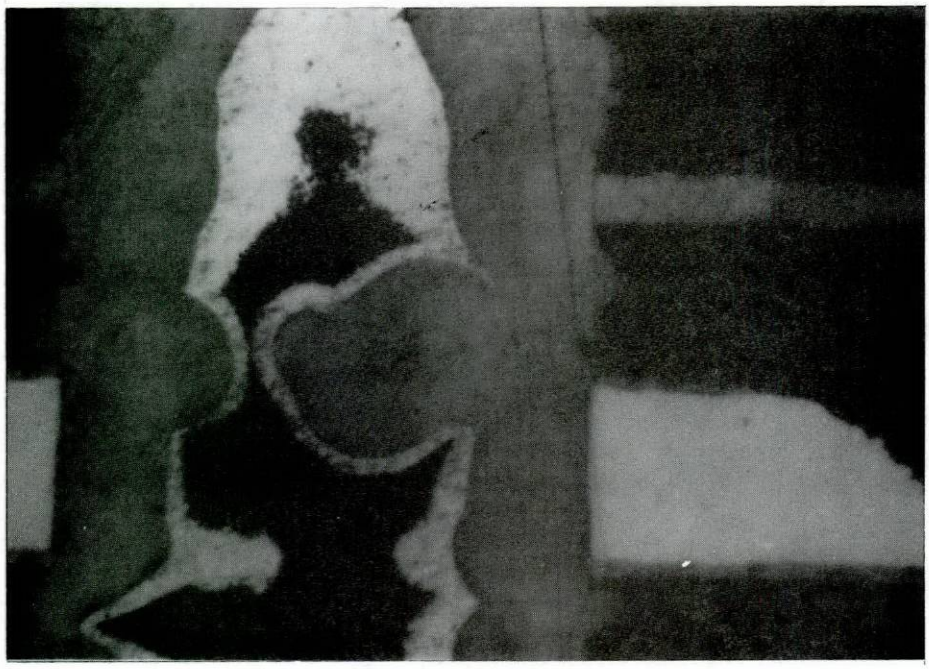

FIG. 4. PLATED-UP WHISKERS THAT GREW OUT OF THE INVAR

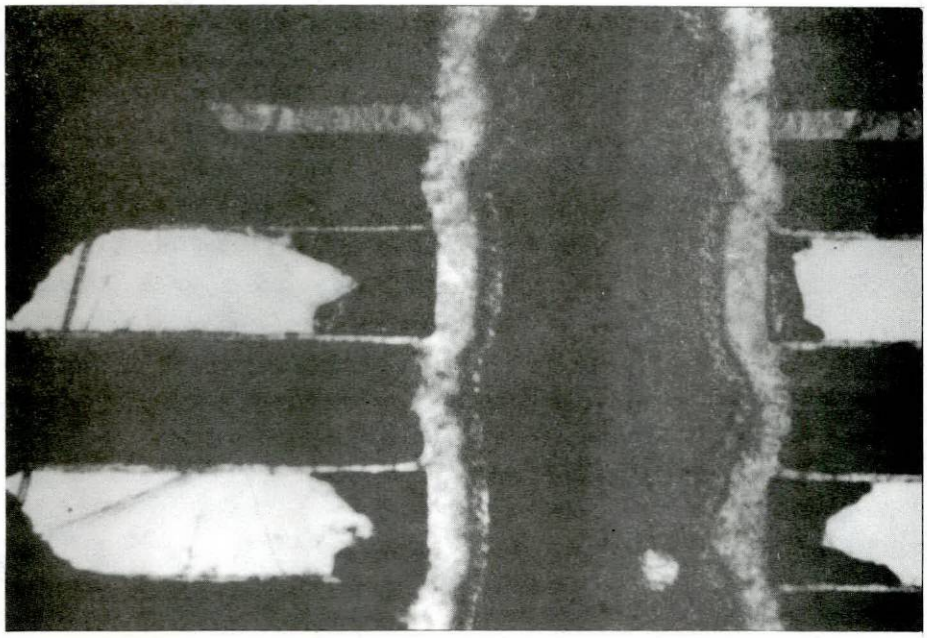

FIG. 5. ETCHOUT OF INVAR BY THE ELECTROLYTIC COPPER PLATING SOLUTION

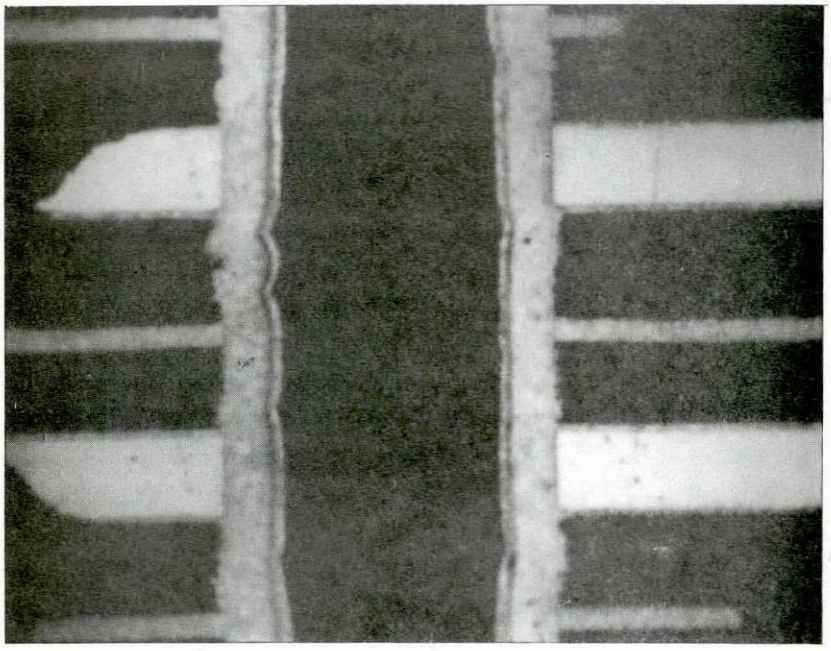

FIG. 6. PROPER HOLE PREP. AND ELECTROLESS COPPER TECHNIQUES PRODUCE ACCEPTABLE INTERNAL CONNECTIONS

G-4

Electronics III
Session G

Automation of Plating Rack Loading for Printed Circuit Panel Electroless Processing

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AUTOMATION OF PLATING RACK LOADING FOR PRINTED CIRCUIT PANEL ELECTROLESS PROCESSING

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ABSTRACT

Automated panel loading into and out of electroless plating racks is an integral part of a fully automated plating operation. Discussed here are a number of considerations that need to be addressed in integrating such automation into a plating facility. Emphasis is on planning for product flow, automatic process record keeping, control system requirements, rack handling options, and rack design. Photographs of scale models of systems being developed and installed are used to illustrate the points discussed. A brief look is also taken at loading of electrolytic processes.

Product Flow

A fully automated plating line can be treated as a long conveyor with work orders flowing one after another through the line and on to the next process in a continuous first in, first out stream. Commonly, an incoming stack of panels will represent all or part of a work order. It is mandatory that this grouping remain the same after plating even though a given work order may be distributed over several plating racks, or a rack may contain panels from more than one work order. To accomplish this we need to look both upstream and downstream from the plating operation.

Upstream the panels need to be stacked on pallets, the panels always in the same orientation. In a fully automated facility a loaded pallet is brought to the plating line load station by conveyor or automatic guided vehicle. The panels are then removed from the top of the stack one at a time and fed to the loader. After plating, the panels are unloaded one at a time and restacked, but with the top panel now on the bottom. The pallets of plated panels are moved to the next operation by conveyor or AGV.

Layout planning of a facility must include space for moving loaded pallets to the load station, transferring empty pallets to the unload station, and moving plated product pallets away from the line. It is particularly critical to have space at the unload station for both empty and full pallets so there is a place to put panels exiting the plating line. Queue space at the load end is less critical but desirable. A plating line starved for parts is under-productive. A plating line stalled because of a downstream bottleneck will create scrap.

Automatic Code Reading

Automatic reading of a hole pattern drilled near the edge of each panel to identify its part number, or work order number, is an integral requirement for a fully automatic load/unload system. As each panel approaches the load station, an on-the-fly reader provides this coded information to the loader control system.

The control system then compares this input with data provided by the facility host system to determine if the panel arriving is expected, and is a process match for the other panels being loaded. If all is in agreement, a data base is created representing the panels as they are loaded in each rack. This data base is then used by the plating line control system to tag any out-of-limit process information to a specific rack load of parts. At the unload station, a second panel reader confirms that the panels being re-stacked are as anticipated and that none have been inadvertently swapped at inspection stations or during manual backup loading.

Automatic panel reading makes it possible to generate accurate quality control and production records for each unit. This, combined with labor savings, can be the major justification for an automated loading system.

Control System

The controller used consists of a personal computer running a true multitasking operating system and communicating with the facility host system and other plating line controllers over an RS-232 network. Residing in a fresh-air pressurized cabinet at the load station, the PC provides a complete display and keyboard for communication with the operator. An optional printer provides hard copy records, reports, or listings as desired.

Because of the computing power available in the PC, it is used for decision making regarding the operation of the load system. Fault display, corrective actions required, re-routing of panels received out of sequence, and count and data base record keeping are all tasks assigned to the PC.

Security passwords allow access to the equipment programs by appropriate level personnel. Within the program all devices and steps are labeled with English names and descriptions. No external programming equipment is required, although the programs can be remotely generated and downloaded if desired. In contrast to programmable logic controllers operating with ladder logic, the personal computer based system is much more tolerant of interruptions in its cycle, can provide an interlock checking routine to prevent machine crashes during manual interaction, and can automatically sequence the machine to a safe starting condition after interruption.

Rack Handling Options

Two options exist for load/unload stations relative to a plating line. The first is for the plating line hoist to service the load station directly. The second is for the racks to be transported a short distance away from the line for loading.

Photos 4-6 represent the former arrangement. The major advantage of this configuration is that no intermediate rack handling equipment is required. The disadvantages are constricted space for product flow to and from the load station, and proximity to the corrosive chemistry environment. For longevity, sensitive components must be isolated from the corrosive atmosphere and the rest of the equipment built of corrosion resistant materials.

Photos 1-3 are of a remote system. Although the rack handling equipment is more complex, if it is combined with rack storage the additional equipment required is minimal. Careful attention must be paid to the rack exchange time as the load station becomes more remote. Because the rack loading time is typically paced by maximum panel delivery rates, delays in exchanging racks will decrease throughput.

Regardless of the arrangement chosen, precise rack positioning is required for automatic loading. A system working from coarse to fine provides the required precision in a series of steps. The large, heavy racks illustrated in photos 1-4 are, for instance, first placed on a platform with a resolution of $\pm$ 1/2". The platform can then be moved $\pm$ 1" to locate the rack against physical stops. The panel loading head or magazine has a limited amount of float so that it can take its final alignment directly from the rack. This third level of positioning accommodates for slight variations between racks and some inevitable distortion of the racks in production.

Electroless Rack Design

The throughput requirements for a line determine the rack capacity and configuration. Solution flow through the loaded rack determines the preferred panel edge guide orientation. The system in photos 1-5 all assume a solution flow of front to back (walkway toward hoist) and so are guided top and bottom, leaving the front and rear as open to solution flow as possible.

Edge guiding should be continuous. PC panel material bears an uncanny resemblance to an abrasive cut-off saw and its effect on a stainless steel rack is similar. Therefore it is recommended that the weight carrying surface on which the panels slide be of large area and easily replaced. A rack design has evolved where the functions of panel support and panel guiding are separated. Panel supports are heavier, intermittent, and anchored in machined details within the rack structure for dimensional control. The guides are light and open to reduce surface area and promote drainage.

The rack frame requires open sides so that the unload mechanism can reach in to push the panels out. Frame structure must be sufficient to withstand production handling both on and off the line, yet minimized for low thermal mass and surface area. Automatic loading demands close dimensional control between individual racks. Hand loaded racks can vary by several inches but automatically loaded racks must be alike. Critical dimensions need to be determined by machining operations and not by welding alone.

The electroless racks illustrated are for constant panel sizes, of self supporting panel thicknesses (1/16" and greater). Varying panel sizes and thinner, inner layers can be accommodated with more complex racks. As rack complexity increases so does the ratio of incidental plate-out relative to the product plating. As panels decrease in size this ratio also increases. The cost of stripping and recycling this material is another factor in determining optimum panel sizes.

Rack Loading Systems

Two options for loading racks are illustrated in the accompanying photos. The first system, shown in photos 1, 2, and 4 uses an intermediate magazine that is pre-loaded at the maximum panel delivery rate. While this is occurring the rack is being positioned for loading. The magazine is then brought into contact with the rack and an entire section of

the rack is filled at one time as the panels are pushed from the magazine into the rack. As the rack is moved to load the next section the magazine is refilled. This "parallel processing" saves a considerable amount of time in a load cycle, and has been found necessary to meet throughput requirements where the rack has more than one section. To supply this parallel system, the feed of panels to the loader must be continuous. The system illustrated utilizes a semi-standard panel "unstacker" with two pallet handling sections to provide this continuous flow of panels while exchanging pallets.

Unloading is done in essentially the reverse order. Panels are pushed from the rack into a magazine, and then fed singly to a dual panel stacker.

The second system, illustrated in photo 5, directly loads one panel at a time into a single section rack. This system is simpler and is recommended when throughput requirements are low enough to permit its use. Unloading this rack must be done from the opposite side to preserve the first in, first out order.

Automatic Loading For Electrolytic Process

Photo 6 shows an adaptation of a single panel, direct loading mechanism to an electrolytic rack. Although it illustrates a single panel rack, any production system that could justify automatic handling would require a 2x2, 2x3 or larger matrix. Ideally the product flow would be normal to the axis of the line with two tiers of panels moving through the rack at a combined load/unload station. This arrangement permits minimum cycle time while preserving the first in first out sequence.

Conclusions

As panel plating facilities become more automated, automatic loading and unloading of racks will take its place along side automatic hoist control and automatic process control as a cost effective system. Planning for automation of the load and unload operations must take into account the product flow both upstream and downstream of the plating line.

Prerequisites for a successful installation are: a well defined panel coding and reading system; a host computer system to manage flow through the facility; a loader control system smart enough to do record keeping, decision making, and communicate with both the host and other equipment controllers; and racks designed for automatic handling.

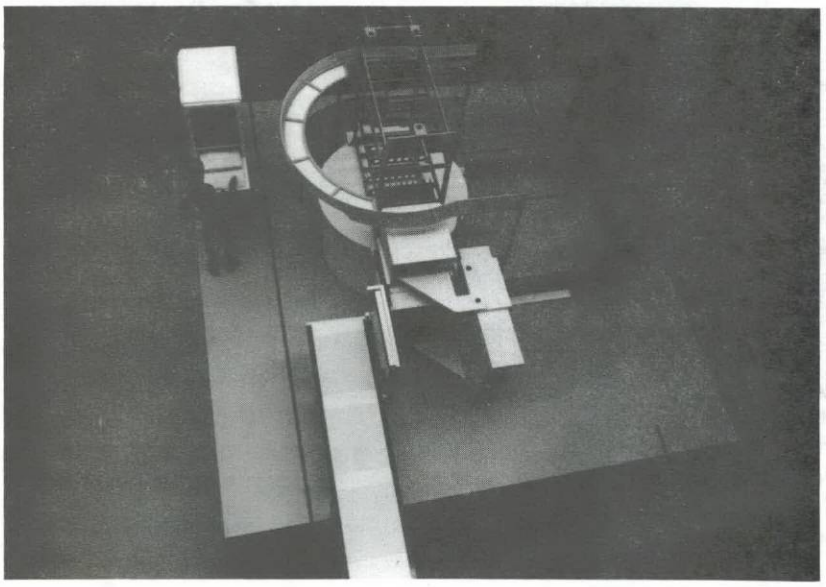

Photo 1

Birds eye view of remote load station - Rack has been raised off rack cart and the cart withdrawn to the right. The first quadrant is being loaded from the accumulating magazine as the pusher transfers the panels into the rack.

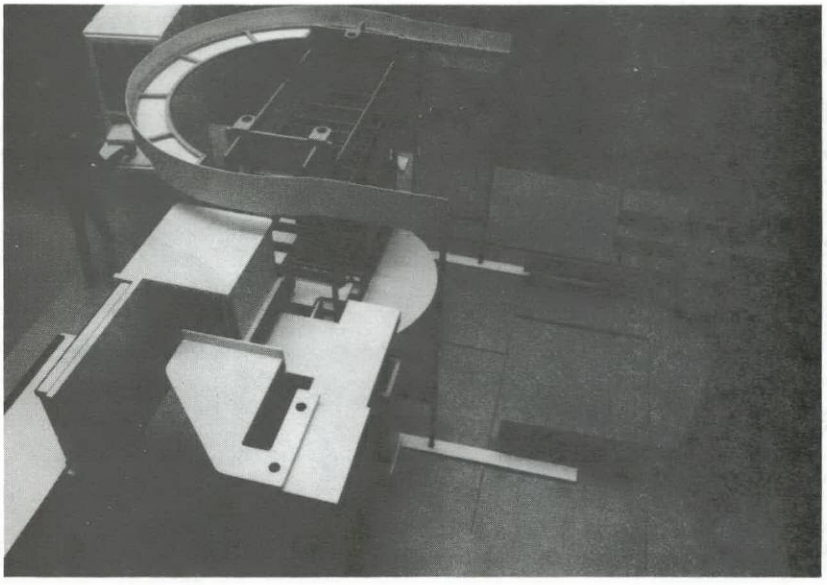

Photo 2

Rack positioned for loading third quadrant - The magazine is nearly filled with panels arriving on the conveyor at the lower left.

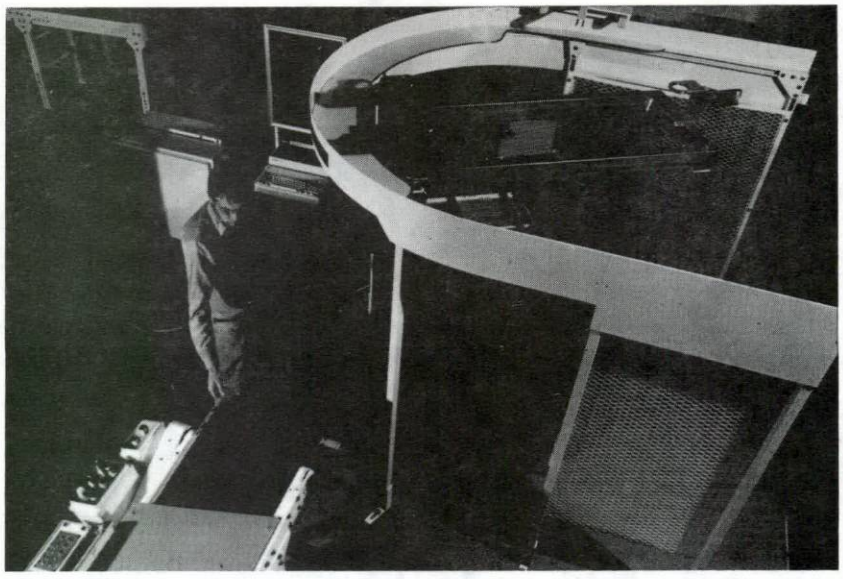

Photo 3

Similar viewpoint to photo 2 - This is the actual machine prior to installation of the loading magazine. Note that the rack is positioned for manual loading of panels. This feature is retained in the automatic system as a backup.

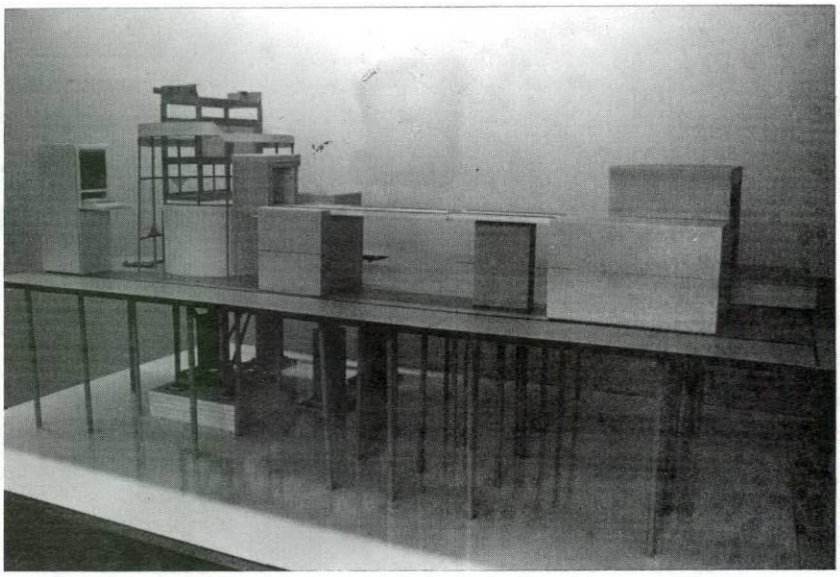

Photo 4

Unload station served by plating line hoist directly - Lift is in the up position. Rack is oriented as it would be left by the plating line hoist running left and right . Structures below the chemical grating are part of the lift mechanism and piers that support the plating line framework. Unit to the right is a dual panel stacker served by an AGV.

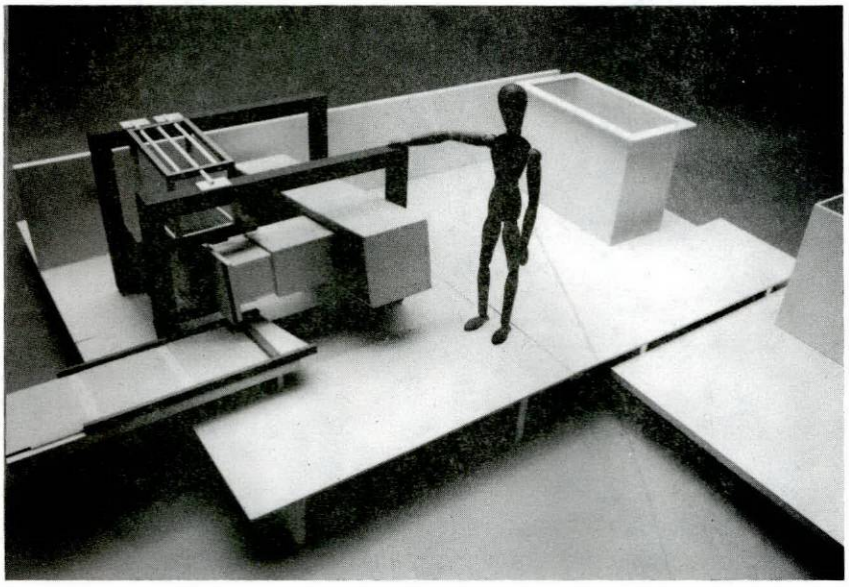

Photo 5

Direct loading machine for smaller electroless system - Rack is delivered to the load station by the plating line hoist. Panels arrive on the conveyor at the left. Space between the load machine and the first tank behind the figure is queue space for racks. Model is of a "U" shaped plating line. A similar mirror image machine will be placed across the walkway in the foreground as an unload machine.

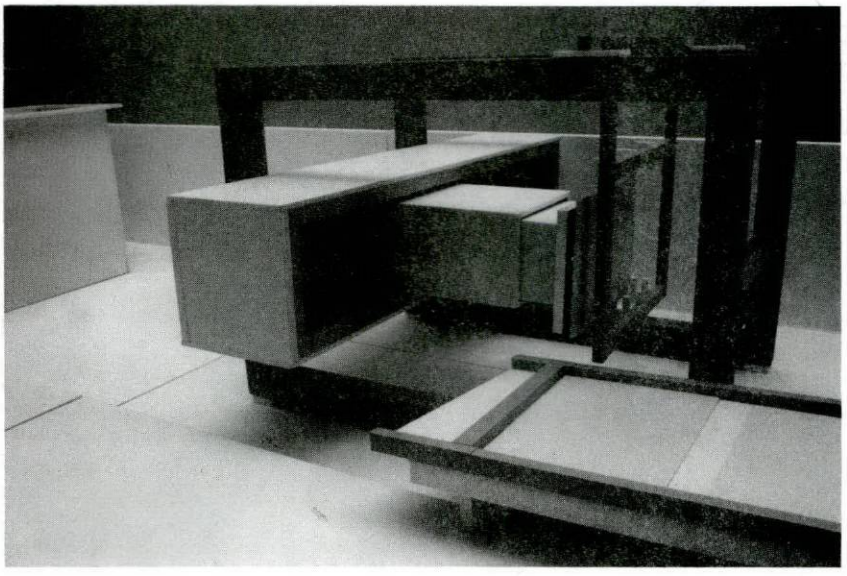

Photo 6

Conceptual arrangement for an electrolytic rack loader - Equipment developed for electroless panel handling can also be used for loading an electrolytic line. The model shown illustrates a single panel rack. Production racks would be multiple panel.

G-5

Electronics III
Session G

Gold Processes for Plating Printed Circuit Boards Processed with Fully Aqueous Resist

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Abstract

Plating printed circuit boards processed with fully aqueous resists with the traditional acid gold electrolytes is problematic due to hydrogen lifting of the resist. This paper describes three novel gold electrolytes that plate at high efficiencies thereby avoiding the hydrogen lifting problem. Discussed are electrolyte operation and deposit properties. Special attention will also be paid to the influences of normally encountered impurities on the operation of the electrolytes.

Introduction

Ever since gold has been plated on circuit boards, changes in technology have impacted the type of gold processes used. Years ago the hot cyanide gold electrolytes, common in the jewelry industry for heavy plating, were found to be totally useless by the printed circuit board manufacturers. These systems yielded deposits with inadequate wear resistance and the alkaline nature of the electrolytes attacked not only the laminate, but also the plating resists themselves. The first silver gold electrolyte introduced in the late 1950's was a step in the right direction. The deposits plated with this system, even though they represented an improvement, still gave insufficient wear protection. Again, in the late 1950's a major breakthrough took place

when it was discovered that potassium gold cyanide is stable in acidic systems down to pH values approaching three. It was also found that the addition of small amounts of salts of cobalt, nickel, and/or indium to a gold electrolyte buffered with an organic acid/salt matrix, capable of complexing the base metal, would result in bright hard deposits when electroplating was accomplished at pH 4, room temperature and 10 amps per square foot. Deposits from these systems gave the printed circuit board manufacturers the wear resistance and constant, low contact resistance that they required. Also, the electrolyte did not attack the plating resists or laminates that were used to manufacture printed circuit boards.

With the rapid growth of the printed circuit board industry, it soon became obvious that these electrolytes were much to slow to satisfy the throughput requirements of that industry. At 10 amps per square foot, it took more than ten minutes to plate the then specified 100 microinch thickness. In order to achieve faster plating rates, some users in the industry resorted to increasing gold concentrations to levels sometimes in excess of four troy ounces per gallon and working at elevated temperatures and higher current densities. It therefore became possible to reduce the plating time from more than ten minutes to less than three minutes for the required 100 microinches. However, working at these high concentrations was costly, especially when the gold price escalated in the late 1970's and problems with solubility were encountered.

These efforts were complimented by the introduction of the bottom anode tab plater, which made it possible to process the tabs on many boards simultaneously in one apparatus. These bottom anode tab platers gave the printed circuit board manufacturers the throughput requirements that were necessary to maintain their elevated production levels. However, they were pigs as far as gold consumption was concerned. This equipment plated the maximum gold thicknesses on the bus bar, which was later sheared from the board and the lower end of the tabs rather than the middle of the tab where the thickness was measured. Due to this waste, printed circuit board manufacturers looked to other types of equipment to plate their tabs. What they found was the first automatic tab plater which was introduced into this industry almost ten years ago. When the first automatic tab platers were introduced, they still required elevated gold concentrations sometimes in excess of three troy ounces per gallon to achieve the then required plating rate of 100 microinches of hard gold in 30 seconds. Shortly after the introduction of this type of equipment, the first truly high speed cobalt

and iron gold plating processes were introduced into that industry. It was now possible to plate the required 100 microinches of hard gold in 30 seconds with a gold concentration of only 1.5 troy ounces per gallon.

Further developments in the printed circuit board industry led to circuit board designs that did not lend themselves to being processed on tab platers. The tabs had to be plated on the full panel with the other areas masked off. Adaptation of the new high speed gold electrolytes to this type of plating, yielded a system that would plate at twenty amps per square foot, but require only 0.5 troy ounces per gallon of gold. Not only was the gold concentration reduced here decreasing drag out losses and investment costs, but these electrolytes yielded better plate distribution then their forerunners. These systems worked well until the introduction of fully aqueous resists. The hydrogen gassing action of these systems, which had proven beneficial working with solvent resists, resulted in undercutting of the fully aqueous resists and the subsequent scrubbing action cleaned these resists right off the circuit board. A new type of gold electrolyte had to be developed to accomodate fully aqueous resists.

The fully aqueous resists were introduced because of problems that the chlorinated solvents, used to strip solvent resists, had on the environment. The desire of the printed circuit board industry was the elimination of these solvents. The way this was accomplished was the development of first semi- and finally fully aqueous resists which are strippable with alkaline aqueous solutions. Unfortunately, advances in an industry are many times accompanied by unwanted disadvantages. In the case of the fully aqueous resists, the disadvantage was that the acid gold electrolytes used to plate tabs on boards stripped these resists. The stripping phenomenon is based on two factors. First, the higher the pH of the solution, the weaker is the bond to the substrate. The second factor, which appears to be the more predominant one, is the undercutting of the resist by the hydrogen gassing. In the case of boards processed with solvent resist, the hydrogen gassing was beneficial in that the scrubbing action enhanced the adhesion of gold to the nickel underplate eliminating the need for a gold preplate; but in the case of boards processed with fully aqueous resists the hydrogen gassing must be drastically reduced or if possible totally eliminated. There are essentially two methods of accomplishing this. The first is to modify the chemistry of existing gold baths which utilize either cobalt or nickel hardening agents so the plating efficiency is increased and the hydrogen gassing reduced. The second method would involve developing a

totally new electrolyte which plates at close to the theoretical 100% cathode efficiency, eliminating hydrogen gassing. This would be possible because these electrolytes would not contain the traditional hardening agents such as cobalt or nickel which generally reduce plating efficiencies. The rest of this paper dedicated to these two types of systems.

Modified Cobalt and Nickel Gold Electrolytes

Increasing the operating pH of cobalt and nickel gold electrolytes will also increase the cathodic plating efficiency. Unfortunately, an increase in pH will also result in the dulling of the deposit appearance, usually before that point at which the efficiency is sufficiently high to eliminate hydrogen lifting. What is needed here is a bright range extender to prevent the dulling of the deposit appearance and an accelerator to further increase the cathodic efficiency thereby reducing the hydrogen gassing effect. Inclusion of these two additives in cobalt and nickel gold electrolytes will result in systems that are operable under conditions and yielding the plating rates indicated in Table 1.

Deposits from these electrolytes exhibit a hardness in the 130-200 KHN range and a gold purity in excess of 99.7% which allows them to meet the requirements of Mil G 45204B Type I, Grade C and Type II, Grade C. Because these deposits also possess excellent wear resistance and a low, constant contact resistivity, they are ideally suited for the plating of printed circuit board edge contacts (tabs). The deposits from these modified electrolytes exhibit less stress cracking than is encountered with many of the traditional nickel and cobalt golds. This is evidenced by the fact that hardness coupons can be plated in these electrolytes to thickness in excess of 1 mil without the formation of stress cracks visible to the naked eye. Because these systems plate at cathodic efficiencies approaching 70%, they can be utilized to plate most printed circuit boards processed with fully aqueous resists. Obviously the type of resist utilized and the manner in which it has been processed is a prominent factor in the successful gold plating of boards using these resists. In general, the thicker resists, in excess of 2 microns, can be processed with these electrolytes with little or no problems. Other meaningful factors are the age of the resist, the preplate operations, as well as the thicknesses of copper and nickel that have been deposited prior to plating the gold. The one disadvantage of these modified gold electrolytes is, because of their high cathodic efficiency, one can encounter

adhesion problems to the nickel undercoat. To avoid this the nickel deposit must be activated non-electrolytically and sometimes a gold preplate must be included prior to depositing the hard gold. Unfortunately, the use of the preplate will enhance the lifting of the resist; so its usage must be limited to providing the absolute minimum thickness needed for adhesion purposes.

High Efficiency Gold Electrolyte Without Nickel or Cobalt Hardening Agents

As indicated previously, cobalt and nickel tend to decrease the cathodic efficiency of gold electrolytes. Therefore, the driving force here is to develop a new system utilizing a brightener which hardens the deposit, but does not decrease the plating efficiency. A system giving these characteristics was developed and operates under the conditions yielding the plating rates indicated in Table 2.

Deposits from this electrolyte exhibit a hardness of 250 KHN and a gold purity in excess of 99.9% enabling them to meet the requirements of Mil G 45204B Type I Grade D and Type II Grade D. Inspite of this relatively high hardness, these deposits possess excellent ductility which eliminates the fear of stress cracking when tabs are routed. The deposits also possess an extremely low contact resistance, however, their wear is inferior to those of deposits plated in the traditional cobalt and nickel gold electrolytes. The wear resistance can be enhanced by top coating these deposits with either the cobalt or nickel gold previously mentioned in this paper.

Because the plating efficiency of 110 mg/amp minute is 90% of theoretical value, these electrolytes operate with almost no hydrogen gassing. Because the hydrogen gassing effect is the main factor that causes lifting of resists, this electrolyte is the most ideally suited one for plating boards processed with fully aqueous resists, in spite of the pH value of the bath being 6.

In general, prior to using a new electrolyte in production, the effects of commonly encountered impurities must be determined. In the event that these impurities are harmful, their removal potential should also be investigated. Impurities that one would anticipate to contaminate a gold bath utilized to plate printed circuit boards are lead, iron, copper, nickel and possibly zinc. The effects of critical concentrations of these impurities on the gold electrolyte and removal potential are listed in Table 3.

Deposits from the high efficiency electrolyte exhibit other interesting properties. Due to the ductility of the deposit and the fact that those deposits possess low internal stress, it is possible, many times, to plate with this electrolyte directly over nickel without the use of a gold preplate. Nevertheless, the preplate is advantageous in case passive nickel is encountered.

Conclusion

Throughout the development years of printed circuit boards, gold electrolytes have been successfully modified to satisfy the end point requirements of the printed circuit board manufacturers, and to operate with a minimum waste of gold. The lastest innovation in the printed circuit board industry, which specifies the use of fully aqueous resists, has rendered the more traditional gold electrolytes totally unsatisfactory. This is due to the fact that the hydrogen scrubbing action, which accompanies gold deposition, will undercut and lift these resists. Once again, novel gold electrolytes have been developed which resolve this problem and also meet the end point requirements of the printed circuit board industry.

TABLE I

OPERATING PARAMETERS AND PLATING RATES

FOR MODIFIED COBALT AND NICKEL GOLD ELECTROLYTES

	Recommended	Range
Metallic Gold Content	1.0 tr. oz./gal (8.2 g/L)	0.75 - 1.5 tr. oz./gal (6.1 - 12.3 g/L)
pH	4.7	4.5 - 4.9
Specific Gravity	14°Be (1.11 g/cc)	12° - 19°Be (1.09 - 1.15g/cc)
Bath Temperature	90°F (35°C)	86° - 104°F (30°-40°C)
Current Density	10 ASF	Up to 20 ASF
Anodes	Platinized titanium	
Agitation	Vigorous solution flow is required	
Filtration	Continuous through Dynel or polypropylene cartridges	
Plating Rate	80 mg/amp-min at 10 ASF pH 4.7 and 1.0 tr. oz./gal gold concentration	Up to 85 mg/amp-min
Gold Consumption	Approx. 1 tr. oz. gold per 400 amp-min at 10 ASF, ph 4.7 and 1.0 tr. oz./gal gold concentration	1 tr. oz. gold for every 350 to 600 amp-min
Time to deposit 40 microinches (1 micron)	2.5 min at 10 ASF pH 4.7 and 1.0 tr. oz./gal gold concentration	As low as 1.3 min

TABLE II

OPERATING PARAMETERS AND PLATING RATES FOR HIGH EFFICIENCY GOLD ELECTROLYTE

	Recommended	Range
Metallic Gold Content	1.0 tr. oz./gal (8.2 g/L)	0.8 - 1.25 tr. oz./gal (6.5 - 12.3 g/L)
pH	6.0	5.8 - 6.2
Specific Gravity	10°Be (1.074 g/cc)	8° - 14°Be (1.058 - 1.106 g/cc)
Bath Temperature	125°F (52°C)	120° - 130°F (49°-54°C)
Current Density	8 amp/sq. ft.	
Anodes	Platinized titanium	
Agitation	Vigorous solution flow is required	
Filtration	Continuous through Dynel or polypropylene cartridges	
Plating Rate	110 mg/amp min	
Gold Consumption	Approx. 1 tr. oz. gold per 285 amp-min	
Time to deposit 40 Microinches (1 Micron)	2.2 min at 8 amp/sq. ft.	

TABLE III

EFFECTS OF IMPURITIES ON HIGH EFFICIENCY GOLD BATH

Impurity	Critical Conc. mg/L	Effect	Percent Removable
Lead	2	Brown Deposits	50%
Iron	200	Drop in Efficiency	No Method
Copper	30	Red/Brown Deposits Drop in Efficiency	55%
Nickel	350	Drop in Efficiency	60%
Zinc	50	Green Deposits in High CD	80%