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AESF Heritage: SUR/FIN 2000 – European Academy of Surface Technology Throwing Power Measurement: The Assaf Cell

by
Y. Assaf
Bohak Plating Company; Hollon, Israel
and
M. Ward and D.R. Gabe
Loughborough University of Technology
Loughborough, England, UK

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ABSTRACT

A new throwing power cell is described in detail; it has the virtue of being usable as a small jig which can be positioned in an electroplating tank. This so-called Assaf Cell is particularly useful for simulating small recesses, typically through-holes found in printed circuit boards (PCBs). This paper demonstrates how a Throwing Power Index - given by the ratio of metal thickness on the front and rear faces of the Assaf-Cell test panel - may be used to evaluate/optimize electrodeposition conditions. Data are presented from work using various electrolytes, including high-throw acid copper solutions, thereby illustrating its usefulness and application.

1. Introduction

The ability to 'throw' metal into a recess, hole or cavity during electrodeposition is an important characteristic of an electroplating process and is related primarily to the type of solution and its constituents. Additional factors include the cell design, the agitation employed and the disposition of the anodes. This characteristic was recognized during the last century but it was in the 1920s that Haring and Blum[1,2] in the USA and Field[3] in the UK attempted to measure throwing power and to define a Throwing Power Index.

The Haring Cell is well known (but not actually well used!) as a box in which a channel of electrolyte is contained, with a central anode and cathodes either side at movable distances away. The ratio of distance (x_1 / x_2) is then related to the weight (w_1, w_2) respectively or thickness of cathode deposit when current is passed. The difference in thickness is attributed to the solution's resistance (iR drop), the electrode reaction efficiency and the electrode overpotentials. Field[3] first proposed a formula for the Throwing Power Index, so that:

$$T.P. = \frac{100(L - M)}{(L + M - 2)} \quad [1]$$

where $L = x_1 / x_2$ and $M = w_2 / w_1$.

Since that time developments have been such that both other cells and other formulae have been employed, e.g., Gabe.[4] The variety of cells studied is substantial but none have become established as standard, the Hull Cell being often used as the basis for novel design:

- Hull Cell used in throwing power mode[5]
- Modified Hull Cells for agitation, heating and scale linearity
- Gornall Cell for PCB applications[6]
- Rotating electrode 'Hull-type' Cells[7,8,9]

The formulae used have depended upon two issues: firstly, the range of values; secondly the sensitivity of the value obtained. For example, the Field formula extends from +100 (very good) through 0 to -100 (very poor). For many years this has been found to be convenient (see British Standard 205, Part 5) but ranges involving ∞ and of 0 to 100 have protagonists, while most recently the use of personal computers has enabled other measures to be used, e.g. Luke.[10] Table 1 summarizes some formulae and Throwing Power Index ranges that arise from their use.

Table 1 - Throwing Power Index formulae.

Author	*Formula*	*Range of values*
Haring-Blum	$100\,(L - M)\,/\,L$	+80 to -∞
Heatley	$100\,(L - M)\,/\,(L - 1)$	+100 to -∞
Field	$100\,(L - M)\,/\,L + M - 2)$	+100 to –100
Subramanian	$100\,(L - M)\,/\,M\,(L - 1)$	+100 to –25
Luke	$100\,L\,/\,(L + M - 1)$	+100 to 0

There is no shortage of ideas but practicality is important! Consequently a number of other suggestions[11] and patents[12,13] remain to be exploited to general acceptability.

2. The Assaf Cell

The Assaf Cell[14] was proposed to overcome three shortcomings of the Haring Cell:

1. Difficulty of providing uniform agitation.
2. Differing anode current densities on each side with consequent differing voltage drops.
3. Need for specific relevance to PCB through-holes.

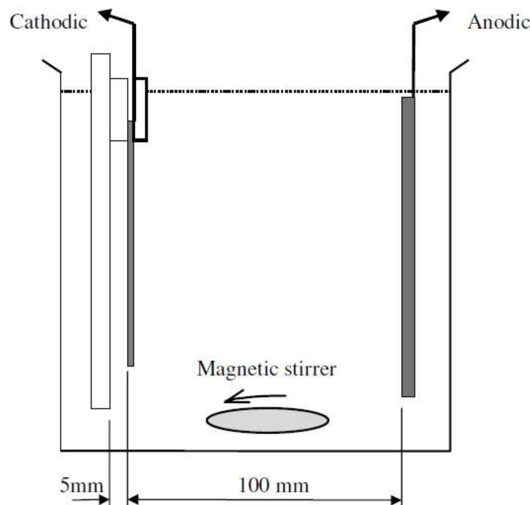

Figure 1 - Schematic of the Assaf Cell design.

An obvious advantage of the Assaf Cell is that it is in effect a small fixture that can be placed in the corner of a tank or even clipped on a plating rack. A further advantage to practical users is that it offers a narrow recess which can be adjusted and can be used as a PCB through-hole simulator where the aspect ratio (i.e. board thickness to hole diameter ratio) is large.[15]

The cathode fixture comprises a Perspex backing board and a 4 mm thick spacer onto which a 40 x 40 mm cathode sheet is fixed, as shown in Figure 1. In an alternative format a circular cathode may be used (40 mm diameter ≅ 0.25 dm^2) and different thickness spacers may be preferred to simulate specific recess geometries. Whatever the choice of shape (based on convenience or applicability) it is important to maintain the desired anode:cathode area ratio for that particular electrolyte.

Although no anode-to-cathode spacing and size ratio are prescribed, a spacing of 150 mm has been reported previously.[16] A 100 mm spacing, 1.5:1 size ratio and 40 x 40 mm cathode have been preferred in this work.[15] Electrolyte agitation is achieved by either attaching the cathode assembly to a reciprocating rod, by a magnetic stirrer or by conventional air agitation. Following deposition, the cathode is rinsed and dried and the minimum deposit thickness values (located around the central region of the cathode surfaces) are recorded. Throwing power is calculated by expressing the minimum metal thickness values as a percentage ratio:

$$\%\,T.P. = \frac{Rear\ surface\ thickness}{Front\ surface\ thickness} \times 100 \qquad [2]$$

3. Experimental results and discussion

3.1 Previous Work

In his original paper, Assaf[14] pointed out that in a conventional silver plating bath with a typical thickness of 8 to 10 μm the throwing power ratio was 2:3 to 3:4, but using pulsed current it could be reduced to 1:1. This was the demonstration of its value. It is also true that the method can identify solution contamination as shown by the values in Table 2.

Table 2 - Variation in throwing power using different electrolyte conditions.

Electrolyte	*Back:front thickness ratio*
Well-formulated silver bath, d.c.	2:3 to 3:4
Pulsed current	1:1
Aged bath with contaminants	1:17
Aged bath after filtration treatments	2:3

In a more detailed study of throwing power in silver cyanide solutions, Leisner, *et al*.[17] reported a series of results for various pulse current schedules and showed that the values were within the range 0.64 to 0.95, with DC plating giving values as low as 0.49 or 0.62. They also showed that graphs of throwing power enabled favorable pulsed current conditions to be identified and in one case, to establish an optimal current density for the system. Rasmussen[18] has used the Assaf Cell to study pulse plating of Sn-Zn alloys from an acid solution. When his values are converted to back:front thickness ratios, values of 50 to 65% have been obtained, with a slight decrease as current density was increased. A small change in alloy composition was also noted but the increasing current density could be at least partly responsible for such a change.

3.2 IPTME Research

In our work,[15] high conductivity acid-copper solutions for a PCB electroplating process were investigated and the influence of pulsed current measured. This investigation was also concerned with the use of eductors for electrolyte agitation. Initial trials (Figure 2) illustrate the reduction in throwing power that occurs with increasing current density and compare the "standard" electrolyte containing no additives and its proprietary counterpart[*] under direct current conditions. This throwing power reduction is attributed to the change in slope ($d\eta/di$) of the polarization curve as current density rises:

- At lower current densities when $d\eta/di$ is high, the current tends toward a secondary-type distribution, producing a more even metal coverage.
- As current density increases and $d\eta/di$ falls, the current assumes a more primary-type distribution and consequently throwing power falls.

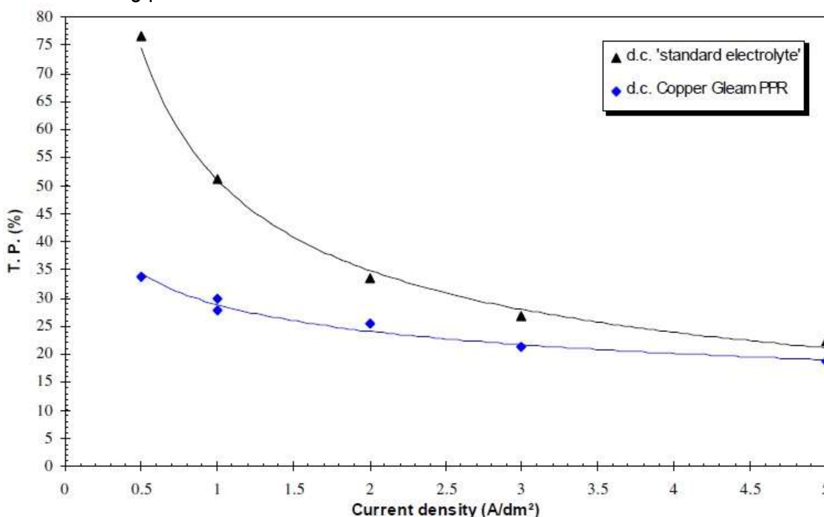

Figure 2 - Comparison of throwing power ratio between "standard" and proprietary PPR electrolytes using direct current.

The aim in analyzing such data is to identify high throwing power values at as high a current density as possible and hence upwards shifts of the trendlines in Figure 2 are sought. It should be recognized that the proprietary solution contains additives designed for periodic pulse reverse (PPR) operation. However, it is interesting to note that for the duration of this initial experiment, bright and lustrous electrodeposits were produced. By comparison those produced from the "standard" solution were level but relatively dull. Longer-term operation of the former electrolyte under DC produced progressively duller deposits, presumably as additive degradation

[*] Copper Gleam PPR©, Shipley-Ronal, Marlborough, MA.

occurred. It should also be noted that at higher current densities, the throwing power of both electrolytes tended towards similar values.

Figure 3 illustrates the effect of pulsed current on throwing power using pulse waveforms as follows:

Cathodic:anodic cycle time: 10,1 and 20,1 ms
Current density ratio, i_a:i_c: 2.8:1

It was found that at mean current densities up to 2.3 A/dm², improved throwing power may be obtained (20,1 ms waveform) when compared to direct current; beyond this limit, DC throwing power remains the most effective. This transition may be explained by the fact that a pulse reverse waveform requires a higher cathodic current density than the equivalent DC condition in order to maintain the same deposition rate. Since it has been reported[19] that the overall current distribution tends toward a primary distribution under pulse conditions, this would explain the reduction in throwing power between the pulse and DC data. The higher throwing power achieved by the 20,1 ms pulse versus 10,1 ms is attributed to the same phenomenon. Occurrence of the throwing power transition at a particular magnitude of current density is understood to be related to the type of additives used and would be expected to vary with additive concentration. Thus certain additives can be expected to be preferred in pulse-sensitive terms.

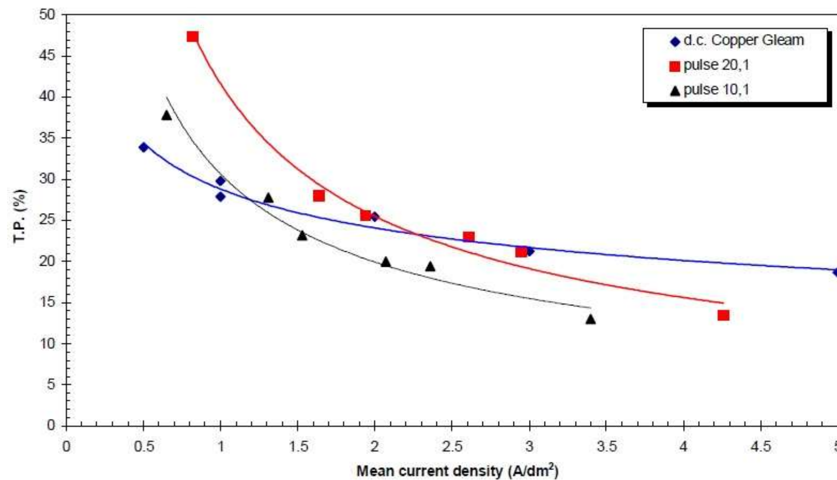

Figure 3 - Comparison of throwing power ratio between DC and PPR current in the proprietary PPR electrolyte.

Figure 4 illustrates the improvement in throwing power that was achieved beyond the 2.3 A/dm² threshold through the use of other cathodic:anodic cycle times but still with an i_a:i_c ratio of 2.8:1. The results show that throwing power may be significantly increased up to mean current densities of 3.5 A/dm² using a (cathodic:anodic) cycle time of 25,1 ms. This experiment was repeated to validate the accuracy of these particular results. Furthermore, there is a point of inflection in the throwing power behavior that occurred in the range 2.7 to 4.0 A/dm² using the 25,1, 30,1 and 40,1 ms conditions. It is reasonable, therefore, to state that:

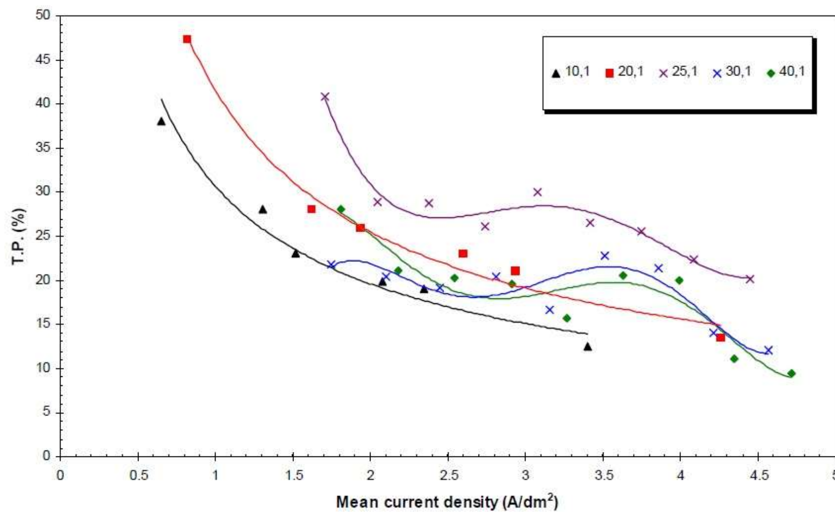

Figure 4 - Comparison of throwing power ratio between DC and PPR with modified cathodic:anodic pulse times in the proprietary PPR electrolyte.

- Changes sometimes occur at mean current densities of 3 A/dm² or above.
- Through-hole throwing power using 20,1 ms pulsed current with additives at "high" current densities is comparable with that from direct current at "low" current densities.

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As mentioned previously, improved throwing power at longer pulse on-times can be expected since a lower peak current density is required and therefore the current distribution would tend toward DC conditions. While this may explain the improved throwing power recorded for the 25,1, 30,1 and 40,1 ms timings, it cannot however account for the fact that 25,1 ms was the optimum in this study. It may be that there was a synergistic effect between this particular timing and the additives (i.e., the pulse-sensitivity of the additive is quantified), which becomes suppressed at 30,1 and 40,1 ms timings. If so, there must be scope for optimizing additives further if the 25,1 ms timing was proven to be applicable in a commercial process. It should be noted that while it is advantageous to increase throwing power, operation at higher current densities must not compromise the physical/mechanical properties of the electrodeposit.

The applicability of the Assaf test method to high aspect ratio through-hole PCBs may be of concern when considering the results obtained. This is a consequence of the cell geometry and also the annular gap behind the cathode surface (normally 4 mm), which is considerably larger than a through-hole. Electrolyte flow across the cathode surface is also somewhat different in this cell compared to full-scale process. However, Assaf Cell studies have been successfully carried out elsewhere as a means of analyzing PPR behavior in copper electrodeposition[16]. In terms of determining *trends*, therefore, this method is simple and allows a wide range of parameters to be studied relatively quickly.

Finally, it should be noted that in this study no attempt has been made to present a critical experimental comparison of the available methods of measuring throwing power. Instead, it has been considered more useful to illustrate the way in which the Assaf Cell test is performed and to show how the data obtained can be constructively used.

4. General discussion

Industrial users of commercial plating solutions have shown the virtues of the Assaf Cell as an analysis tool. Practical experience with a number of common plating solutions including chromium, zinc, copper and tin, plus less common solutions such as bismuth has shown that *in situ* analysis of problematic baths can indicate:

- Incorrect current density
- Metal ion depletion (including the effects of ineffective agitation)
- Additive and/or brightener depletion

One example cited is for data obtained from a commercial plating shop, in which process adjustments were made using Assaf Cell analysis. An acid-copper plating solution had become depleted of brightener content, achieving 75% throwing power. With brightener additions, throwing power fell to 35-50% depending upon current density (noting that that throwing power usually falls with increased current density). Results also indicated that the bath producing samples with best back-surface appearance achieved a throwing power of 47%; this represented the optimum brightener content. Thus this case serves as a reminder that metal distribution is not always related to visual appearance!

In practice, it is clear that a throwing power value of 100% represents 'perfect' thickness distribution between panel faces which can only be achieved with ideal solutions (probably complexed) and conditions. In practice, a range of 30-80% has been found normal for acid copper using d.c, noting that care must be taken when measuring deposit thickness: experience has shown that this will vary slightly between the cathode edge and middle regions, even when using a small surface area in experiments.

5. Conclusions

The Assaf Cell and jig have been used to measure throwing power in a number of solutions and for small recesses, typically as represented by through-holes on PCBs. Useful data has been generated which has enabled optimal pulsed current conditions to be identified. The graphical representation of data (%T.P. vs. Mean current density) has been shown to give clear indications of preferred pulse conditions.

This approach to throwing power measurement has been claimed to be of greatest use in the context of through-holes on PCBs. For this reason, it has not so far gained wide usage but appears to have been limited to the aforementioned research exercises; in commercial solutions the requirements have been adequately met by traditional methods. Nevertheless, the use of the Assaf Cell in these fields could offer a degree of convenience, making further studies worthwhile.

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About the authors (written at the time of publication)

Dr. David R. Gabe is Professor of Materials Engineering at Loughborough University of Technology, England, and formerly the Director of the Institute for Polymer Technology and Materials Engineering. He is a graduate of the University of Wales (Cardiff) and received a Ph.D. from the University of Sheffield. He has published more than 250 papers on electrodeposition and related coating processes, and was the recipient of the AESF Scientific Achievement Award in 1995. He also served a two-year term as President of the Institute of Metal Finishing.

Dr. Matthew Ward is a research technologist at Mars UK Ltd. Prior to this, he was a Research Associate at the Institute of Polymer Technology and Materials Engineering (IPTME), Loughborough University in the UK, where he was involved in researching properties of hard anodic films as part of a collaborative program with the European Union and three anodizing companies. Dr. Ward holds a B. Eng. In mechanical and materials engineering, and a Ph.D. for research into the electrodeposition of copper for printed circuit board manufacture. He is a member of the Institute of Metal Finishing, and to date, has published 15 papers on his research interests, which include low-friction-anodized surfaces, agitation system design, and pulsed-current technology for electrochemical processing.

Yair Assaf has owned and operated Bohak Plating Co., Ltd., Israel, since 1974. He also spent several years in the research and development of fishing fear for the government of Israel, including underwater research. He worked for seven years at the Corrosion and Surfinishing Lab, Technion Haifa, Israel, and two years as director of the plating shop of Tademon Company.