

Throwing Power Measurement: the Assaf Cell

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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.

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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 recognised 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:

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

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 - see 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 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 summarises some formulae and Throwing Power Index ranges that arise from their use.

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.

The Assaf Cell

The Assaf Cell [14] was proposed to overcome four 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. Large solution volume needed.
4. Need for specific relevance to PCB through-holes.

An obvious advantage of the Assaf Cell is that it is in effect a small jig that can be placed in the corner of a tank or even clipped on a work jig. 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 jig comprises a Perspex backing board and a 5 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 and other spacers can 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.

Table 1. Throwing Power Index formulae

<i>Author</i>	<i>Formula</i>	<i>Range of values</i>
Haring-Blum	$100 (L - M) / L$	+80 to $-\infty$
Heatley	$100 (L - M) / (L - 1)$	+100 to $-\infty$
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

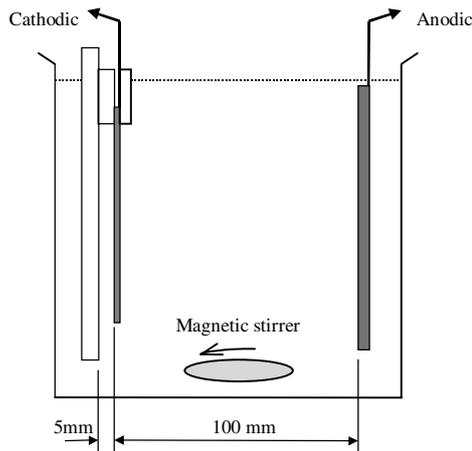


Figure 1 - Schematic of the Assaf Cell design

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 surface) are recorded. Throwing power is calculated by expressing the minimum metal thickness values as a percentage ratio:

$$\%T.P. = \frac{\text{Rear surface thickness}}{\text{Front surface thickness}} \times 100 \sim \{2\}$$

Experimental Results and Discussion

Previous Work

In his original paper, Assaf [14] pointed out that in a conventional silver plating bath with a typical thickness of 8-10 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.

In a more detailed study of throwing power in silver cyanide solutions, Leisner et al [17] reported a series of results for various pulsed current schedules and showed that the values were within the range 0.64 to 0.95, with d.c. plating giving values as low as 0.49 or 0.62. They also showed that graphs of throwing power enabled favourable 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 50-65% 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.

Table 2 - Variation in throwing power using different electrolyte conditions

<i>Electrolyte</i>	<i>Back:front thickness ratio</i>
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

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In our work [15], high conductivity acid-copper solutions for a PCB electroplating processes 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 Copper Gleam PPR ($\text{\textcircled{C}}$ Shipley-Ronal) counterpart under direct current conditions. This throwing power reduction is attributed to the change in slope ($d\eta/di$) of the polarisation 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.

The aim in analysing 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 recognised that the proprietary Copper Gleam PPR 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; in comparison those produced from the 'standard' solution were level but relatively dull. Longer-term operation of the former electrolyte under d.c. produced progressively duller deposits, presumably as additive degradation occurred. It should also be noted that at higher current densities, the throwing power of both electrolytes tended towards similar values.

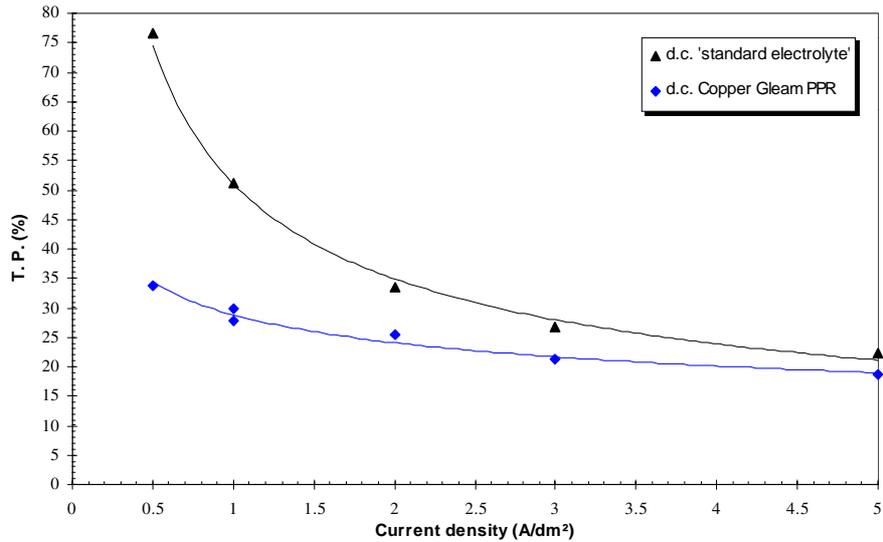


Figure 2 - Comparison of throwing power ratio between 'standard' and Copper Gleam PPR electrolytes using direct current

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, d.c. 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 d.c. 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 d.c. data; the higher throwing power achieved by the 20,1 ms pulse compared to 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.

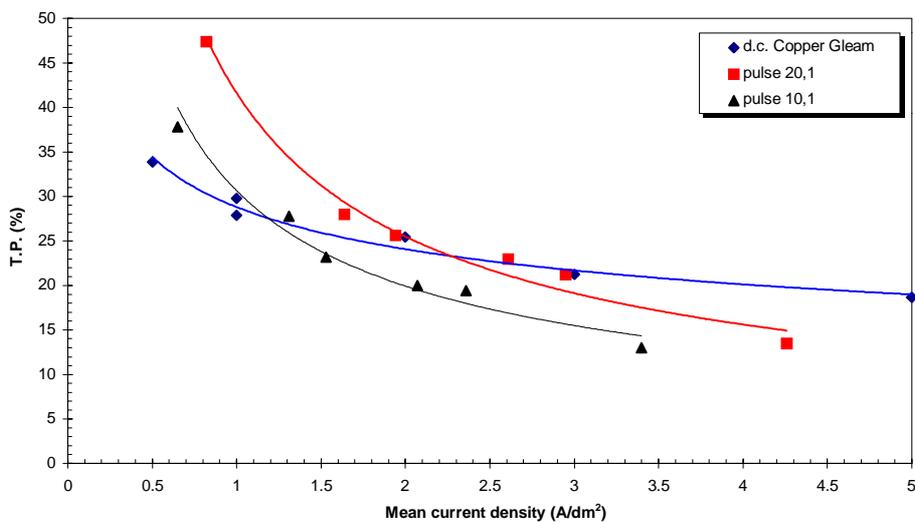


Figure 3 - Comparison of throwing power ratio between d.c. and PPR current in Copper Gleam PPR electrolyte

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 behaviour that occurred in the range 2.7-4 A/dm² using the 25,1, 30,1 and 40,1 ms conditions. It is reasonable, therefore, to state that:

1. Changes sometimes occur at mean current densities of 3 A/dm² or above.
2. 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.

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 d.c. 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 optimising 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 5 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 analysing PPR behaviour 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.

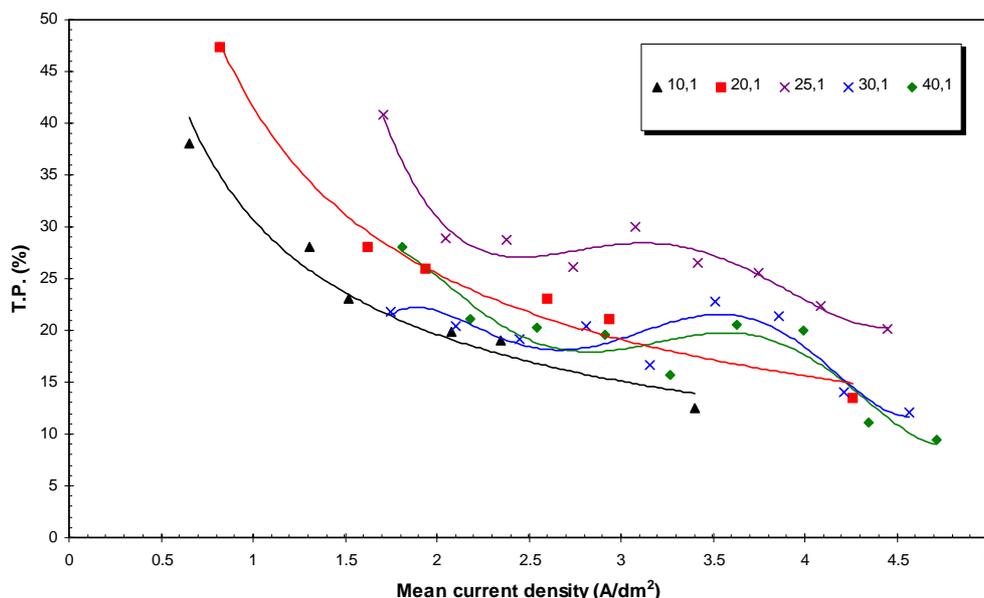


Figure 4 - Comparison of throwing power ratio between d.c. and PPR with modified cathodic:anodic pulse times in Copper Gleam PPR electrolyte

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.

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, use of the Assaf Cell in these fields could offer a degree of convenience, making further studies worthwhile.

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