

A Method towards Infinite Bath Life for Acid Copper Electrolytes

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Abstract

A new method to control and maintain electrolyte and plating performance for acid copper electrolytes has been developed. This method is based on the application of combined H₂O₂ /UV treatment on parts of the electrolyte. This treatment method can be applied as a by-pass solution for continuous production. We have shown in independent lab and technical center experiments that this method can be successfully used for such different plating techniques as Reverse Pulse Plating and DC Plating. Especially, for life time of the Via filling electrolytes which is usually less than 100 Ah/l, this method delivers the possibility to gain a quasi infinite life time leading to significantly lower costs and production down times. A second promising application is pulse plating for high aspect ratio panels (HARP). The electrolytes for this application also show usually a significant decrease of the throwing power with increasing TOC and bath life.

Working principle of the H₂O₂ /UV method is the destruction of organic additives and their breakdown products by OH radicals formed by UV- light and hydrogen peroxide. These OH radicals oxidize organic molecules to volatile decomposition products without any precipitation or oily sludge. The method is much more effective than traditional carbon treatment. Comparative experiments were performed in a 600l scale of an aged electrolyte for via filling application with TOC values of more than 1 g/l and demonstrated the superior cleaning potential. The TOC value of the aged bath of 1180 mg/l could be reduced down to 90 mg/l by H₂O₂ /UV treatment whereas traditional carbon treatment with hydrogen peroxide results in a TOC of 600 mg/l. HPLC investigations and CSB values were used to determine the quality of the cleaning procedure proving its effectiveness. Subsequent plating results with the cleaned electrolyte showed comparable plating results and life times as a new make up.

Key words: H₂O₂, UV treatment, Via filling, HDI, back panels

Introduction

In the last few years demands and product requirements for PCBs reached a level which could only be fulfilled by new products and/or improved electrolyte control mechanisms. Some of these applications include production of high aspect ratio panels and boards with blind micro vias. Both panel types require extensive electrolyte control and an extremely constant plating quality. But constant plating quality can only be achieved by a constant electrolyte constitution and quality. Unfortunately, every electrolyte ages during production thus leading to changes in the plating performance. After make up of new electrolytes one can often observe different and normally better plating results than after several hundred or thousand Ah/l. As a consequence, new make ups are a necessity. An application for which this undesired aging process is often observed is the filling of Blind Micro Vias (BMV)

Filling of BMV has become over the past 2 years more and more important for plating industry. Common approach for filling up BMVs is the traditional Cu DC setup with soluble anodes. This enables many companies to run their production in existing standard tanks without additional investment costs. For this set up only specially designed electrolytes have to be used which sometimes can be used for normal (non filling) applications. Unfortunately, it has become apparent that life time of these designed electrolytes is significantly restricted. Life times of 100 Ah/l or less have been reported leading to substantial maintenance and make up costs.

Some PCB producers apply carbon treatment to revive the bathes, others prefer a completely new make up of the electrolytes. Carbon treatment has its restrictions and it has been reported that life time after carbon treatment is even shorter than for a new make up (about 50 % of a new make up). Trials with repeated carbon treatment are even less effective so that after a short while new make ups are necessary.

Reasons for the break down of the filling ability can be different. Contaminations from leached photo resist as well as breakdown products of the inherent additive system can be responsible for the limited life time. Since nature of the breakdown products and contaminations are very different, it is not to be expected that carbon treatment can be a general answer. Active carbon usually extracts preferentially polymers with longer chain length but leaving small molecules in the electrolytes.

Therefore, we were looking for a more general approach, extracting or destroying every organic molecule, either small or long polymeric ones. A combined peroxide/UV treatment could be an alternative for the usual carbon treatment. It is known that this technique delivers good and reliable results for waste water treatments, reducing significantly the organic contamination. It has been applied for destroying complexing agents like EDTA and Ni additives.

So our intention was a) to investigate the quality of the cleaning process with peroxide /UV for copper electrolytes and b) to prove the cleaning quality by plating and filling BMVs with copper. Additionally, we wanted to show its applicability to reverse pulse plating (RPP) electrolytes.

Experimental

Cleaning procedures with peroxide/UV were performed in a lab scale unit as well as with a pilot plant. The lab scale unit is equipped with a 10 l treatment tank, a 1 KW UV lamp (200 nm up) and power supply unit for the lamp. The solution is cooled during treatment by a water cooling system

A pilot unit at A.C.K. Aquaconcept with a 12 KW UV lamp (200 nm up) for cleaning in a larger scale has been used . This pilot unit is capable of treating volumes larger than 600 l and is equipped with a cooling tower to reduce the heat which is transported into the electrolyte by the 12 kW lamps. Electrolyte circulation during treatment: 10,5m³/hr

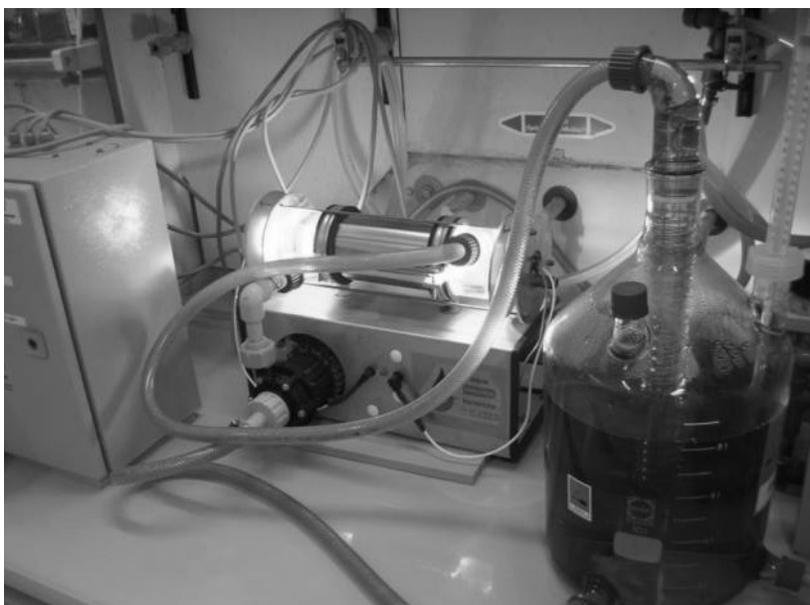


Figure 1 - Treatment Set Up with a 1 KW UV Lamp; Capacity is about 10 l; Center of the Picture is the UV Reactor

Tests for filling up BMVs were done with Cupracid HLF and for RPP we chose Cuprapulse S4 since both electrolytes are production proven. For RPP life time is significantly larger (some 1000 Ah/l) than for the BMV filling application. Here, our intention was to show that the peroxide /UV treatment is not restricted to a special acid copper electrolyte type since RPP and Filling electrolytes contain different additives.

For Via filling 600 l of a Cupracid HLF were made up in a vertical tank equipped with air agitation, soluble anodes (5 mm balls). We plated complete 18" x 24" panels. Plating results were achieved with 1,3 ASD by plating 25µm copper on the surface. The Cupracid HLF bath contained: H₂SO₄:130-140 g/l ; Cu 2+: 40-44 g/l ; Cl⁻: 40-45 mg/l, Brightener HLF: 0,5-1,0 ml/l and Leveller HLF 15-20 ml/l.

Test panels for filling the BMVs were reinforced panel types. BMV have a depth of 50-60 µm and a width of 100-110 µm. BMVs have a barrel shape, which a more difficult to fill than V-shaped BMVs.

For RPP test we asked for 600 l used Cuprapulse S4 electrolyte of a customer (bath age 2000 Ah/l) , plated test panels in a test tank, cleaned the electrolyte in the pilot plant and tested the electrolyte again.

Brightener:0,2 - 0,4 ml/L; Leveller: 33 - 39 ml/l; Cu: 20 g/l; H₂SO₄: 240 g/l;Chloride: 50 - 60 mg/l; Plating parameters I eff: 2,5; Forw. /rev 1: 2,5 Time forw./Rev: 10: 0,5 ; Expo time: 52 min .

Test panels for RPP were reinforced pattern boards with 1,8 mm thick and 0,3 mm holes. Test parameters include surface appearance, throwing power and solder shock stability. Temperature cycling test (TCT) were also performed but results are not known yet due to the long test time.

Results

Filling of BMV:

We plated test panels after make up, after every 20 Ah/l and stopped plating after 100 Ah/l, since BMVs were not filled anymore. We treated the whole volume of the electrolyte with H₂O₂/UV, refilled the tank and added our additives again. Test panels have been plated again to see whether BMVs were filled or not.

HPLC measurements with different elements and TOC values were taken after new make up at 100 Ah/l and after the treatment. Additionally, we monitored TOC values of the electrolyte during treatment with peroxide /UV.

Results are given in table 1. Plating results are given as a dimple in μm . Values of the dimple are the measured difference between the copper deposition on the surface and the deposition in the BMV. A larger dimple means no filling, dimple = 0 would mean a completely flattened BMV.

Table 1 - Cross Section and TOC Values before and after Treatment of Cupracid HLF

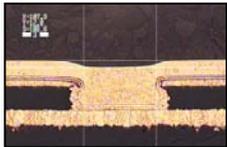
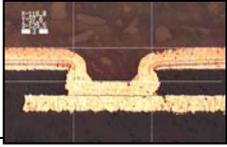
Bath age Ah/l	TOC (± 20 mg/l)	Dimple μm	Cross section
2 (new make up)	480	10-15	
100 before UV treatment	1180	50-60	
100 after UV treatment	80	No plating	
102 after UV treatment plus additives	520	10-15	

Table 1 clearly shows

1. that the TOC value could be reduced below 100 mg/l and
2. via filling performance was identical to the new make up.

The life time of the via filling electrolyte was further controlled and compared to a new make. We found that life time of the treated bath was with 80-100 Ah/l identical to a completely new made up bath.

During cleaning we monitored TOC and COD value also. Fig 2 shows the development of the TOC during the treatment. The electrolyte was treated for 24 h with 90 l 35 % hydrogen peroxide solution = 150 ml H₂O₂ per liter electrolyte. This value seems to be high but costs for hydrogen peroxide are rather low (1 l H₂O₂ = 0,40 E).

The cleaning efficiency is rather good. The TOC value could lower down to 7% of the original value.

The COD value of the electrolyte is given in table 2. The cleaning efficiency based on this value is also extraordinarily good. The COD is lowered down to only 3 % of the original value

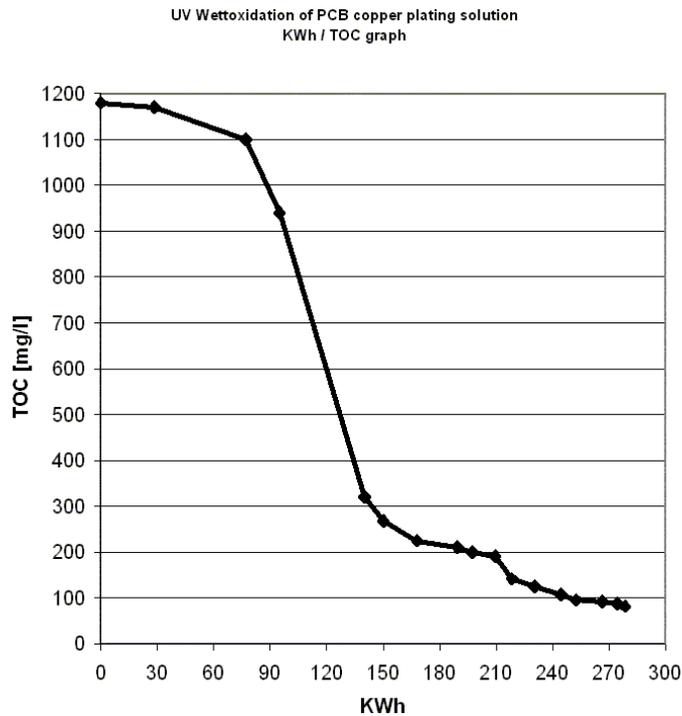


Figure 2 - Development of the TOC During UV/H2O2 Treatment Procedure took 24 hours : 120 kWh = 10 Hours

Table2 - Development of COD during Treatment

Treatment time (h)	Energy kWh	COD (± 50 mg/l)	Percentage
0	0	3490	100
2,3	28	3450	99
10	120	1560	45
20	240	120	3

The electrolyte is clear blue after the treatment, no sludge formation has been observed. Quality of the cleaning is controlled by HPLC method with different UV detector. Since none of the Cupracid HLF additives is UV active only contaminations and/or breakdown products are visible. Fig. 3 shows the chromatograms of the 100 Ah/l old bath before and after UV treatment.

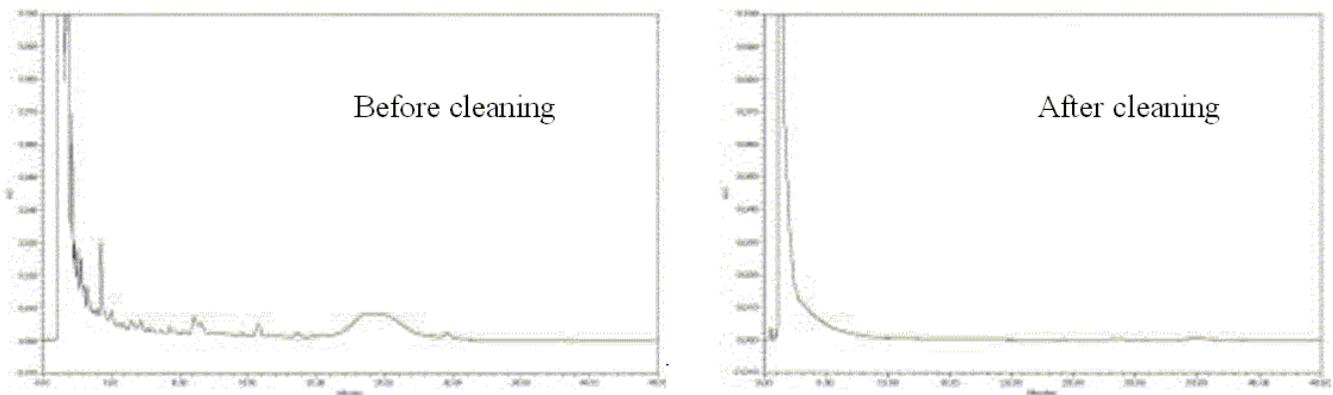


Figure 3 - HPLC-UV for Cupracid HLF with 100Ah/l (left) and after Treatment UV/H2O2 (right)

The HPLC of the treated electrolyte is identical to one of a new made up electrolyte.

Tests were repeated in our small lab line with Production electrolyte from customer. The TOC value of these electrolyte was 0,700 g/l and we added different amounts of peroxide to see which TOC value could be reached. Additionally, we aged the

electrolyte and controlled again via filling with the aforementioned parameters. All electrolytes showed proper filling results and showed identical life times as newly made up electrolytes!

Table 3 summarizes the results for different H₂O₂ concentrations, treatment times and the cleaning efficiency.

Table 3 - Effect of Different Peroxide and Treatment Parameters

Plant	ml/l H ₂ O ₂	Treatment time h	TOC before mg/l	TOC after mg/l	Cleaning efficiency
Pilot	150	24	1180	80	93%
Lab scale	90	8	700	280	60%
Lab scale	60	5	700	350	50 %

Reverse Pulse Plating

600 l of a 1,5 year old production electrolyte with a TOC value of 2,6 g/l has been treated in the pilot plant with identical treatment parameters as with the HLF bath. Results are given in table 4. The cleaning efficiency was again with 85% very good.

Table 4 - Results of a Cleaned Cuprapulse S4 Electrolyte - Test Boards: 1,8 mm with 0. 3mm Holes

	Before cleaning	After cleaning	After addition of additives
TOC mg/l	2600	400	950
Solder shock test 6 x 10 s 288°C	passed		passed
Throw IPC %	132		137
Throw Min	117		124
Copper µm	31		32
Sludge	No	No	No

Results before and after cleaning were comparable.

Application

The title of this paper is a promise. A promise that this paper should show a way how to achieve an infinite life time. But how can we realize this. The way we believe that infinite life time could be achieved is outlined in the following chapter.

We have shown that the cleaning procedure works with an extraordinary efficiency so that the cleaned electrolyte can be used again for plating again, without quality losses for the production. The advantages compared to a traditional cleaning procedure with Active Carbon (even with peroxide or permanganate)

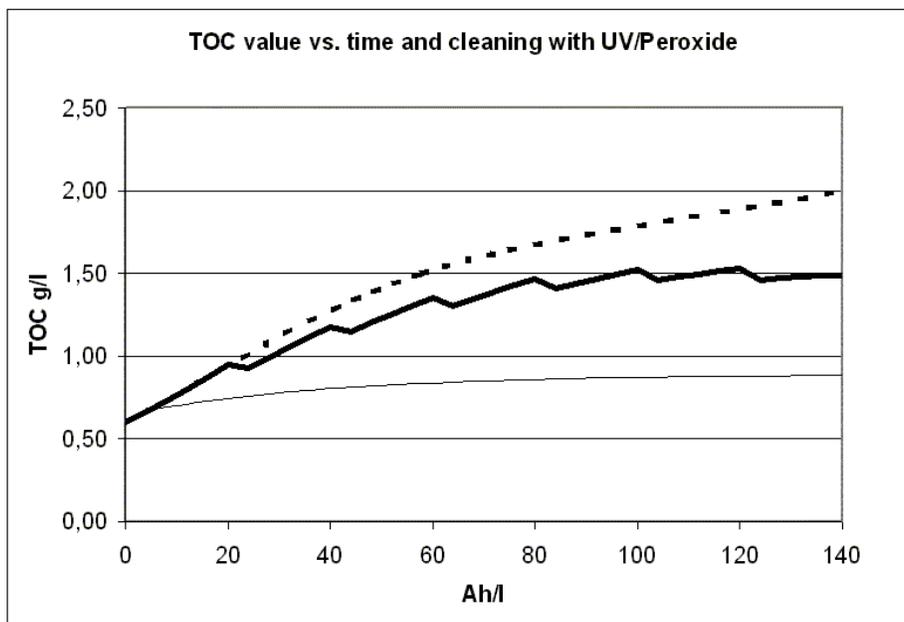
- No sludge formation
- Higher efficiency
- No contamination

A possible production scenario could be like this:

- 10-15 % percent of the production solution are transferred into a treatment tank
- At the same time 10-15 percent newly made up electrolyte (in a second tank) are transferred into the production line.
- The 10-15 % old electrolyte are treated with peroxide /UV over a period of 1-1,5 days. The cleaning procedure is controlled by the analysis of TOC and Peroxide, so that no peroxide is left.
- The cleaned electrolyte is than transferred into the second tank, brightener and leveler are added and can therefore be used for the replacement next cycle.

This procedure allows for a continuous production, since the small volume exchanges do not require any dummy plating. This set up requires the UV cleaning set up with UV lamp, a peroxide dosing system, a treatment tank about a size of 10-15 % of the production line, a second tank of the same size for the new make up and piping system.

To demonstrate how the frequent cleaning procedure would influence the TOC we calculated the TOC value which results with two different cleaning frequencies. Fig 4 shows the development of the TOC with time. The calculation is based on the measured TOC of a production electrolyte (Cuprapulse S4, dotted line) without any cleaning procedure. Calculation of the other two curves are based on following assumptions: 10 % of the solution is cleaned, additives are readjusted and retransferred into the tank. The TOC value after cleaning before readjustment of additives is 0,30 g/l. Cleaning frequencies are every 4 Ah/l (thin line) and every 20 Ah/l (thick line).



Dotted line = without cleaning
 Thick line = every 20 Ah/l
 Thin line = every 4 Ah/l

Fig. 4 TOC of a Cuprapulse S4 Electrolyte vs Bath Age for Different Cleaning Frequencies

As a result, the TOC value reaches a constant value after several Ah/l. The value depends strongly on cleaning frequency. For the 20 Ah/l cleaning frequency this value is with 1.5 g/l significantly higher than for the 4 Ah/l cleaning. After reaching the saturation TOC, the TOC changes only in very small amounts, thus leading to a constant plating performance! This value and performance should be kept for years without any changes!

This setup requires substantial investment costs which depend strongly on the frequency of the treatment, and the size of the production line. Investment costs range from 70-150 thousand € for production lines with capacities of 20 000 – 70000 l. Nevertheless, we believe that installation of such a line will pay off within a few years. The costs for one liter of new copper electrolyte (without additives) are very high especially for the via filling electrolytes with the high copper loading. A liter of this electrolyte can be about 1,25 € including waste water costs.

Treatment costs of 1 liter electrolyte (including peroxide and energy) range from 0,05 to 0,30 € per liter depending on the desired efficiency. Thus, a complete cleaning cycle of 60000 l acid copper electrolyte would save about 57 000 to 72 000 €. For electrolytes with a lower copper concentration savings would be lower, since the main cost driver is copper.

Summary

We have shown that peroxide/UV treatment of acid copper electrolytes is a much more effective cleaning procedure than the traditional AC treatment. We showed the performance of the electrolytes after the treatment is comparable or identical to newly made up electrolytes. We could not observe any quality problems with the electrolytes. This offers especially for μ -Via filling electrolytes an interesting possibility to increase life time of the electrolytes thus leading to substantial cost savings. We developed a procedure where portions of the electrolyte are cleaned batch wise, but without any production down times. The setup requires investment costs which should pay off in a few years since savings by cleaning the acid copper electrolytes are enormous.

Acknowledgement

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