Cupric Chloride-HCl Acid Microetch Roughening Process

by Kesheng Feng, Nilesh Kapadia, Brian Jobson, Steve Castaldi,
MacDermid

Copper surface roughening is an important step to achieve good adhesion for dryfilm photo resist and solder mask in PCB fabrication. The roughening process can be accomplished by mechanical means, such as pumice scrubbing or brushing, or by chemical micro etching means. Mechanical cleaning methods are not suited to the processing of thinner core or fine line boards. The micro etch chemical methods commonly used are ferric chloride, persulfate salt, and hydrogen peroxide-sulfuric acid. Recently, a new micro etching chemistry, cupric chloride-hydrochloric acid-additives, was introduced. The chemistry creates unique roughened copper surface topography. This type of roughness can be used for various processes where good adhesion to copper surfaces is needed.

Reviewing the history of printed circuit boards, for each copper etchant, there is a correlated micro etchant. For examples, peroxide-sulfuric acid, persulfate salt, ferric chloride systems are used for both etching copper and micro etching copper surface. Cupric chloride systems have always been interesting for micro etching applications just like the cupric chloride etching system developed in the 1960's. However, the roughness from cupric chloride micro etching depends on the organic components in the system. It has been reported that a micro etching solution containing cupric chloride (or ferric chloride), peroxysulfuric acid and quaternary ammonium cationic surfactant provided a smooth, polished surface rather than a roughened one. It has also been reported that the chemistry of cupric chloride with organic acid provided a roughened surface, which offered good adhesion for solder mask and dryfilm photo resist and for bonding the copper layer and the prepreg layer. In order to resolve the environment and waste treatment issues deriving from the use of the cupric chloride-organic acid micro etching solution, a recycling system for this chemistry was presented in which the micro etchant is recycled by solvent extraction.

Cupric chloride-hydrochloric acid micro etching solution

Cupric chloride with hydrochloric acid has been the basic chemistry for etching solution in printed circuits board industries, in which a constant etching rate can be maintained indefinitely. Based on this chemistry, a new micro etching technology, MultiPrep, composed of cupric chloride, hydrochloric acid and additives, has been developed at MacDermid. This technology provides excellent solder mask adhesion through ENIG, nickel-gold plate, Immersion Tin, HASL, silver, OSP and other alternative final finishes. It also can be used as a micro etching cleaner for dryfilm photo resist applications to promote the adhesion between dryfilm and copper surface.

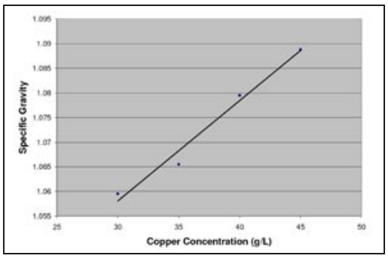
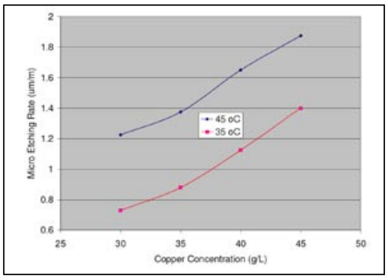


Figure 1 – The relation between Cu concentration and specific gravity

Figure 2 – Micro etching rate versus copper concentration at a temperature between 35°C and 40 °C



The micro etching chemistry of cupric chloride and hydrochloric acid with additives, MultiPrep, provides uniquely roughened copper surface topography, which offers a uniform micro etched appearance on copper substrates including electrolytic pulse plated panels (PPR).

Due to the nature of the chemistry from cupric chloride and hydrochloric acid, the cupric chloride-hydrochloric acid based micro etching solution provides stable and consistent micro etching rate, uniform rough surface, high copper capacity, long bath life and easy to control. There is no organic acid involved in the chemistry.

Chemistry maintenance

Specific gravity

In the cupric chloride etching solution, the copper concentration is maintained between 125 to 175 g/L. This corresponds to a specific gravity range of 1.2393 to 1.3303. In order to reach a reasonable micro etching rate, the copper concentration in the micro etching solution is maintained between 35 g/L to 45 g/L for MultiPrep chemistry in order to also get a steady micro etching rate.

The copper concentration is controlled by a specific gravity controller, and kept between 1.065 to 1.088, as shown in Figure 1. The relationship between copper concentration and micro etching rate is shown in Figure 2: under free acid at 0.18 N, higher copper concentration provides higher micro etching

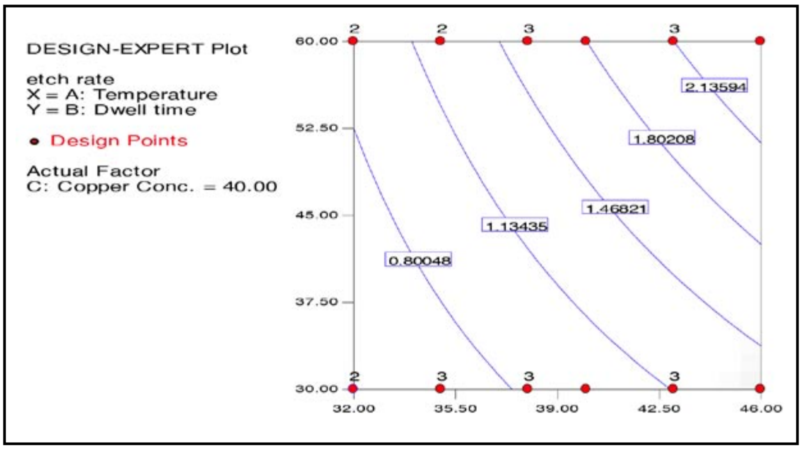


Figure 3 – DOE for micro etch rate change

rate. Feed/bleed steady state could be controlled by a specific gravity controller, which maintains copper concentration within 40 ± 1.5 g/L. When the specific gravity controller is used, the micro etching rate affected by copper concentration is within 0.125 µm/m.

Temperature vs. micro etching rate

As shown in the Figure 2, the micro etching rate is higher with higher bath temperature. When copper concentration is at 40 g/L, bath temperature (°C) was studied. The micro etch rate is predictable on the basis of Figure 3.

Depending on the dwell time required, the micro etching rate (amount) is easily controlled by bath temperature. For example, the micro etching amount was about 0.8 µm when bath temperature was at 33°C, dwell time of 45 seconds, which is good for inner layer, such as dryfilm photo resist applications. It becomes 1.13 µm when temperature is 37°C, which will give great roughness for outer layer, such as solder mask applications.

Besides the micro etching rate, another important factor for the cupric chloride-hydrochloric acid micro etching solution is the roughness and the topography of the micro etched surface. Roughness as measured by Zygo profilometry instrument, Ra (average surface roughness) indicates the chemistry provides higher roughness under higher micro etching amount.

A higher temperature will yield a rougher surface even under the same micro etching amount.

For example, roughness is above 0.4 µm when the micro etching amount is above 1.00 µm at the temperature between 40 and 43°C under the conditions tested, while the roughness is below 0.40 µm under the same micro etching amount when the temperature is between 35 and 38°C. The SEM images in Figures 4 and 5 show the topography under two micro etching rates at a temperature of 40°C.

Free acid level versus micro etching rate and roughness

Free acid is a measurement of the amount of hydrochloric acid in the system. Cupric chloride micro etchant must have at least some detectable free acid for optimum etch efficiency and for preventing copper hydroxide solid formation. Hydrochloric acid keeps the relatively insoluble cuprous chloride complex molecule in solution where it can be regenerated.

Higher acidity provides higher micro etching rate as shown in Figure 6. The free acid is controlled by conductivity under feed/bleed steady state. The relationship between acidity and roughness, Ra, is shown in Figure 6. It shows that the roughness is not affected by acidity once the etching rate is above 1.40 µm/m. With lower etching rate, the chemistry gave a roughness above 0.40 µm as long as the acidity is within the range of 0.30N to 0.50N.

HCl post rinse and equipment design

After the micro etch chemistry of cupric chloride-hydrochloric acid, a layer of copper complex or copper oxide is formed on the copper surface, and a hydrochloric acid post rinse is needed to clean the copper surface. The acidity for the post rinse is normally 4-6%. This post acid rinse solution can also be used to maintain the acidity needed for micro etch bath to reduce the waste treatment, by replenishing the acid solution to the micro etching bath. Based on the control on the specific gravity and acidity in the micro etching solution, and the control on the acidity in hydrochloric acid post rinse, a controlling system was designed. Concentrated hydrochloric acid is mixed with water in a ratio to get the concentration about 1.4 N (5.1%) in post rinse bath, which is used to remove the copper complex or copper oxide on the micro etched copper surface. The hydrochloric acid in the post rinse bath is pumped into the micro etching bath along with the additive when the acidity is low, which is consumed by the reaction from copper (I) to copper (II). Copper concentration in the micro etching bath is controlled by specific gravity.

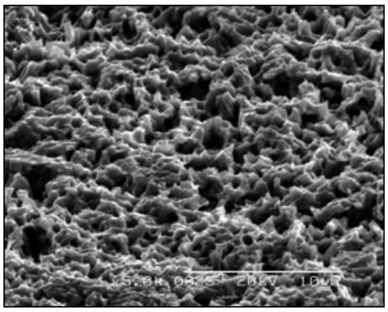
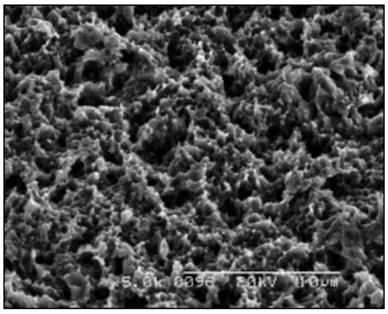


Figure 4 – SEM, x5000, for temperature 40 oC, micro etch amount 1.88 µm, Ra 0.667 µm

Figure 5 – SEM, x5000, for temperature 40°C, micro etch amount at 0.90 µm, Ra at 0.445 µm



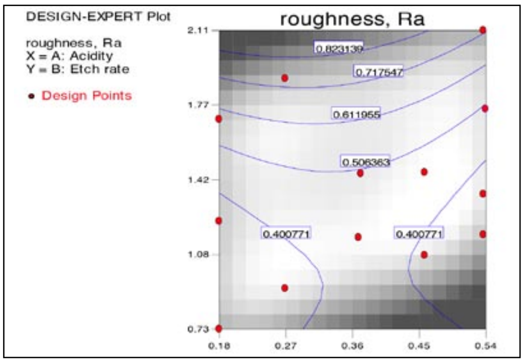


Figure 6 – Influence of acidity and micro etch rate on surface roughness, Ra

Applications

Both SEM and Zygo profilmetry showed that MultiPrep yields a roughened surface. The performance, including dryfilm photo resist, solder mask, prepreg resins, was tested on the roughened copper surfaces comparing it to the mechanically scrubbed copper surfaces.

Dryfilm adhesion/resolution performance

As is known, the surface preparation is important for dryfilm applications in order to get acceptable adhesion. There is no doubt that current cupric chloride-hydrochloric acid micro etching process provide good adhesion for dryfilm application, but it must be balanced between adhesion and resolution for the applications where fine lines, such as 30-40 µm, are involved (Figures 7 and 8).

In the tests, board surfaces were processed through cupric chloride-hydrochloric acid micro etching solution. The micro etching amounts were 1.0 µm and 1.38 µm, respectively, and the resulting roughness was 0.40 µm and 0.55 µm.

MacDermid's Aquamer LF 106 dry film, was laminated onto copper surfaces treated by the cupric chloride-hydrochloric acid micro etching chemistry, comparing it to the one mechanically scrubbed. It was then run through the photoimaging and developing processes (Exposure: 30 mJ/cm^2; Development: 1% sodium carbonate, 33°C).

The line resolution at 30 µm was evaluated under microscope. It was found that the dryfilm on the roughened surface treated by cupric chloride-hydrochloric acid micro etching solution had excellent adhesion, while the one on scrubbed surface lost adhesion.

Resolution was checked by SEM pictures. 30 µm of dryfilm lines/spaces was resolved well when surface roughness was at 0.40 µm under micro etching amount 1.0 µm, while some areas had foot-reside left when the surface roughness was 0.55 µm under micro etching amount of 1.38 µm. Therefore, for fine line applications, the surface roughness should be controlled within a certain range to balance adhesion and resolution.

Solder mask performance

It is known that the peel-off problem of solder mask occurs during nickel-gold plate and immersion tin plate processing.

Solder mask adhesion was tested on the roughened surface treated by the cupric chloride-hydrochloric acid micro etch system, comparing it to the surface treated by mechanical scrubbing. The micro etch amount for copper surface was about 1.0-1.3 µm.

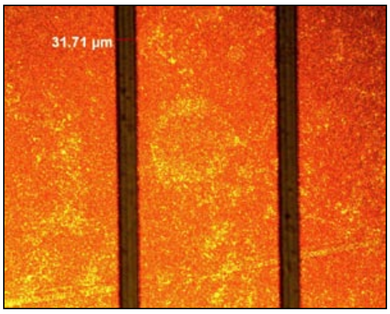
Solder mask, Taiyo 4000 BN (HV), was applied to the treated copper surfaces, then processed through final finish plating applications according to the flowing parameters

- Solder mask: PSR 4000 BN (HV) (Taiyo)
- Drying: 80°C, 30 min
- Exposure: 300 mJ/cm^2
- Development: 1% sodium carbonate, 35°C
- Postcure: 150°C, 60 min.

Tape test is applied to the target patterns (3.0 mil lines) after Electroless Nickel-Gold and MacStean HSR immersion tin final finishes. The panels processed with the cupric chloride-hydrochloric acid micro etch chemistry had no damage, while the one processed by mechanical scrub had a lot of damages for both final finish applications (under microscope).

Figure 7 – Dryfilm picture under microscope. Surface was treated by MultiPrep chemistry (left)

Figure 8 – Dryfilm picture under microscope. Surface was mechanically scrubbed (right)



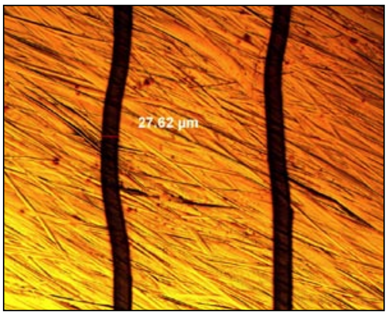
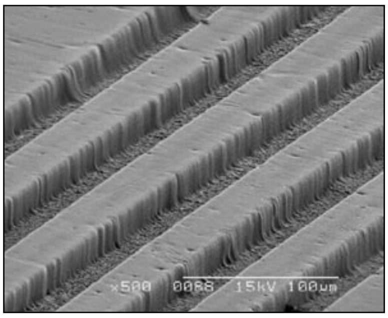
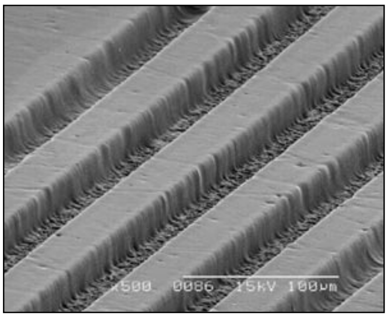


Figure 9 – SEM of dryfilm, whose surface was treated by MultiPrep chemistry. Micro etch amount 1.0 µm (left)

Figure 10 – SEM of dryfilm, whose surface was treated by MultiPrep chemistry. Micro etch amount 1.38 µm (right)





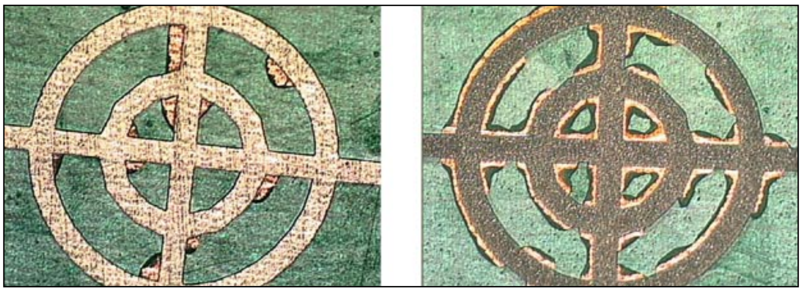
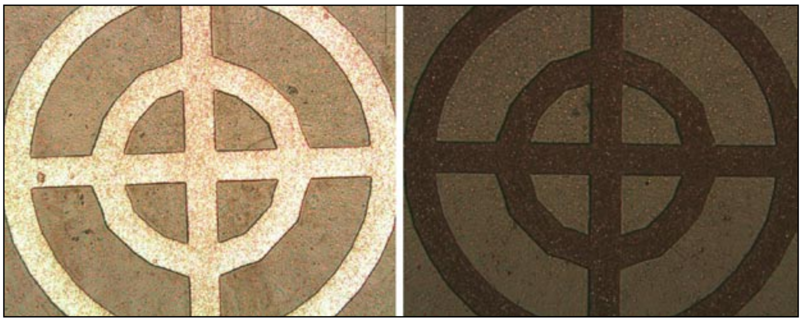


Figure 11 – Tape tests on solder mask, scrubbed copper surface: nickel-gold plating (left) and immersion tin plating (right)

Figure 12 – Tape tests on solder mask, copper surface treated by MultiPrep chemistry: nickel-gold plating (left) and immersion tin plating (right)



The finished boards whose underlying copper had been treated with cupric chloride-hydrochloric acid micro etching process were tested for solderabilty and solder spread using IPC J-STD-003 Test A (solder dip test):

- Conditioning: 2x lead free reflows with peak temp of 250°C
- Solder temperature: 250°C.
- Flux Type: 2% adipic acid in 2-propanol
- Solder Immersion Time: 3 and 10 seconds

All panels showed excellent soldering with uniform wetting as shown in Figure 13 and 14.

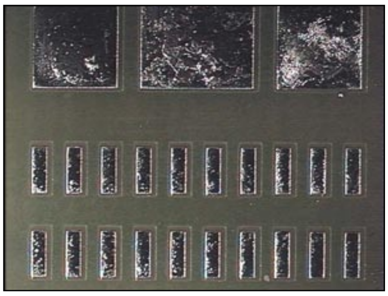
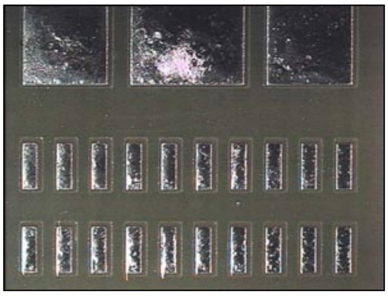


Figure 13 – Edge Dip Test after 3 sec

Figure 14 – Edge Dip Test after 10 sec



The samples were also tested according to IPC J-STD-003 Test E (Surface Mount Process Simulation):

- Conditioning: 1 and 2x lead free reflow cycles
- Peak temperature: 250°C
- Solder Alloy: 96% tin, 3.5% silver and 0.5% copper
- Time above Liquidus: 60 seconds

All panels displayed intermetallic layers free of any voiding. All panels also displayed uniform wetting over all SMD pads. The solder wetting angle was about 90° which is perfect according to the IPC standard. The tests showed that the cupric chloride-HCl micro etching process produced a reliable and good quality for solder mask adhesion in combination with e'less final finishes.

Bond strength to prepregs

Peel strength was examined between prepregs and copper surface after being pressed. The panels were solder shocked at 288°C for 10 seconds, 3X and 6X times. Peel strengths were determined using a Diventco peel tester. The surfaces processed by cupric chloride-hydrochloric acid micro etchant, brown oxide, alternative brown oxide, and the combinations were compared.

From these tests, the surface treated by cupric chloride-hydrochloric acid micro etchant offered excellent roughness to get peel strength before any thermal shock treatments, but it lost the adhesion after thermal shock. When brown oxide or alternative organic metallic oxide was applied to the surface, the peel strength increased remarkably.

Conclusions

Copper chloride-HCl micro etching chemistry offers uniform roughened surface, which provides great adhesion for solder mask and dry-film photo resist applications. The chemistry could be controlled just like to run a mini copper chloride etcher. The micro etching rate or micro etching amount is predictable from this chemistry. A higher temperature will give a rougher surface even under the same micro etching amount. The acidity has little effect on surface roughness, but it affects the micro etching rate due to increasing chloride concentration. The chemistry is organic acid free, creating less VOC issues. The performance of dryfilm photo resist shows that the surfaces treated by the cupric chloride-HCl micro etching chemistry provide excellent adhesion, but the micro etching rate and roughness should be balanced where fine line applications are required. The roughened surface offered excellent adhesion for solder mask applications and prepreg resins in PCB fabrications.

This article is based on a paper originally presented at the IPC Printed Circuits Expo, APEX and the Designer's Summit 2008

Table 1 – Peel strength on different surfaces, prepreg Isola 406

Process	Surface processed by	No Solder Dip	3X Solder Dip	6X Solder Dip
1	Cupric chloride-HCl micro etch	5.9	4.6	0.5
2	Brown oxide	7.2	5.1	3.8
3	Alternative brown oxide	6.3	4.9	3.8
4	Process 1+ brown oxide	9.0	6.5	4.4
5	Process 1 + Alternative brown oxide	7.9	6.8	4.2