Cupric Chloride-Hydrochloric Acid Microetch Roughening Process and its Applications

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Abstract

We have developed a cupric chloride-hydrochloric acid based microetchant process. This process provides a unique roughened copper surface, which yields excellent adhesion for both solder mask and dry film photo resist applications. The process also yields excellent solder mask adhesion through subsequent silver, tin and nickel plating post solder mask application.

The amount of copper etched using cupric chloride-hydrochloric acid based microetchant is not as high as that seen typically in cupric chloride etching systems. Airborne oxygen is efficient enough to be used as an oxidizer in the system. Hydrochloric acid maintains the proper hydrogen and chloride ion concentrations. The cupric ion maintains itself throughout the process.

The chemistry and process are both easily controlled. The process operation is comparable to a mini cupric chloride etcher, whereby copper concentration is maintained by specific gravity and acidity can be controlled by conductivity. It is not necessary to control oxidation-reduction potential, hence the difference as compared to conventional etching processes.

This technology provides highly roughened copper surfaces for conventional acid plated copper such as PPR and DC, and standard regular copper clad, which offers great adhesion for solder mask and dry film photo resist. For solder mask applications, it is necessary to produce a rougher topography by controlling micro etching rate at 1.0-1.5 µm/m to get good adhesion between copper surface and solder mask when the final finish is involved in immersion or electroless plating process with tin or nickel. For dry film photo resist applications, the processed copper surface is rough enough to improve the adhesion at micro etching rate below 1.0 µm/m. The copper surface roughness should be controlled within a range to balance the adhesion and resolution when dryfilm photo resist is used for fine line boards.

Introduction

At Electronic Circuits World Convention 11 Conference, Shanghai, China, March 17-19, 2008, 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 is needed to copper surfaces.

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.

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 system has been always interesting for micro etching application just like the cupric chloride etching system developed in 1960's. However, the roughness from cupric chloride micro etching depends on the organic components in the system. Rudolf Sedlak (RD Chemical Company, US 4,956,035, September, 1990) 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. While Maki Yoshiro et al (MEC Co. Ltd., US 5,807,493, September, 1998) reported that the chemistry of cupric chloride with organic acid provided a roughened surface, which offered good adhesion for solder mask, dryfilm photo resist and for bonding the copper layer and the prepreg layer. In order to resolve the environment and waste treatment issues from cupric chloride-organic acid micro etching solution, Sachiko Nakamura (ECWC 8, Tokyo 99) presented a recycling system for this chemistry, in which the micro etchant could be recycled by solvent extraction method.

In this paper, the new chemistry of cupric chloride-hydrochloric acid is reviewed along with its applications.

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, is developed in MacDermid, Inc. This technology provides excellent solder mask adhesion through ENIG, Nickel-Gold plate, Immersion Tin, HASL, Silver, OSP and other alternative Final Finishes etc. It also can be used as a micro etching cleaner for dryfilm photo resist applications to promote the adhesion between dryfilm and copper surface.

The micro etching chemistry of cupric chloride and hydrochloric acid with additives, 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.

1. **Chemistry Maintenance**

(1). Specific gravity

In cupric chloride etching solution, copper concentration is being controlled 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 to get a steady micro etching rate. The copper concentration is controlled by specific gravity controller, between 1.065 to 1.088 as shown below 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 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.

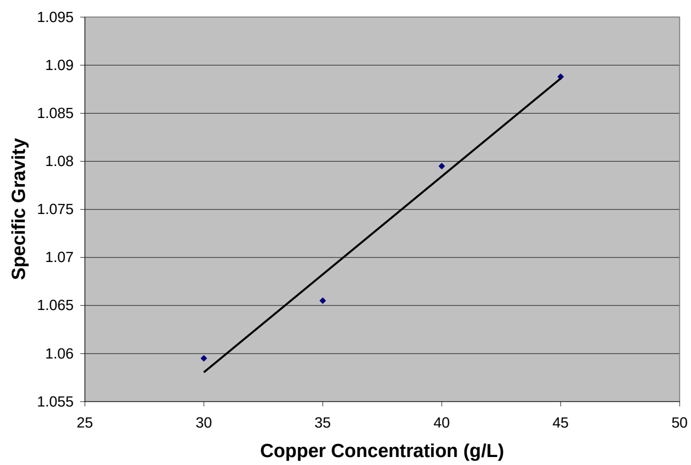


Figure 1 - The relation between copper concentration and specific gravity

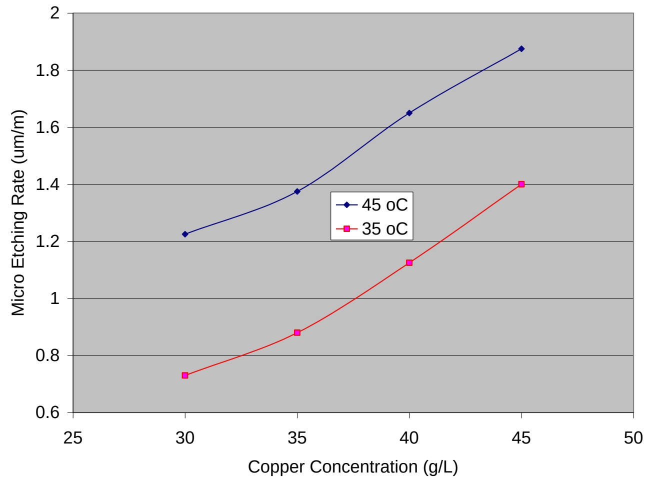


Figure 2 – Micro etching rate versus copper concentration under temperature at 35 ºC & 40 ºC

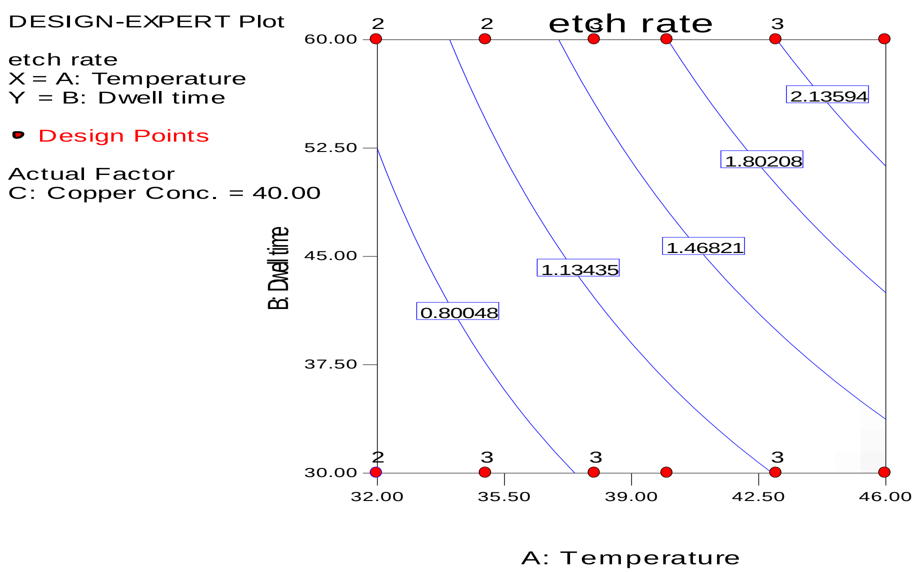


Figure 3 – DOE for micro etch rate change

(2). Temperature versus 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 (ºC) was studied. The micro etch rate is predictable based on the 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 ºC, dwell time of 45 seconds, which is good for inner layer, such as dryfilm photo resist applications. It will become 1.13 µm when temperature was at 37 ºC, which will give great roughness for outer layer, such as solder mask applications.

Besides the micro etching rate, another important factor for 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) indicated 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 as shown in the figure below.

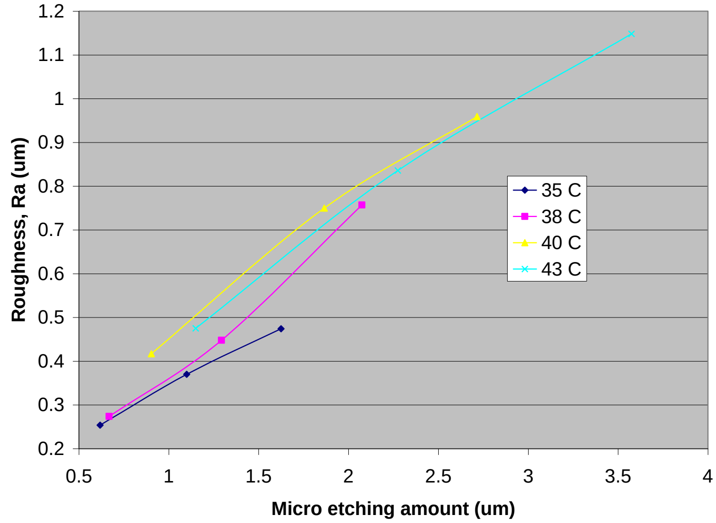


Figure 4 – Micro etch amount versus roughness under different temperature

For example, roughness, Ra, is above 0.4 µm when the micro etching amount is above 1.00 µm at the temperature 40 and 43 ºC under the conditions tested, while the roughness is below 0.40 µm under the same micro etching amount when the temperature is 35 and 38 º C. SEM below showed the topography under two micro etching rate at temperature of 40 ºC.

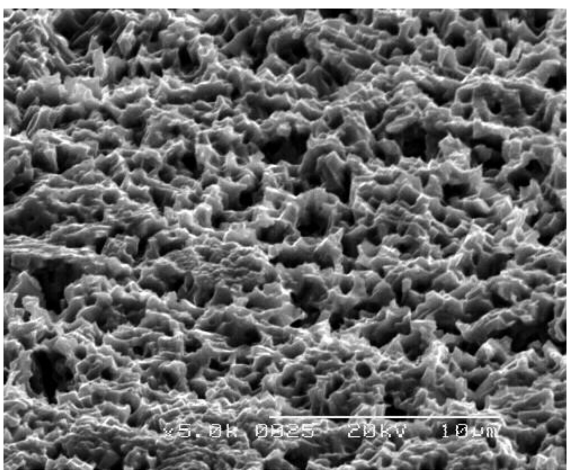


Figure 5 - SEM, x 5 K, for the conditions on temperature at 40 ºC, micro etch amount at 1.88 µm, Ra at 0.667 µm.

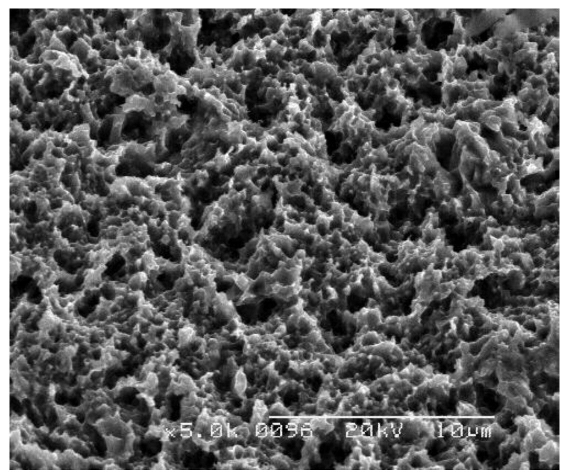


Figure 6 – SEM, x 5 K, for the conditions on temperature at 40 ºC, micro etch amount at 0.90 µm, Ra at 0.445 µm

(3). 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 the chart. The free acid is controlled by conductivity under feed/bleed steady state. The relationship between acidity and roughness, Ra, was shown in the figure below. It shows that the roughness, Ra, is not affected by acidity once the etching rate is above 1.40 µm/m. With lower etching rate, the chemistry gave a roughness, Ra, above 0.40 µm as long as the acidity is within the range of 0.30 N to 0.50 N.

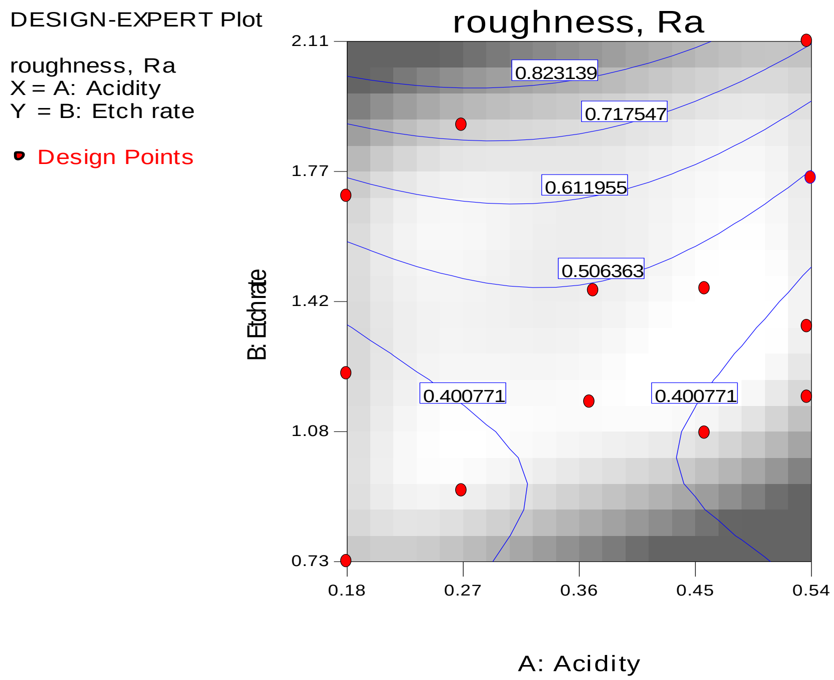


Figure 7 – Influence of acidity and micro etch rate on surface roughness, Ra.

2. Hydrochloric acid 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 as shown in the figure below.

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.

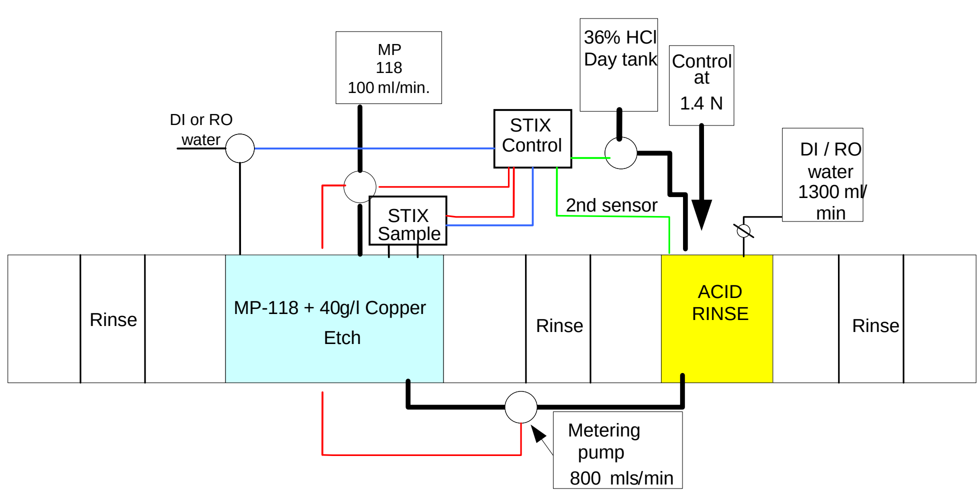


Figure 8 – The controlling system for the micro etching system

3. Applications

Both SEM and Zygo profilmetry showed the new microetchant yielding a roughened surface. The performance, including dryfilm photo resist, solder mask, prepreg resins, was tested on the roughened copper surfaces comparing to the mechanical scrubbed copper surfaces.

(1). Dryfilm adhesion/resolution performance

As it is known, the surface preparation is important for dryfilm applications 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 as shown below.

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, to get roughness, Ra, 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 to the one mechanically scrubbed, then through the process of photoimaging and developing.

Exposure: 30 mJ/cm^2
Development: 1% sodium carbonate, 33 ºC.

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 has excellent adhesion, while the one on scrubbed surface has already lost adhesion.

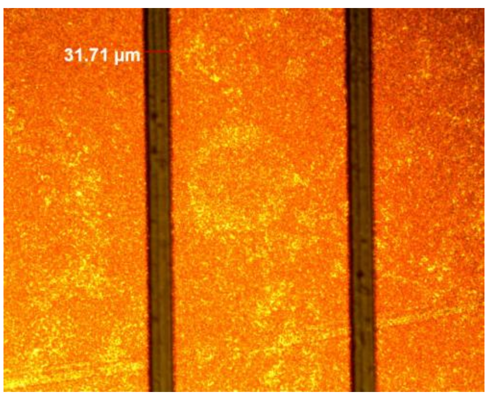


Figure 9 – Dryfilm picture under microscope, Surface was treated by MultiPrep chemistry

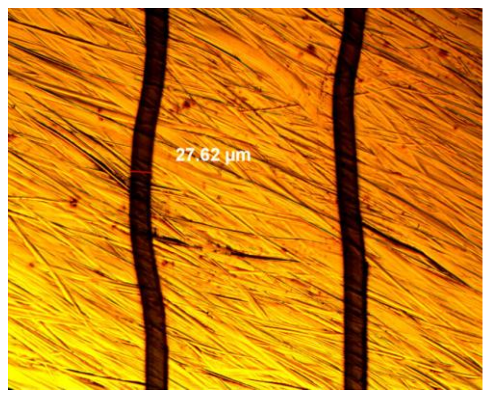


Figure 10 – Dryfilm picture under microscope, Surface was mechanical scrubbed

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 at 1.0 µm, while some areas had foot-reside left when the surface roughness was at 0.55 µm under micro etching amount at 1.38 µm. Therefore, for fine line applications, the surface roughness should be controlled within a certain range to balance adhesion and resolution.

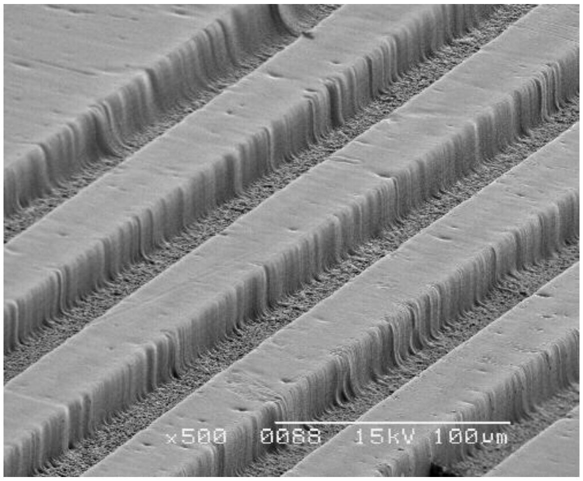


Figure 11 – SEM of dryfilm, whose surface was treated by chemistry, micro etch amount at 1.0 µm

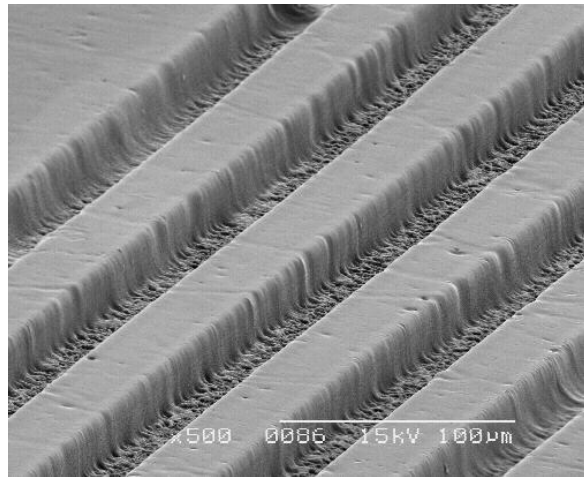


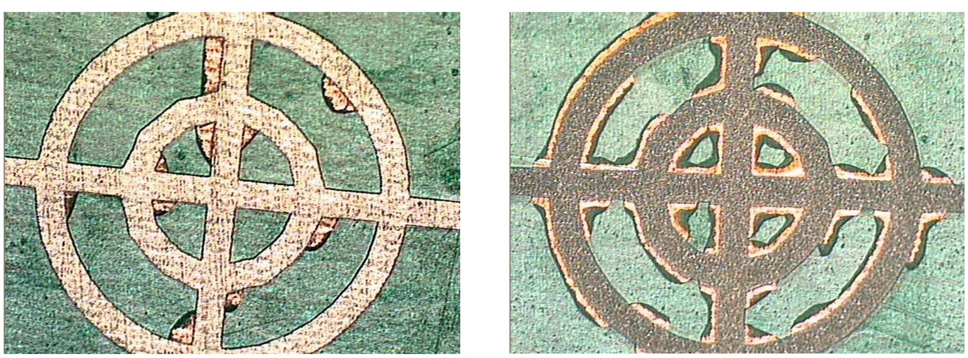
Figure 12 – SEM of dryfilm, whose surface was treated by chemistry, micro etch amount at 1.38 µm

(2). 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 to the surface treated by mechanical scrub. 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, and then processed through Final Finish plating applications.

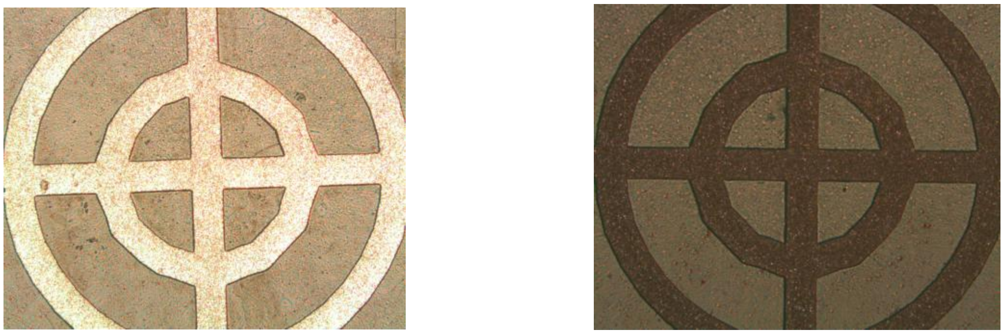
Solder mask:	PSR 4000 BN (HV) (Taiyo Inc)
Drying:	80 ºC, 30 min
Exposure:	300 mJ/cm^2
Development:	1% sodium carbonate, 35 ºC
Postcure:	150 ºC, 60 min.

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).



Nickel-gold plating **Immersion tin plating**

Figure 13 – Tape tests on solder mask, scrubbed copper surface



Nickel-gold plating **Immersion tin plating**

Figure 14 – Tape tests on solder mask, copper surface treated by MultiPrep chemistry

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.
Solder Alloy:
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 15 and 16.

The samples were also tested according to IPC J-STD-003 Test E (Suface 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

Analysis
- Quality of the intermetallic alloy
- Solder Spread Angle and Quality

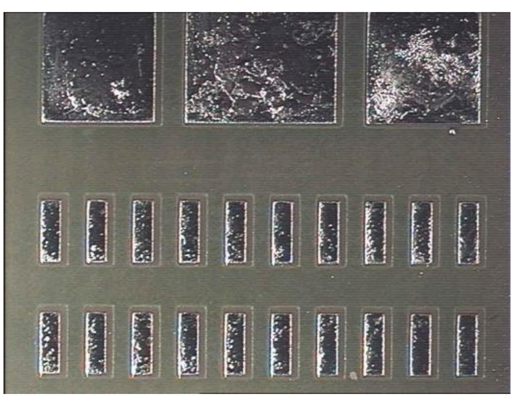


Figure 15 - Edge Dip Test after 3 sec

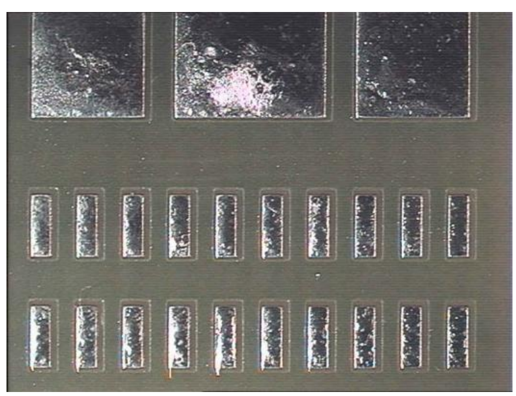


Figure 16 - Edge Dip Test after 10 sec

All panels displayed intermetallic layers free of any voiding. All panels also displayed uniform wetting over all SMD pads both after 1 and 2 lead free reflow conditions. The solder wetting angle was about < 90° which is perfect according to the IPC standard.

The tests above showed that the cupric chloride-hydrochloric acid micro etching process produced a reliable and good quality for solder mask adhesion in combination with e'less final finishes.

(3). Bond Strength to Prepregs

Peel strength was examined between prepregs and copper surface after being pressed. The panels were solder shocked at 288 ºC 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.

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

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 was remarkably increased.

Conclusions

Copper chloride-hydrochloric acid micro etching chemistry offers uniform roughened surface, which provides great adhesion for solder mask and dryfilm 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. Roughness, Ra (average roughness), indicated higher micro etching amount provides higher roughness and 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 on micro etching rate due to increasing chloride concentration. The chemistry is organic acid free, which has less concern on VOC issue.

The performance of dryfilm photo resist showed the surfaces treated by the cupric chloride-hydrochloric acid micro etching chemistry provide excellent adhesion, but the micro etching rate and roughness should be balanced where fine line application was required. The roughened surface offered excellent adhesion for solder mask applications and prepreg resins in printed circuit board fabrications.