

# The Use of a Chemical Fixing Agent with Colloidal Graphite for Producing High Reliability Through Vias and Microvias

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## **Abstract**

High density (HDI) boards utilize through via and microvia technology to achieve the required circuit density present in current electronic applications. As a board manufacturer integrates through vias and microvia fabrication capabilities into their operations, concerns for the long term reliability of the metalization needs to be investigated.

The use of colloidal graphite incorporating a chemical fixing step has been tested and found to produce highly reliable plated through holes, target pads and interconnections on circuit boards featuring both through vias and microvias.

IST™, hot oil thermal cycling and 5 cycle solder shock testing were used to evaluate if any performance enhancements were achieved when a chemical fixing agent and colloidal graphite was used verses electroless copper or colloidal graphite alone.

It was found that the chemical fixing agent, by causing partial polymerization between the hole wall conditioning polymer and the colloidal graphite, could be varied mechanically where as to ensure complete removal of excess colloid from the copper interconnections and target pads yet leave a consistent, tightly adherent, conductive coating that produced highly reliable electroplating and interconnections.

The reliability test data presented clearly shows that the resulting product produced with the chemical fixing method out-performed electroless copper or colloidal graphite alone.

## **Introduction**

OEMs using high density chip on board, flip chip, and chip scale packages are finding build up multilayers and HDIS, the substrates of choice. Because of miniaturization: 33% reduced area, 60% more boards/panels, layer count reduced from 8 to 6 layer, product cost is dramatically reduced. Some high-volume board manufactures have installed and developed new processes utilizing lasers. Drilling resin coated copper and graphite based direct metallization to accommodate the demands of the computer and cell phone manufactures. The cellular market alone offers enormous opportunity for build up multilayers. Two million cell phones with microvias are already being produced in Asia today. The future demand will be even greater yet, with the introduction of new “smart” cell phones that are capable of changing frequency from country to country. The demand for use with the new notebook computers and flash memory devices will also be

incredulous. The focus now is how to produce build up multilayers that meet the reliability standards for thorough via and blind micro vias. Many OEMs require that a daisy chain type test vehicle containing both types of vias pass 40 cycles through hot oil at 288°C. Others require 5 solder floats at 288°C for 10 seconds. The Interconnect Stress Test® vehicle is also considered by most as a state-of-the-art, reliability test method. The primary failure points on build up multilayers vias are: separation of electrolytic plating from the target pad or interconnect copper cracking during thermal stress at the bottom junction where the plated copper meets the target pad and lastly voids or thin plating. This paper describes the chemical and mechanical mechanisms when using a fixing agent with colloidal graphite to produce high reliability through vias and microvias.

### Making the Vias Conductive

The graphite direct metallization process that is the scope of this paper can essentially be broken down into 6 steps: 1. conditioning the dielectric, 2. flocculation of the colloidal graphite on the conditioned surfaces, 3. fixing or partially cross-linking colloidal graphite particles between themselves, 4. mechanical rinsing away of the coating excess, 5. full cross-linking of the coating by heat, 6. chemical cleaning of the copper surfaces by micro etching.

### Conditioning the Dielectric

After drilling and desmearing the hole wall exhibits a net negative charge due to the Si-O bond on the glass and the linkage on the epoxy. The amine based conditioning agents are designed to place a highly cationic static charge on the hole wall (Figure 1).

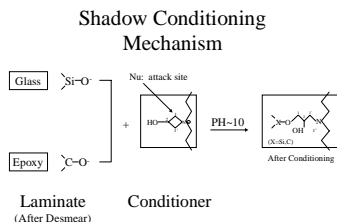
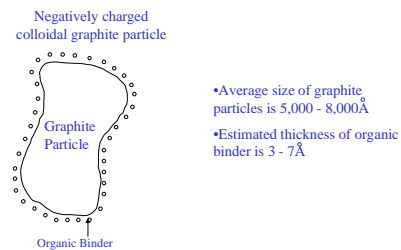


Figure 1 illustrates how through nucleophilic substitution creates a ring opening reaction with the dielectric and polymer. Because the conditioner is

highly substitutive, the hole wall now exhibits a strong cationic charge to promote flocculation.

### Flocculation of the Conductive Colloid

The highly conductive graphite particles are very hydrophobic in their natural state and can only be suspended with vigorous agitation. To overcome this a polymeric anionic binding is used to coat graphic particles as to cause the particles to repel each other rather than link together via the attractive Van Der



Waals forces (Figure 2).

Once the graphite is coated with the anionic polymer the colloid can now be easily dispersed in water and is sterically stable. Zeta potential is a very good index of the magnitude of repulsive interaction between colloid particles and measurements of a colloidal solution. If stability is caused by the particle charge, the repulsion force depends on the degree of the double layer overlap (Figure 3).

## Zeta Potential

$$U_e - \varepsilon \zeta / \eta \text{ (Smoluchowski's equation)}$$

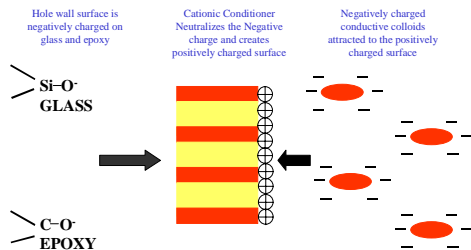
$$U_e - 2\varepsilon \zeta / 3\eta \text{ (Hückel equation)}$$

$$U_e - 2\varepsilon \zeta (1 + \kappa a) / 3\eta$$

Where  $u_e$  is the electrophoretic mobility,  $\varepsilon$  is the permittivity of the liquid,  $\zeta$  is the zeta potential,  $\eta$  is the viscosity of the liquid,  $1/\kappa$  is the thickness of double layer, and  $a$  is the radius of particle.

The attractive force that is provided by the Van Der Waals interaction must be overcome. The total potential energy of the interaction can readily be altered by changing the magnitude of the repulsion, by increasing the ionic strength of the solution i.e. adding in a different electrolyte. This is exactly what the conditioning agent on the hole wall does. The cationic potential energy is great enough to cause the anionic colloidal graphite to precipitate or flocculate onto the hole wall (Figure 4).

### Adsorption Mechanism

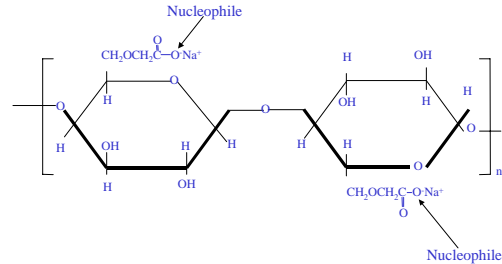


### Fixing or Gel Formation of the Graphite Coating

As we have learned from extensive testing and reliability data; the fixer step is probably the most important and critical aspect in producing of highly reliable vias and through vias. The fixer is a proprietary acidic solution that is used at typically  $120 \pm 5^\circ \text{F}$ . The fixer provides protons (hydrogen ions) to the neutralizer and the anionic charged

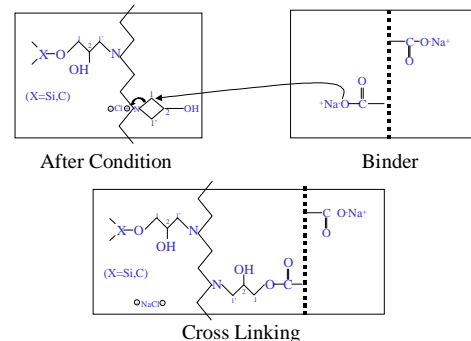
binder surrounding the graphite particles (Figure 5).

### Typical Binder



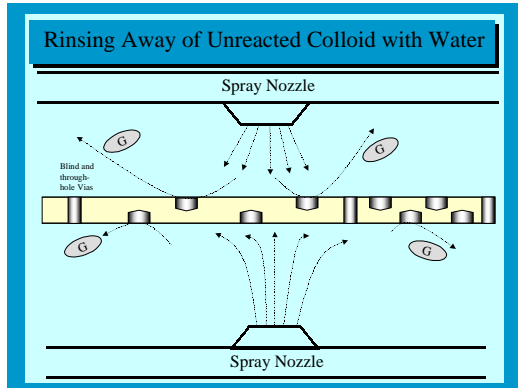
Once the charge is neutralized the colloidal graphite becomes insoluble so only a thin tightly coherent coating is left, which is attracted and partially polymerized to the conditioner. The excess of coating can be rinsed away (Figure 6).

### Gell Formation

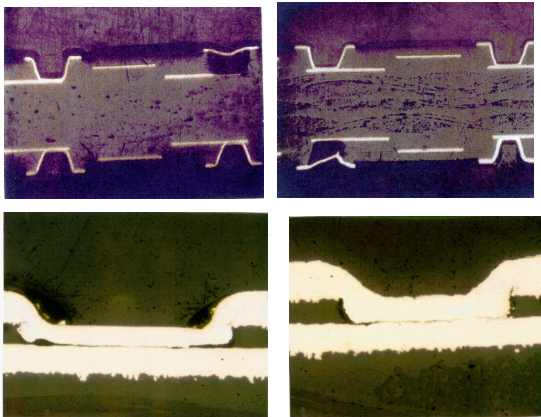


### Mechanically Rinsing Away the Excess Colloidal Graphite

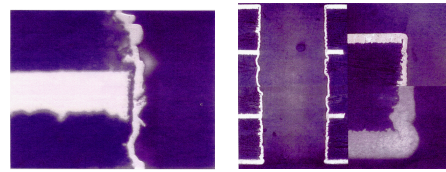
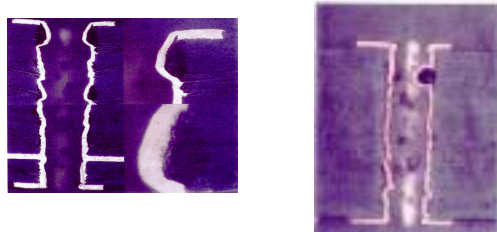
Because of the gel formation the excess neutralized colloidal graphite can be rinsed away and the insoluble, partially polymerized conductive coating is left behind (Figure 7).



This leaves a very continuous, thin conductive coating on the dielectric and copper. Being able to control the thickness of the coating is paramount to ensuring good reliability of the vias and through vias. When air drying alone is used to control the thickness of the coating the results are very inconsistent. It is extremely difficult to use an air knife to clean the target pad of a blind via and hole wall of the through via. The air knife inherently will force or jam colloid into the bottom of the blind vias (Figure 8).



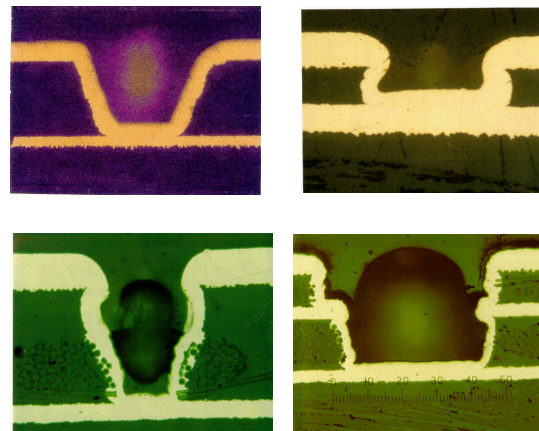
This also leaves a very inconsistent thickness of coating in the through vias (Figure 9).



By chemically and mechanically controlling the thickness of the colloid with fixer and rinsing, it will ensure the consistency of each hole. When conductive coating is fully cured or cross-linked the micro etch can remove the colloid from the interconnects and the target pads.

Figures 8 and 9 clearly show that when using an air knife or oven alone, to dry, the colloid residue can be left on the target pads and interconnects.

Where as with the fixer no residue was found (Figure 10).



Under hot oil testing this residual colloid left on the target pad was found to cause separation, thus failure. Out of 17 lots of test daisy chain panels (54/lot) all the test panels were able to pass the 40 hot oil cycles that were processed with fixer. Only \_\_\_\_% of panels with air knife failed.

## **Thermal Stress Results**

## **References**

- (1) "How one OEM is implementing HDI" HDI Express Vol 1 Editor Mike Bueow I.P.