

## Enhancing the Performance of a Graphite Direct Metalization Process

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### Abstract

Colloidal graphite direct metalization processes have proven their usefulness as a replacement for electroless copper. This is especially the case in high technology and quick turn applications. The consistency of colloidal graphite direct metalization processes has been improved through a better understanding of the influence of contaminants. The contaminants cause degradation of the colloid and thus reduce coating effectiveness. This paper will discuss the importance of reducing contamination of the colloidal graphite. The benefits of a newer generation graphite colloid process will be highlighted.

### Introduction

While direct metalization processes utilizing palladium or carbon black have been commercially available for at least 15 years, the development of a colloidal graphite direct metalization process in 1993 accelerated the use of direct metalization in place of electroless copper. Based upon experience gained over the last 10 years improvements have been made that help to maintain the consistency of the colloidal direct metalization process. Major advancements have been made to improve the understanding of contaminant sources, implement analytical methods to detect these contaminants, and to develop a colloidal graphite that is more resistant to contaminants. In addition, improvements were made to the processing equipment to reduce the introduction of contaminants.

### Overview of the Colloidal Graphite Process

The colloidal graphite direct metalization process involves the following steps:

1. Cleaner/Conditioner
2. Colloidal Graphite
3. Fixer
4. Dry
5. Microetchant
6. Anti-tarnish (optional)

The purpose of the Cleaner/Conditioner is to coat the hole-walls with a compound having a positive charge. This is typically accomplished by the use of a cationic conditioner such as a quaternary amine polymer.<sup>1</sup> The cationic conditioner has a strong attraction to the slightly negatively charged resin and glass materials along the hole-wall. The coating of conditioner is not easily removed and can withstand aggressive spray rinsing. Following conditioning the printed wiring board is coated with the colloidal graphite. Since the colloidal graphite has a negative charge it is easily attracted to the conditioner and forms a uniform layer of graphite on top of the conditioner. The graphite particles themselves have a negative charge. This charge is further enhanced by the use of a binder attached to the graphite that also has a negative charge. A proprietary polysaccharide material with carboxylate groups is used as the binder. The purpose of the Fixer is to form an adherent coating of graphite. The Fixer solution is an acidic solution having a fairly high ionic strength. Following Fixer, the graphite coating is dried to provide proper adhesion. The panel is then passed through a microetchant. The purpose of this step is to remove graphite from the copper surface and copper interconnections along the hole-wall. This provides a good copper-to-copper bond during electroplating. As a final, optional step an anti-tarnish coating may be applied to protect the copper surface during storage prior to resist application or electroplating.

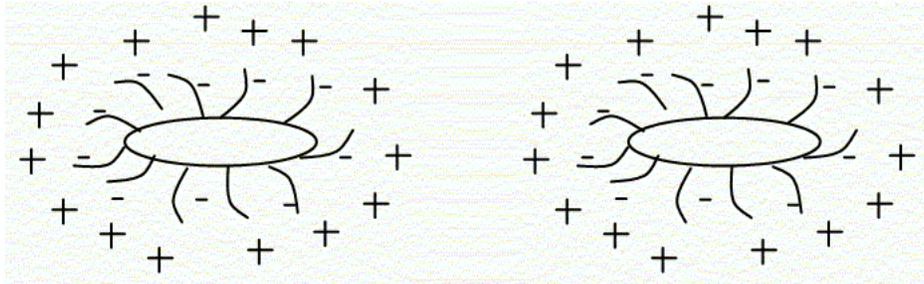
### Science of Colloidal Graphite Dispersions

When discussing the consistency of colloidal graphite processes the stability of the colloid is a major consideration. Stability is defined as 1) the ability to maintain a consistent particle size without aggregation and 2) the ability of the particles to remain suspended in solution without settling. Each definition of stability involves different factors and will be discussed separately.

#### *Consistent Particle Size*

Colloidal graphite is a hydrophobic colloid, which means it is not strongly attracted to water. Hydrophobic colloidal particles are repelled from each other in two ways, sterically and electrostatically. Steric repulsion involves forming physical barriers to prevent the particles from aggregating. Electrostatic repulsion involves an electrostatic charge preventing the particles from coming into contact with each other. While both methods of stabilization are involved in keeping colloidal graphite particles from aggregating, electrostatic repulsion is of most interest due to the influence of contaminants on the electrostatic charges.

As previously stated, the graphite particle has a net negative charge. This negative charge is further increased by the addition of a proprietary binder, which at the operating pH also has a negative charge due to the presence of carboxylate groups (R-COO<sup>-</sup>). Surrounding this particle is a cluster of counterions having a net positive charge. This unequal distribution of electrical charges sets up a potential across the interface and forms an electrical double layer. A schematic representation of this electrical double layer is shown in Figure 1.



**Figure 1 - Electrical Double Layer Surrounding the Graphite Particle**

The effective thickness of this electrical double layer,  $1/\kappa$ , is called the Debye length and is defined as follows:<sup>2</sup>

$$1/\kappa = (\epsilon_r \epsilon_0 RT / 4\pi F^2 \sum C_i Z_i^2)^{1/2} \quad \text{(Equation 1)}$$

- where
- $\epsilon_r = \epsilon / \epsilon_0$  = the relative dielectric constant of the solution
  - R = the gas constant
  - T = the absolute temperature
  - F = the Faraday constant
  - $C_i$  = the molar concentration of any ion in the solution phase
  - $Z_i$  = the valence of any ion in the solution phase

A thicker electrical double layer causes the particles to be repelled at a greater distance. As seen from the Equation 1 this thickness is inversely proportional to the concentration and valence of each ionic contaminant. Therefore, ionic concentration should be reduced as much as possible especially when the ion is divalent or trivalent. Zeta potential is a practical measure used to determine the effective charge on a colloidal particle. The more negative the zeta potential, the more stable the colloidal graphite dispersion. Zeta potential is a useful tool in evaluating the effect of contaminants on colloid stability.

### **Resistance to Settling**

Colloidal graphite exists as a stable suspension in water. Like any particle in solution the settling rate of the colloidal graphite particle is given by Stoke's law:<sup>3</sup>

$$v_\infty = \frac{2r^2 (\rho_p - \rho)g}{9\mu} \quad \text{(Equation 2)}$$

- where
- $v_\infty$  = rate of settling ( cm/s )
  - r = radius of the particle ( cm )
  - $\rho_p$  = density of the particle ( g/cm<sup>3</sup> )
  - $\rho$  = density of the solution ( g/cm<sup>3</sup> )
  - g = the gravity constant ( 980 cm/s<sup>2</sup> )
  - $\mu$  = the viscosity of the solution ( g/cm-s )

If a graphite particle with a radius of 0.5 micron ( $5 \times 10^{-5}$  cm) and a density of 2.1 g/cm<sup>3</sup> is dispersed in a solution having a density of 1 g/cm<sup>3</sup> and the viscosity of the dispersion is 40 g/cm-s the rate of settling,  $v_\infty$ , is  $1.5 \times 10^{-8}$  cm/s. If the graphite radius is reduced to 0.25 micron the settling rate in the same solution is  $3.7 \times 10^{-9}$  cm/s. This example shows that it is beneficial to reduce the particle size in order to reduce settling.

### **Sources of Contamination**

As seen from the above discussion on colloid stability, ionic compounds can have a detrimental effect on maintaining a stable colloid. The presence of ammonium hydroxide in the colloid can cause the attack of copper on the printed wiring board and thus potentially results in copper ion contamination of the colloidal graphite.



Another source of contamination is that, like any alkaline solution, the colloidal graphite will react with carbon dioxide in the air to form carbonate ions:



Depending upon pH some of the carbonate will exist as bicarbonate:



This reaction has a pK value of 10.25. Which means that at a pH of 10.25 the ratio of ( $\text{HCO}_3^-/\text{CO}_3^{2-}$ ) would be 1.0, in other words 50% of the molecules would exist as bicarbonate and 50% as carbonate. At a pH of 9.25 the ratio would be 10.0 and approximately 90% of the molecules would exist as bicarbonate. This ratio of bicarbonate to carbonate is important due to the fact that bicarbonate has a valence of 1 and carbonate has a valence of 2. As seen in Equation 1 divalent ions have a more detrimental effect on the electrical double layer thickness and thus have a greater influence on reducing stability of the colloidal graphite. Therefore, the pH of the solution should be kept below 9.25 for two reasons. It will lower the rate of carbon dioxide dissolution and also keep any dissolved carbonate in the bicarbonate form.

## Test Methods

### *Methods for Detecting Contaminant Levels*

In general standard analytical techniques are used to accurately detect contaminants. These techniques enable determination of common contaminants, such as copper and carbonate, as well as less common contaminants, such as chloride, sulfate and nitrate.

- For the analysis of copper ions, graphite particles are removed before the solution is titrated with EDTA. This is accomplished by acidifying the solution to flocculate the graphite followed by filtration.
- Total alkalinity is determined by titrating the working bath with 0.1 N sulfuric acid to an endpoint of 7.3. Bicarbonate concentration is determined by continuing to titrate from a pH of 7.3 to 4.2. The concentration of bicarbonate is determined by measuring the amount of 0.1 N sulfuric acid used to titrate from 7.3 to 4.2.
- In practice we have found that conductivity of the bath is a good measure of contamination from carbonate/bicarbonate in solution. Conductivity is determined with a conductivity probe having a working range of 0.5-3 mS/cm. This is a useful method to quickly evaluate contamination of a bath without taking the time to do a titration.
- Non-typical contaminants such as chloride, sulfate and nitrate are analyzed using ion chromatography. A Dionex Ion Pac AS4A-SC column is used with a carbonate/bicarbonate mobile phase. In most cases these contaminants are not found in high enough concentrations to influence colloidal stability.

### *Methods for Evaluating Colloid Stability*

Evaluating the stability of the colloid involves several techniques including particle size measurement, viscosity, and a magnified optical inspection using a specialized backlight technique.

- Particle size is measured on a Microtrac S3000 Particle Size Analyzer. This analyzer uses laser diffraction to determine particle size distribution. This analyzer plots a scan of the distribution of particle size for a colloidal solution. Typical scans for normal and contaminated colloidal dispersions are shown in Figures 2 and 3, respectively. Figure 3 shows the increase in average particle size. In this case the particles are aggregating due to the presence of ionic contaminants.
- Viscosity is measured using a Brookfield viscometer. Colloidal graphite solutions are thixotropic, which means that the viscosity of the solution is dependent upon the shear rate. Therefore, selection of the proper rotation rate and spindle is important. For this application a rotation rate of 60 rpm is used, and the spindle is chosen so that the torque range is within acceptable limits for the viscometer. A stable colloid with a concentration of 4% solids is typically less than 7 centipoise (Cp). As the colloid becomes unstable the viscosity will rise. If the viscosity is too high coating uniformity may be diminished.
- Optical inspection of the colloid is conducted in two ways. The first way is to place a few drops of colloid on a glass slide and visually examine the colloid for signs of particle aggregation. The second method involves placing the colloid between two glass slides and examining them at a magnification of 1000X. For this method it is necessary to use a light source to backlight the sample. The advantage of the second method is that it is less subjective because it can be compared to a standard scale. This method also allows utilization of a video camera so that you can save the image on a computer for later reference. Images of normal and contaminated colloidal dispersions are shown in Figures 4 and 5, respectively. Figure 4 shows a uniform dispersion of particles, while Figure 5 shows the aggregation of the colloidal graphite particles due to contamination.

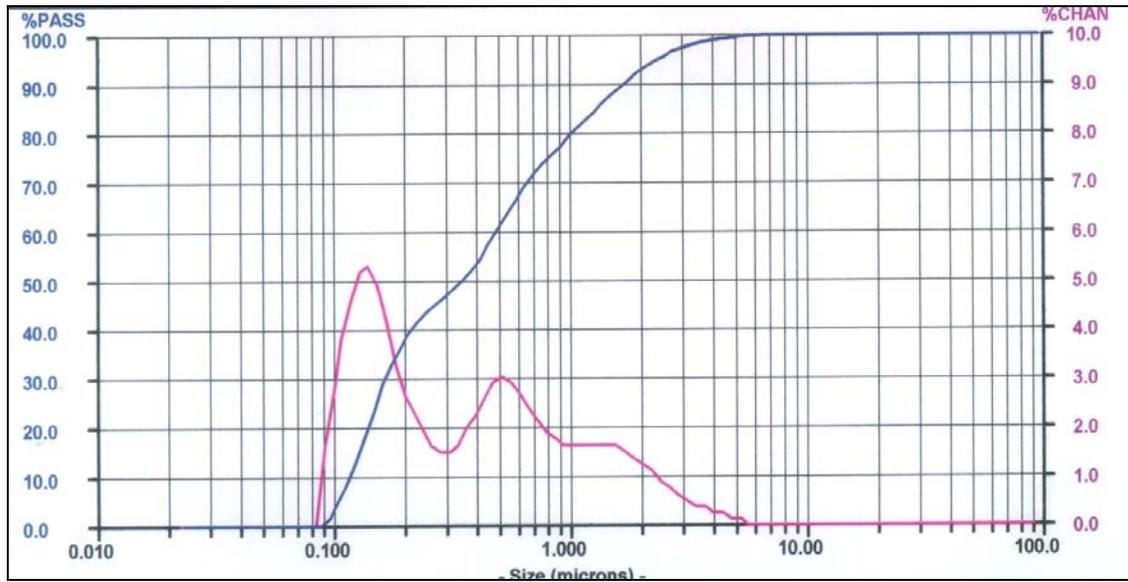


Figure 2 - Particle Size Scan of a Normal Colloid

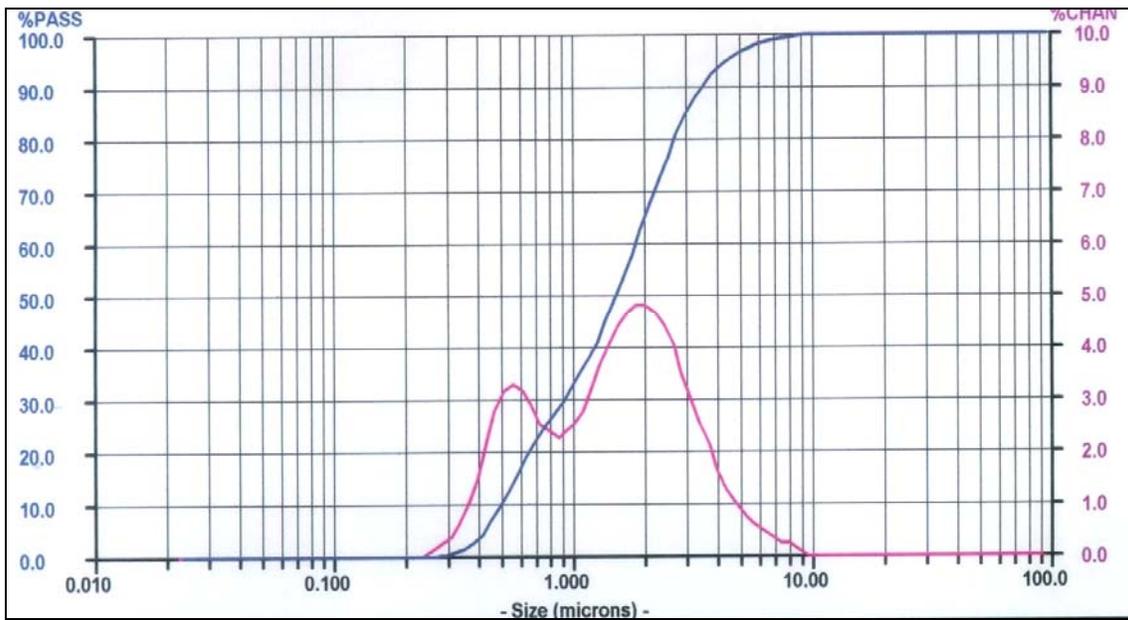


Figure 3 - Particle Size Scan of a Contaminated Colloid

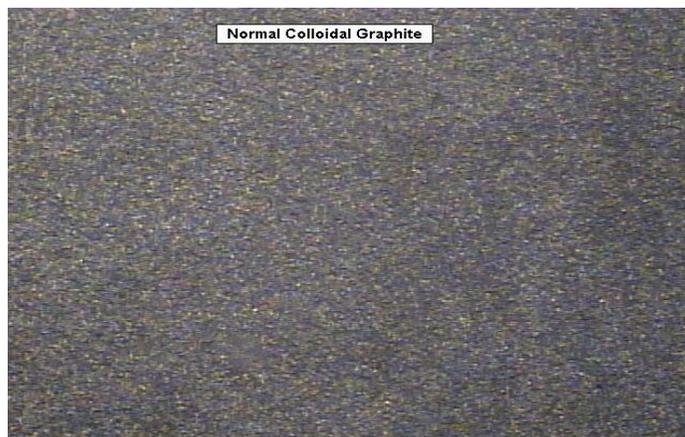


Figure 4 - Magnified Glass Slide of a Normal Colloid

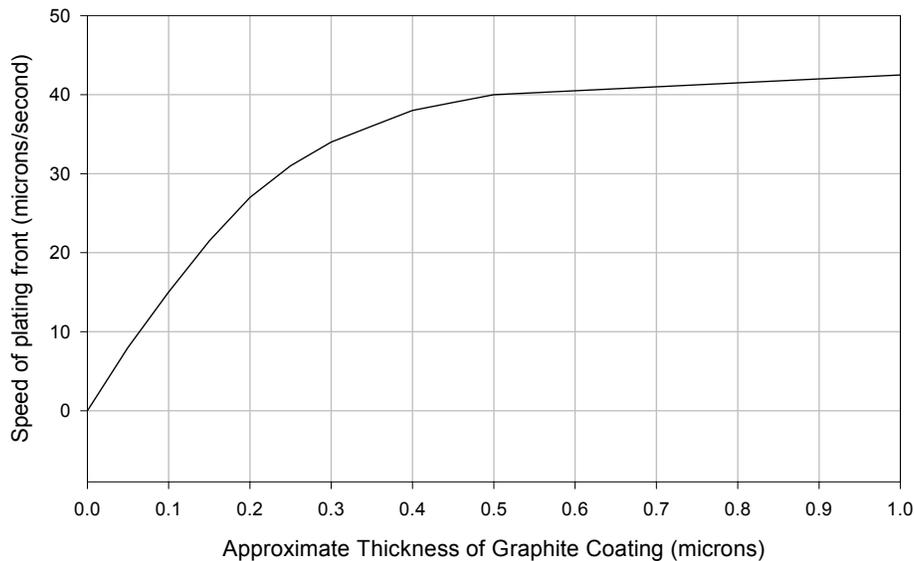


**Figure 5 - Magnified Glass Slide of a Contaminated Colloid**

*Methods for Evaluating Plating Quality*

Copper plating quality of panels processed through the colloidal graphite is evaluated using a standardized flash plate test or by use of a video camera.

- For the standardized flash plate test a panel is plated for 5 minutes in an acid copper solution at a current density of 20 ASF. The panel is then sectioned so that the coverage of copper along the hole-walls can be evaluated by shining a light source from behind the hole. The plating coverage is then rated compared to a standard backlight scale.
- One plating characteristic that is important in the plating of direct metalization coatings is plating front velocity. This is a measurement of how quickly the copper moves across the direct metalization coating. Monitoring the plating using a video camera allows the determination of the front velocity as well as evaluating the uniformity and completeness of the plating. The front velocity of the coating can be very fast but localized areas may not plate as quickly due to the non-uniformity of the direct metalization coating. For a standard colloidal graphite coating the front velocity vs. coating thickness is shown in Figure 6.



**Figure 6 - Front Velocity vs. Approximate Coating Thickness**

## Process Improvements

Based upon our knowledge of the role of contaminants in reducing stability of the colloidal graphite dispersion we were able to make modifications to the process that reduced the influence of these contaminants. These modifications involved two areas 1) reducing the amount of contaminants getting into the colloidal graphite and 2) modifying the colloidal graphite dispersion so that it was more resistant to contamination.

To reduce the amount of carbonate/bicarbonate the conveyerized equipment was modified to maintain proper mixing while reducing aeration of the solution. Working with our equipment suppliers, free-fall of the solution from the top process tray to the bottom sump was eliminated. This was accomplished by putting an angled drop pipe that flowed from the top tray to the bottom sump. Sump mixing was also improved. Sloping of the bottom of the sump allowed sufficient mixing while eliminating dead spots in corners. In many cases eductors were incorporated to improve mixing.

Allowing adequate mixing time for a new colloid bath prior to starting production will also reduce the influence of aeration. This allows ammonia to be removed before it has a chance to dissolve copper from printed wiring boards or convert carbon dioxide to carbonate. Some customers mix in the working sump while others utilize a separate mixing tank. The advantage of using a separate mixing tank is that it allows evaporation of the ammonia without aerating the solution. Mixing in the working sump may still incorporate air into the solution.

To reduce the influence of contaminants, a new colloidal graphite dispersion was developed. The new colloid has a smaller particle size and the distribution of particle size is narrower. As seen in Equation 2, based upon Stoke's law, a smaller size results in less settling. A particle size scan of the new colloidal graphite dispersion is shown in Figure 7.

The new colloidal graphite dispersion also incorporates a new combination of stabilizers that help to improve the colloid's resistance to contaminants. Figure 8 shows a comparison of the two colloidal graphite dispersions with respect to resistance to contamination. In each case a controlled amount of copper and carbonate ions provided the source of contamination.

The most recent development is a new additive, which is incorporated into the colloidal graphite dispersion. This additive reduces the effect of copper dissolved in solution and helps to reduce the dissolution rate of copper from the printed wiring board.

Comparing Figures 9 and 10 you can see the benefits of the additive on colloidal stability. Figure 9 is a glass slide of a standard colloid contaminated with 500 ppm of copper. Figure 10 shows the same colloid with the new additive, also with 500 ppm of copper. While the standard colloid shows some particle aggregation, the presence of the additive allows the colloid in Figure 10 to remain stable.

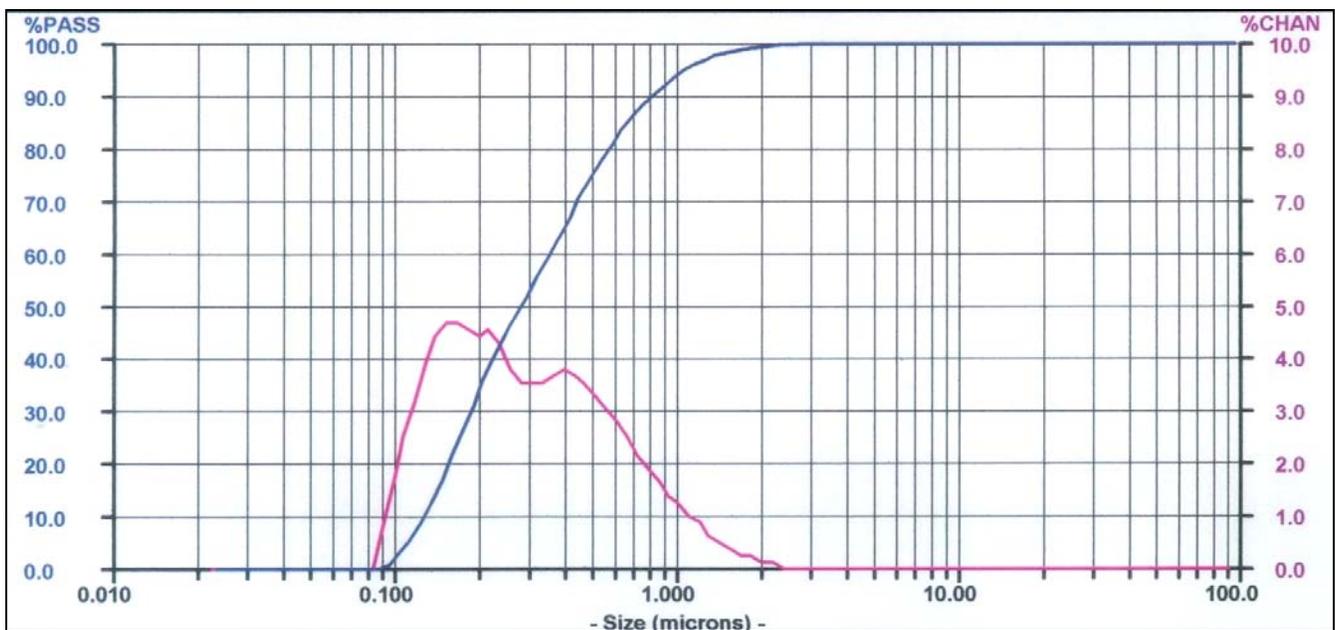
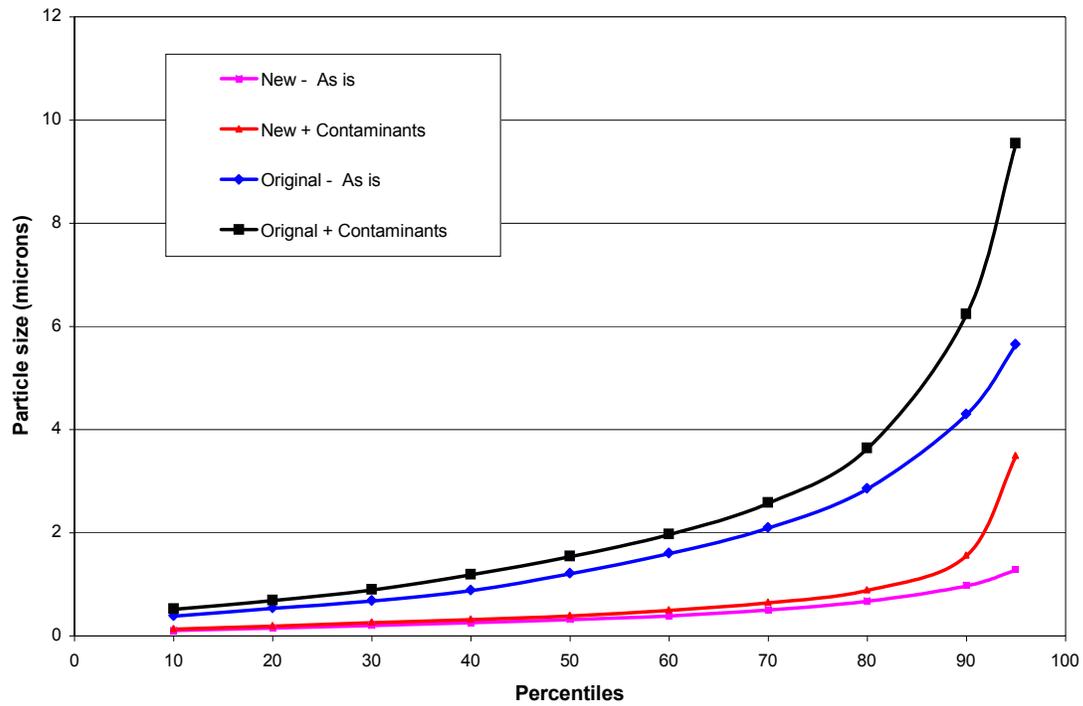
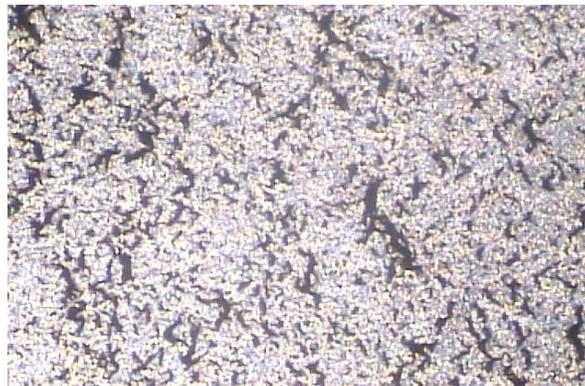


Figure 7 - Particle Size Scan of the New Colloid



**Figure 8 - Comparison of Original and New Graphite Dispersions**



**Figure 9 - Magnified Glass Slide of a Contaminated Colloid without the New Stabilizer**



**Figure 10 - Magnified Glass Slide of a Contaminated Colloid with the New Stabilizer**

Since the new additive limits aggregation of particles it also helps to maintain low bath viscosity. In one test, baths with and without the additive were contaminated with approximately 600 ppm of copper ions. The effect on bath viscosity and plating coverage is shown in Table 1. While each solution started out with a viscosity of 3 Cp the viscosity of the colloid without the additive increased to a viscosity of 20 Cp. The solution with the additive only increased to a viscosity of 6 Cp. This de-stabilization of the colloid without the additive also resulted in a decrease in plating coverage as seen in the flash plate test.

**Table 1 – Effect of Copper Contamination**

<b>Copper (ppm)</b>	<b>Viscosity (Cp)</b>		<b>Flash Plate Rating</b>	
	<b>With Additive</b>	<b>Without Additive</b>	<b>With Additive</b>	<b>Without Additive</b>
0	3	3	9.2	8.7
600	6	20	9.0	8.0

### **Summary**

Recent studies relating to the influence that contaminants have on colloidal stability of graphite dispersions have resulted in improvements in the colloidal graphite direct metalization process. The recent developments help to reduce the detrimental effect of common contaminants such as copper and carbonate. Test methods provide a way to monitor contamination and colloid stability on an on-going basis. The end result is a more reliable, more consistent direct metalization process.

### **References**

1. U.S. Patent No. 5,389,270
2. Surfactants and Interfacial Phenomena (2<sup>nd</sup> edition), Milton J. Rosen, 1989
3. Surface and Colloid Science - Course Manual (July 10-14, 2000), John C. Berg, University of Washington