# The Nature of Plating Solution Turbidity and its Effects on Plated Parts

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Methylsulfonic Acid (MSA)-based tin-lead plating solution produces suspended solids that may cause rough plating and excess solder on plated parts. The composition of these particles is identified and, based on the experiments done and historical data, a mechanism illustrating the formation of the rough surface morphology is proposed.

The ability of the suspended particles to absorb or scatter light (absorbance) is used as a measure of solution's turbidity. Experiments are performed to establish the relationship between the air, current and anti-Tin oxidant concentration with absorbance as the response parameter. The results enable the rootcause determination of a problem in the line and appreciate the importance of monitoring the plating solution clarity.

Previously, plating solution is dumped because the colloidal properties of the particles make filtration impossible. A quick recovery process for the affected solution that effectively extends the plating bath life is recommended. Reliability implications will also be investigated.

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# Introduction

A high-speed magazine to magazine equipment is used to solder-plate components in strip form. Fresh preparations of methyl sulfonic acid (MSA)-based plating solutions yield almost problemfree plating process. However, through extended use, solution becomes turbid. Rough plating, which seem to be more pronounced at the edges, was observed in packages having high current densities. Figure 1 shows an optically magnified photo of a 28ld SSOP (Small Shrink Outline Package) termination processed when the plating solution was turbid (absorbance=3.3).



Figure 1. Rough plating

Published literatures confirm the presence of suspended particles as one of the causes of rough plating <sup>1,2</sup>. Although it is generally known by plating experts that the turbidity is caused by the oxidation of  $Sn^{+2}$  to  $Sn^{+4}$ , the primary cause of  $Sn^{+2}$  oxidation and how the suspended particles induce the formation of rough plating were rarely discussed <sup>3</sup>. In addition to this, solution clarity is rarely monitored as an important process variable.

## **Experimental Section**

*UV/VIS Spectroscopy:* In the absence of a turbidimeter, which is an extension of colorimetry in the sense of its absorbing visible light, the absorbance function of the UV-Vis Spectrophotometer<sup>4</sup> was used. A dual beam spectrophotometer with 1, and 5 mm matched quartz cells was used to relate the amount of suspended particles with absorbance. The absorbance reading of 3 different concentrations of turbid solution was taken at different wavelengths (300 – 760 nm) and was found to be stable at 380nm.

The correlation between the amount of suspended particles (turbidity) and absorbance was then determined. Virgin plating solution was prepared using an optimized make-up formulated in the line. Particulate solids from a previous affected solution was dried, and varying amounts of it were weighed then mixed with a measured amount of the virgin plating solution. An aliquot from each of the prepared solution was withdrawn and its corresponding absorbance read at 380nm.

*X-ray Diffraction (XRD):* Two liters of the turbid plating solution was allowed to settle and the bone-colored sludge was sent to Metallurgical Laboratory of University of the Philippines (Diliman) for analysis. XRD was used to identify the sample.

*Tin Oxide Formation Studies :* For every experimental run, 500ml of freshly-prepared plating solution was placed inside a wide-mouthed glass container. Current and Airflow settings and Anti-tin oxidant concentration were adjusted as per Experimental Conditions in Table 1. A 90/10 SnPb solder bar and a copper panel were used as anode and cathode, respectively. Throughout the experiment, the temperature was kept within 40-50°C range. A portable rectifier was used to control the current settings. A small amount of the solution was withdrawn and its absorbance read every 30 minutes.

**Table 1. Experimental Combinations** 

Parameter	Low	High
Current Density (A)	2	4
Air (bar)	0.1	0.2
Anti-Tin oxidant	0	20
(ml/l)		

*Flocculation Treatment Evaluation:* The plating solution's absorbance was monitored at 380nm from the time it was prepared until it turned turbid. A flocculant of known concentration was added to the turbid plating solution with constant stirring 100rpm (minimum) for 30-45mins. The treated solution was then allowed to stand for 24hrs to settle suspended particles. The clear liquid (overflow) was transferred to another clean container and was used to plate sample panels.

Scanning Electron Microscopy/ Energy Dispersive Xray (SEM/EDX): The surface morphology of plated parts was studied closely using SEM and the elemental composition within the areas of interest was identified using EDX. *X-ray Fluorescence (XRF):* Plating thickness of sample units was measured by X-ray Fluorescent coating thickness gauge using Sn-Pb/Cu composition measurement file. Random sampling was performed on plated parts, 32 plating thickness readings per sample.

*Solderability Test (ST):* The solderability test (ST) procedure referred herein is based on Method 2003.7 of Mil-Std-883E. The usual 8 hours steam aging was extended up to 96 hours.

*Pressure Cooker Test (PCT):* Forty-five sample units plated with treated plating solution were subjected to 24 hour preconditioning, baked @ 125°C, soaked in 48 hours @ 85°C/85%RH. Samples were then subjected to normal PCT in 168 hours @ 121°C, 100%RH and 15psi.

Thermal Shock Test (TST): Forty-five sample units plated with treated solution were subjected to 1000X TST @  $-65^{\circ}$ C and  $150^{\circ}$ C after 24 hour preconditioning, baked @  $125^{\circ}$ C, soaked in 48 hours @  $85^{\circ}$ C/85%RH.

### **Results and Discussion**

### Expressing turbidity in terms of absorbance

A chart was constructed by plotting the known amount of particulate solids (in mg/l or PPM) against the absorbance read at 380nm. Absorbance readings were observed to be exponential when plotted versus the concentration (Figure 2). The readings were noted to be asymptotic to the absorbance value of 4.0.



Figure 2. Absorbance vs. Concentration Graph

### Suspended Particles Identification



Figure 3. XRD readout of the sample

The XRD result shown in Figure 3 reported the particles to be made up of tin oxide. It was observed that during the drying process of the sample (in preparation for the XRD analysis) the tan or bonecolored sludge turned to greenish black. It is possible, though not proven in this paper, that the meta-stannic acid species exist when in solution<sup>5</sup>. These were reduced to tin-oxide when water was allowed to evaporate as shown by the following reaction:

(1)  $H_2SnO_3$  (tan or bone-colored solid)  $\rightarrow H_2O + SnO_2$  (greenish-black solid)

# *Factors Affecting the Formation of Tin Oxide*

Since the suspended particles are primarily composed of tin oxide, the factors that might have a direct influence on the oxidation of  $\text{Sn}^{+2} \rightarrow \text{Sn}^{+4}$  were enumerated. The following were considered: air, current density and the anti-Tin oxidant concentration.

Temperature was initially included as one of the parameters to be studied. However, since the actual plating bath is maintained at  $45^{\circ}$  C, it was decided that temperature be set constant at this value to prevent it from confounding the results.

The different combinations were compared in terms of change in absorbance. As seen from the graph at Figure 4, without anti-oxidant, air is the most significant factor in inducing turbidity in the solution.



Figure 4. Rate of Change in Absorbance at 0mL/L Oxidant Concentration.

The addition of anti-tin oxidant impeded the generation of the tin oxide particles, effectively suppressing the solution's turbidity. Figure 5 shows how it was able to maintain the solution clarity by keeping the change in absorbance very low at all times. Note that at lower air contact, addition of anti-Tin oxidant may not be necessary.



Figure 5. Rate of Change in Absorbance at increased oxidant Concentration.

Reflecting on the implications of these experiments prompted the investigation of possible causes of abnormal air contact with the plating solution. One of the pumps used to deliver plating solution to the cell was found defective, taking in some air, instead of just the solution, with every turn of its impeller.

Figure 6 shows the improvement in the average weekly absorbance of the plating solution after the problem in the pump was detected and corrected.



Figure 6. Absorbance trend of the plating solution

## Inferring the Rough Plating Mechanism

In literature, rough plating is said to be induced when the colloidal particles of tin oxide adsorb the organic additives of the plating solution, thereby upsetting its grain-refining capabilities. This is somewhat contrary to what we experienced in the line. As per historical data, the additive concentration was at its maximum allowable level and yet rough plating was observed. Figure 7 shows how a plating solution with all the components carefully controlled at optimum level results to entirely different surface morphologies when the solution clarity is not controlled.



Figure 7. Surface morphology of SSOP units taken at lead edge @ 2000x magnification (A) when plating solution is clear, absorbance = 1.5 (B) when plating solution is turbid at absorbance = 3.3.

An attempt to explain the participation of tin oxide in the rough plating mechanism was made by considering the following observations:

a) Surface morphology deterioration at optimum additive concentration. Rough plating was observed

when the absorbance readings reach a value of about 3.2 or higher. Increasing the level of additive concentration did not eliminate this product attribute.

b) Unplated Tin-oxide. EDX was used to determine the composition of the surface and cross section of both units in Figure 7. EDX readings detected only Sn and Pb in both good and bad plating. The absence of oxygen peaks implies that tin oxide did not codeposit with the metal ions.

The proposed mechanism is best explained by using the Helmholtz model, an idealized and simplified approach used by Jordan<sup>6</sup> to illustrate how metal ions are plated (Figure 8). This time, however, the presence of tin-oxide particles should be considered (Figure 9).



Figure 8. Helmholtz model. Source: Electrodeposition of Tin and its Alloys, M Jordan 1995.



Figure 9. Helmholtz model with Tin oxide species

The tin oxide suspended in the solution acted as a barrier and induced a localized deposition of Sn metal in the electrode. The resulting layer is uneven and developed miniature protrusions. Since protrusions have more concentrated electric field, metal deposition is higher in that area resulting in rough surface morphology similar to that seen in Figure 7B.

Units with rough plating were also subjected to PCT and ST (with steam aging extending up to 96 hours). No reliability issue attributed to rough plating was reported. At the worst condition if the solder filaments were long enough, the only quality concern may be shorting and burring.

### Extending the Life of the Plating Solution

Previously, when the phenomenon of a turbid plating solution was not yet understood, the plating solution was dumped every year. The plating bath life became shorter as the production volume increased since the existing filter housing was not able to keep up with the amount of suspended particles produced.

Flocculation treatment was implemented to reduce the over-all solution cloudiness. It enabled the colloidal tin compound to aggregate thus facilitating their removal by filtration.

Figure 10 shows how flocculation treatments enabled the extension of plating bath life. Since rough plating started to manifest when absorbance is 3.2 and higher, flocculation was implemented when absorbance reaches 3.0. Without flocculation treatments, plating solution lasted for about a year or less. With flocculation, the present plating solution (which has undergone three flocculation treatments already) was being used for two years now.



Figure 10. Absorbance of Plating Solution in the Line

An improvement was noted in the surface morphology as shown in the hull cell panel plating after the solution underwent flocculation treatment. Figure 12 (after flocculation) shows finer grain structure than Figure 11 (before flocculation).



Figure 11. Surface morphology before flocculation (400 and 1000x)



Figure 12. Surface morphology after flocculation (400 and 1000x)

Several functional and reliability tests were used to evaluate the effect of flocculation treatment on plated parts. The results show no adverse effects resulted from such treatment (Table 2).

#### Table 2. Functional and Reliability Test Results of Units Plated with Flocculated Plating Solution

Test	Results
Solderability Test	
8hrs	0/5
16hrs	0/5
24hrs	0/5
32hrs	0/5
48hrs	0/5
60hrs	0/5
72hrs	0/5
84hrs	0/5
96hrs	0/5
Pressure Cooker Test	
168hrs	0/45
Temperature Cycle	
1000X	0/45
Plating Thickness	Mean: 13.9um (555.5u")
Measurement	S.D: 0.6um (23.2u")
32 readings	Max: 15.1um (605.7u")
(20L SSOP)	Min: 13.1um (523.8u")

## Conclusion

Monitoring the clarity of the plating solution is important in ensuring the quality of the plated parts. Turbidity was brought about by suspended stannic oxide particles which exists as meta-stannic acid in an acidic environment. The protrusions caused by localized deposition of tin in the electrode induced the rough surface morphology of the plated parts.

Available oxygen in air is a significant factor in the formation of stannic compound in the plating solution and should be minimized when Individual plating possible. chemistry and formulation have different absorbance curves and consequently, different values when rough plating will be detected. These values should be determined on a case to case basis. Turbid plating solutions may be immediately clarified through flocculation. If plating bath is monitored and controlled properly, flocculation treatments may even be unnecessary. Understanding the factors in the formation of tin oxide enabled us to detect problems in the plating equipment (e.g. defective pump) in a timely manner and prevented us from installing additional filter housing to address the turbidity problem.

The effects of increased anti-tin oxidant concentration in the plating solution and on the plated parts are beyond the scope of this paper. It is strongly advised that air contact with plating solution be minimized or eliminated first and the filtration process improved before resorting to addition of antitin oxidant.

Monitoring and controlling the generation of suspended tin particles also allowed the efficient deposition of stannous tin in the plating solution and eliminated its hazardous disposal to the environment.

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