

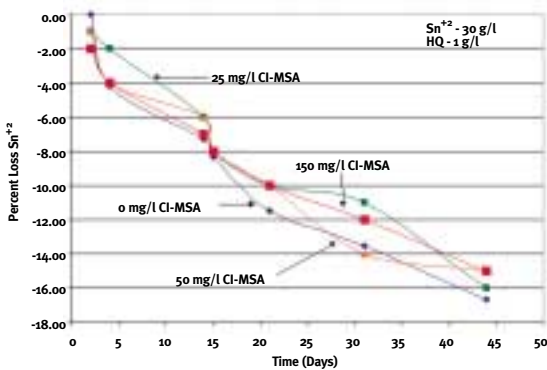
## Influence of Cl-MSA in Acid Tin Methanesulfonate Plating Solutions

*In the development of E-PURE MSA® Arkema studied the effects of various impurities on the electroplating of tin in Methane Sulfonic Acid based plating solutions. The following article summarizes our research on the effect of Cl-MSA in acid tin methanesulfonate plating solutions.*

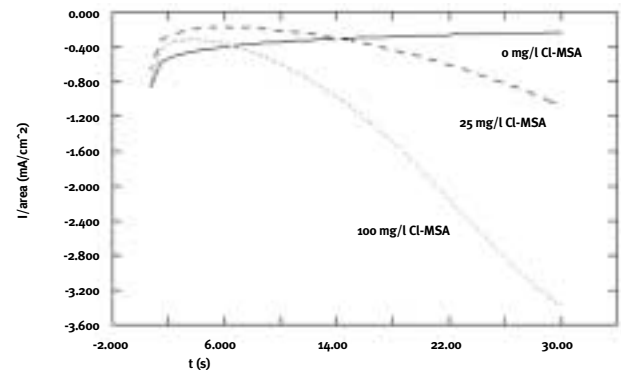
Methanesulfonic acid (MSA) is used in the plating of electronic components such as connectors, leadframes and printed wire boards. MSA is widely accepted as the acid electrolyte of choice because of its non-oxidizing nature (which minimizes stannic sludge formation) and its unique ability to solubilize metals that are insoluble in sulfuric acid. MSA is typically made from the oxidation of methylmercaptan with chlorine gas followed by the hydrolysis of methanesulfonyl chloride,  $\text{CH}_3\text{SO}_2\text{Cl}$ . As a result, trace quantities ( $\leq 75$  mg/l) of chloromethanesulfonate,  $\text{ClCH}_2\text{SO}_3\text{H}$  (Cl-MSA), may also be produced and found in 70% MSA.

Arkema studied the impact Cl-MSA may have in matte tin plating solutions. By using state-of-the-art electrochemical and materials characterization techniques, it has been found that Cl-MSA has little, if any, influence in electronic plating solutions.

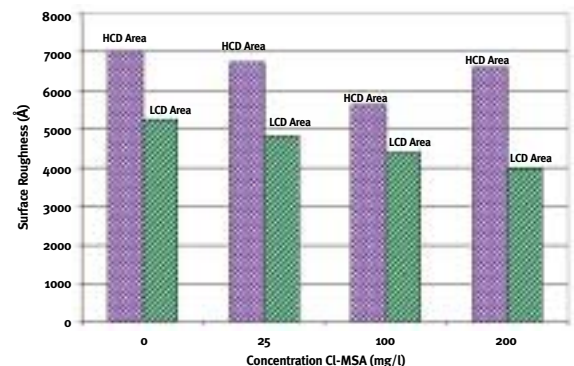
**Chloromethanesulfonate and its Effects on  $\text{Sn}^{+4}$  Formation:** Oxidation studies of  $\text{Sn}^{+2}$  to  $\text{Sn}^{+4}$  were monitored over a 30-day period to determine if Cl-MSA has any effects on sludging. Electrolytes containing from 25 to 150 mg/l Cl-MSA had about the same amount of  $\text{Sn}^{+2}$  loss (~15%) compared to tin solutions containing no Cl-MSA. Any  $\text{Sn}^{+4}$  that is generated under normal operating conditions is easily controlled by constant filtration of the tin plating solutions, thus producing high-quality electronic components.



**Cl-MSA and its Effects on Tin Electrodeposition:** Several electrochemical techniques were used to study the influence of Cl-MSA during the reduction of stannous to metallic tin. Polarization measurements show two types of reduction currents: kinetically controlled and diffusion controlled. Cl-MSA shows a small increase in the kinetically controlled current and no effects on the diffusion-controlled current. The potential-step measurements below show accelerated tin deposition due to Cl-MSA in the plating solutions likely influencing the kinetically controlled current density.

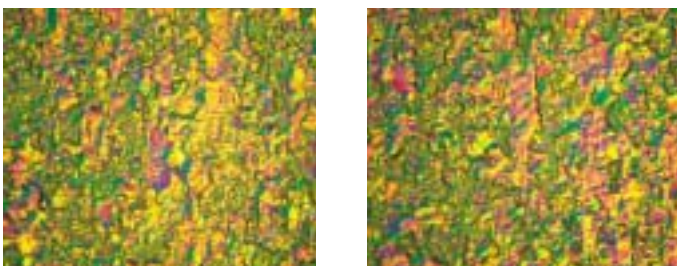


**Surface Roughness and the Role of Cl-MSA:** The influence of chloromethanesulfonate on the roughness of tin deposits is minimal if not slightly improved. Even up to 200 mg/l of Cl-MSA in the tin electrolyte, the roughness is not appreciably different than those tin coatings plated without Cl-MSA. The current density (HCD  $\sim 3.5$  A/dm<sup>2</sup> and LCD  $\sim 1$  A/dm<sup>2</sup>) and type of grain refining additives used in the plating solutions have a dominating influence on the overall coating roughness.



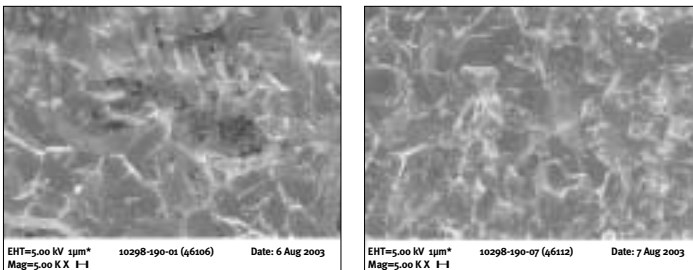
**Cl-MSA and Its Impact on Surface Morphologies:** The surfaces of the matte tin deposits were studied to understand the role Cl-MSA may have on the structures of the electronic coatings. Optical, scanning electron (SEM) and atomic force microscopy (AFM) techniques were used to follow changes in the tin deposit structures plated with increasing amounts of Cl-MSA (from 25 mg/l – 900 mg/l).

The optical images produced using interference contrast methods show very similar surfaces and no large protruding grains or recess areas.



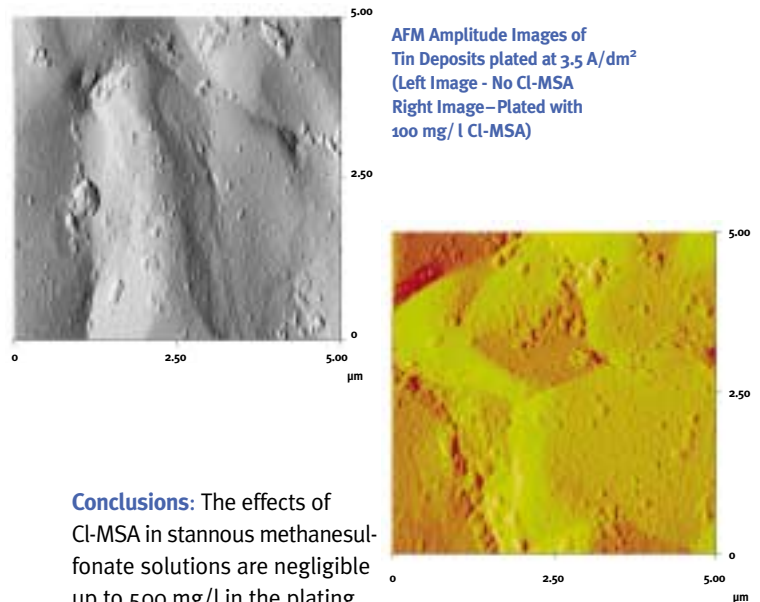
**Interference Contrast Images of Tin Deposits plated at 2.5 A/dm<sup>2</sup>**  
(Left Image - No Cl-MSA • Right Image – Plated with 200 mg/l Cl-MSA)

SEM images show the tin grains are about 1 – 2 μm in size. There are no apparent effects of Cl-MSA on the structures:



**Scanning Electron Images of Tin Deposits plated at 3.5 A/dm<sup>2</sup>**  
(Left Image - No Cl-MSA • Right Image – Plated with 100 mg/l Cl-MSA)

AFM analysis shows the tin coatings in three dimensions. Using tapping mode, height, amplitude or phase images are easily obtained, allowing one to quickly see the effects of Cl-MSA on the tin deposit morphologies, grain sizes, grain size distribution and surface roughness. These images clearly show no significant changes in deposit structures due to Cl-MSA.



**AFM Amplitude Images of Tin Deposits plated at 3.5 A/dm<sup>2</sup>**  
(Left Image - No Cl-MSA  
Right Image – Plated with 100 mg/l Cl-MSA)

**Conclusions:** The effects of Cl-MSA in stannous methanesulfonate solutions are negligible up to 500 mg/l in the plating solution (~2,500 mg/l in 70% MSA). The Cl-MSA is soluble in the matte tin electrolytes and is not co-deposited nor does it adhere to the tin coatings. It has little influence, if any, on the electrochemical reduction or mass transport processes, or the roughness, composition, or morphologies of the matte tin deposits.

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