

Comparison of the Solderability Performances of Inhibitor Containing and Inhibitor-Free Immersion Silver Coatings

**Pan Pacific Conference
Jan. 30 – Feb. 1, 2007
Maui, HI**

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Outline

- **Introduction**
 - Why we have an interest in ImAg finishes
 - Background information
 - Motivation for a coupon study
- **Objectives**
- **Experimental Procedures**
 - Substrate preparation
 - Solders and fluxes
 - Storage environments
 - Test methods
- **Test Results & Discussion**
 - Contact angle
 - Wetting rate
 - Auger surface profiles
- **Summary**



Introduction

- Pb-bearing surface finishes for PCB's are being phased out.
- Potential alternative finishes include OSP's, ENIG, Ni/Pd with a Au flash over Pd, Immersion Sn and **Immersion Ag**.
- **Attributes of ImAg**
 - less expensive than Au or Pd,
 - has excellent wire bondability,
 - inherently solderable with Sn-based alloys,
 - and the intermetallic compound layer formed between Ag & Sn (Ag_3Sn) is not particularly brittle.
- **Limitations of ImAg**
 - Ag tarnishes by reacting with S in air,
 - reacts with airborne Cl to form a Ag-Cl layer,
 - Ag develops a native oxide layer on its surface (Ag_2O),
 - these chemical reactions can have an impact on the solderability performance of ImAg.



Introduction

- **Earlier studies have examined the performance of ImAg for PWB's.**
 - **high temp. aging indicates that Ag coatings can meet a minimum 6 month shelf life requirement unprotected and achieve a 7 year shelf life when wrapped in vapor phase corrosion (VPC) paper and moisture barrier bags.**
 - **the Ag finish exhibits excellent solderability retention after multiple reflow steps often required of double sided boards or more complex PWA's.**
 - **finally, longer-term investigations have not uncovered any reliability concerns with ImAg coatings.**
- **These studies have provided valuable information on the performance of ImAg in applications-related testing.**



Introduction

- **At the coupon level**
 - we seek a science-based understanding to establish a baseline of laboratory solderability data.
- **Benefits include:**
 - an initial insight in the analysis of process failure,
 - and the studies are relatively inexpensive and the data can be rapidly assessed.
- **Moreover, the solderability tests provide a “model system” that identifies factors that control the behavior of the coating.**
 - determine the role of the flux type on solderability and whether the role is derived from surface tension effects or cleaning efficacy.
- **Similarly, the tests provide the means to evaluate the effects of surface finish composition and/or surface degradation on solder wetting—and-spreading behavior.**
- **Therefore, a study was initiated to investigate the solderability performance of ImAg finishes.**



Objective

- Investigate the solderability of an immersion Ag (ImAg) finishes with and without an inhibitor coating, after accelerated aging treatments to simulate long-term exposure.
 - Battelle Class 2 (Industrial Environment) - Duplicated in Facility for Atmospheric Corrosion Test (FACT) at Sandia National Labs
- Determine the effects or pre-assembly heat treatments used to remove water and other volatiles from the printed circuit board.

Test Methods

- Two test methods were used to calculate the contact angle, θ_c , as the “generalized” solderability metric.
 - Meniscometer test
 - Wetting balance test

Meniscometer



Wetting Balance



Experimental Test Methods

- The “absolute” solderability metric is the **contact angle, θ_c** .
- The contact angle is determined by:
 - **Meniscometer Test Method** – measures the meniscus height by measuring the vertical movement of a solder meniscus up the face of a coupon using a traveling microscope.
 - **Wetting Balance Test Method** - measures the weight of the meniscus that forms on the sample as a function of time.

$$\theta_c = \sin^{-1} \left[\frac{4w^2 - \left(\rho g P H^2 \right)^2}{4w^2 + \left(\rho g P H^2 \right)^2} \right]$$

where: ρ = solder density

g = acceleration due to gravity

P = sample perimeter

H = meniscus height

W = weight of solder within meniscus

Preferable solderability is accompanied by contact angles that are generally $< 30^\circ$

Contact Angle (θ_c) Range Relative Wettability

$0^\circ < \theta < 10^\circ$	Perfect
$10^\circ < \theta < 20^\circ$	Excellent
$20^\circ < \theta < 30^\circ$	Very Good
$30^\circ < \theta < 40^\circ$	Good
$40^\circ < \theta < 50^\circ$	Adequate
$55^\circ < \theta < 70^\circ$	Poor

Reference: Klein Wassink

Solderability Optimization

Solderability is **optimized** when the contact angle, θ_c is **minimized**

γ_{SF} = solid (substrate)-flux interfacial tension

γ_{SL} = solid-liquid (solder) interfacial tension

γ_{SF} is maximized by:

- surface cleanliness
- surface oxide removal
- substrate material

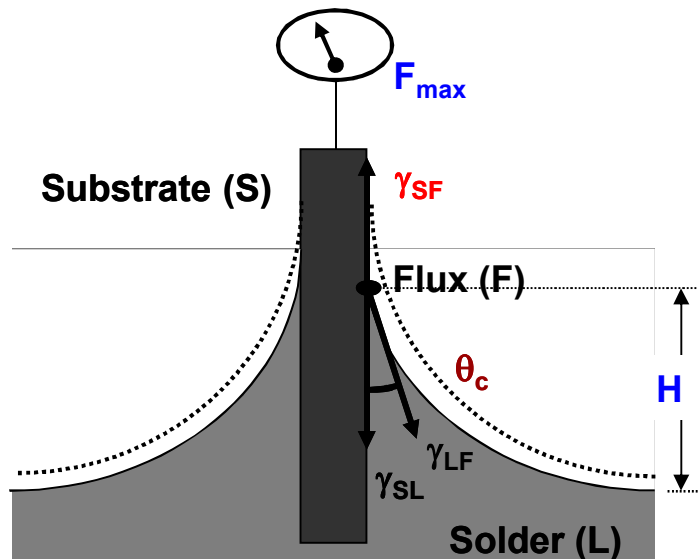
γ_{SL} is minimized by:

- solder alloy
- substrate material (interfacial reaction)

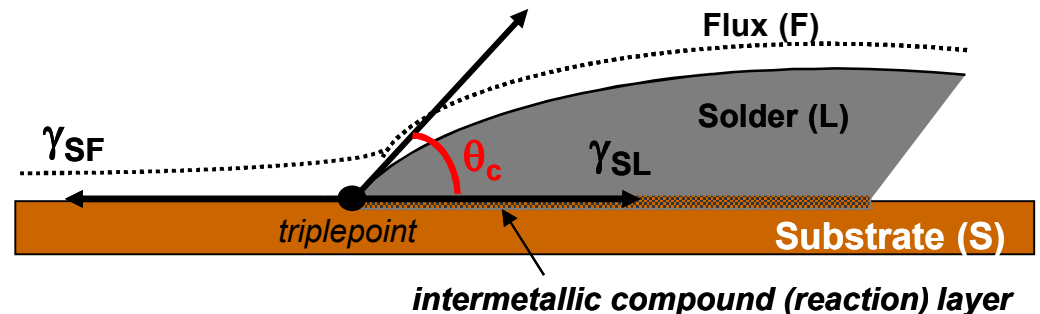
γ_{LF} = liquid-flux interfacial tension

γ_{LF} is minimized by:

- substrate material & protective layer
- flux formation
- solder alloy

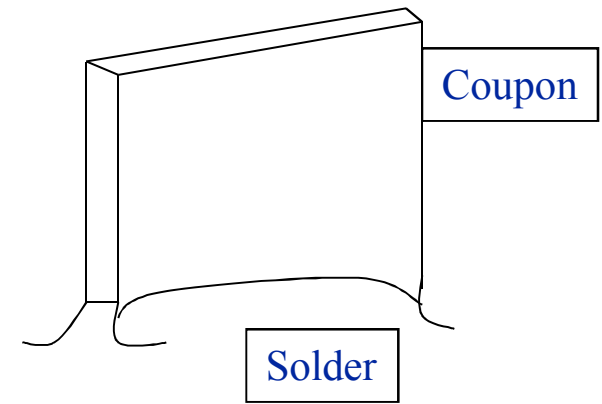


Solderability testing



Experimental Procedures

- **Substrate Preparation**
 - OFE Cu test coupons
 - 2.54 cm \pm 0.013 cm square pieces sheared from 10 mil stock
 - degreased with TCE & IPOH
 - plated with 1mAg
 - coated with a flux
- **The function of the flux coating**
 - removes thin tarnish from the substrate surface
 - prevents substrate re-oxidation during processing
 - reduces the solder surface tension
- **Solder Fluxes**
 - Rosin Based Mildly Activated (RMA)
 - Rosin (R)
 - Low-solids (LS)
- **Solders**
 - 63Sn-37Pb
 - 95.5Sn-3.9Ag-0.6Cu
- **Test Temperatures**
 - 245°C, 260°C



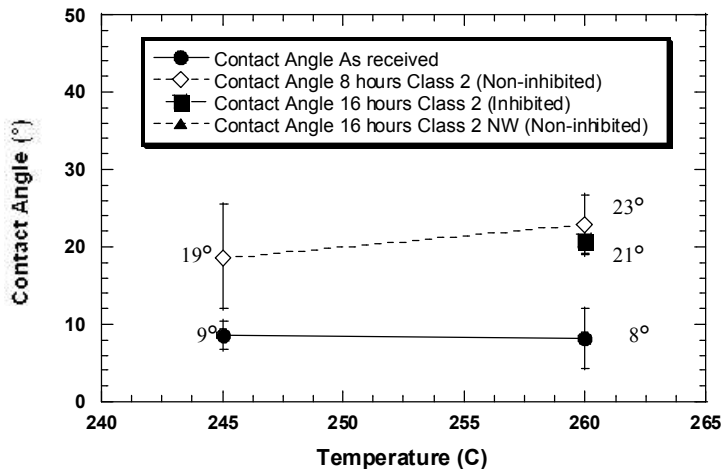


Exposure Environments

- **Battelle Class 2 (Industrial Environment)**
 - The Facility For Atmospheric Corrosion Testing (FACT) at Sandia Labs was used to simulate the Battelle Class 2 environment.
 - target environment contains 10 ppb H₂S, 200 ppb NO₂, 10 ppb Cl₂, 70% RH, and 30°C temperature.
 - coupons were exposed for time periods that are intended to simulate storage durations (i.e., shelf life) of 3 and 6 months, in a light industrial environment (acceleration factor for these conditions is assumed to be approximately 250). **8 hours exposure ~3 months storage life time** and **16 hours exposure ~6 months storage life time**.
- **Pre-assembly circuit board pre-conditioning treatments**
 - Expose coupons for 2 or 4 hours at 72°C in air.
 - Expose coupons for 2 or 4 hours at 93°C in air.

Contact Angle – ImAg As A Function of Temp/Time Battelle Class 2 Environment

Contact angle as a function of temperature with and w/o inhibitor using 63Sn-37Pb solder and RMA flux.

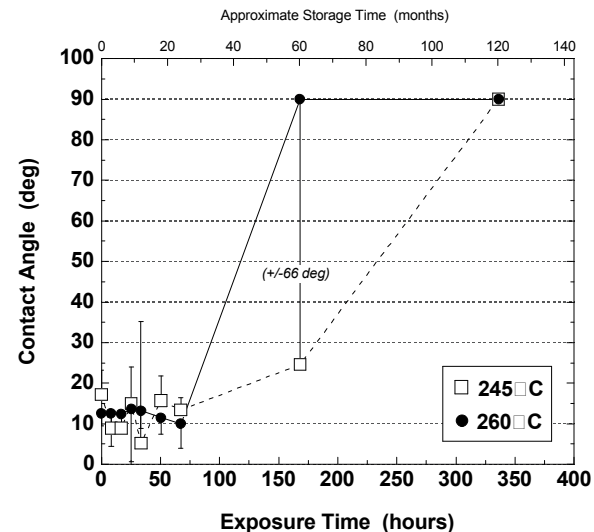


Non-inhibited As-received - Excellent solderability
Non-inhibited - Very good to excellent after 8 hrs.

Non inhibited - Non-wetting at both temperatures
For samples exposed for 16 hours.

On other hand, inhibited ImAg coupons
exposed for 16 hours, a reasonable CA was obtained.

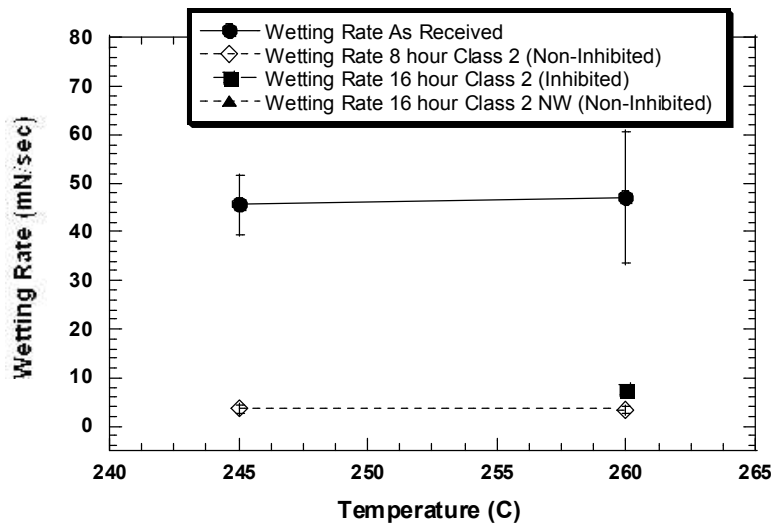
Contact angle as a function of time with inhibitor using 63Sn-37Pb solder and RMA flux.



Prior work showed low CA's when inhibited
ImAg coupons were exposed for up to 66 hrs.
(approx. equivalent to 24 months storage).

Wetting Rate - ImAg As A Function of Temperature Battelle Class 2 Environment

Wetting rate as a function of temperature **with** and **w/o inhibitor** using 63Sn-37Pb solder and RMA flux.

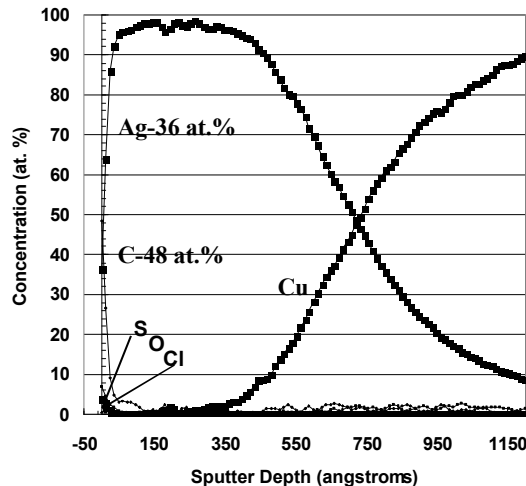


The W_R was much slower for both coupon types after exposure to the Class 2 conditions.

In the case of the inhibitor containing finish, the trend of the W_R extended beyond the 16 hour treatment in a manner similar to the CA's observed up to 66 hrs.

Auger Electron Spectroscopy – ImAg Depth Profile As-fabricated

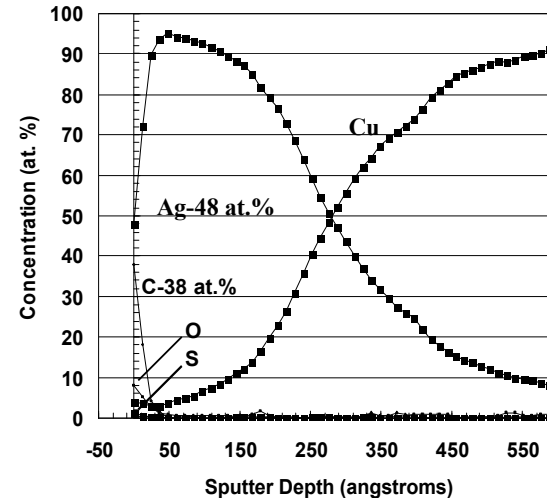
Auger depth profile (with inhibitor)
in as-fabricated condition.



The inhibited ImAg coupon has higher C concentration and lower Ag concentration at the surface than uninhibited coupon.

The higher C content reflects the inhibitor material plus C from the natural environment.

Auger depth profile (w/o inhibitor)
in as-fabricated condition.

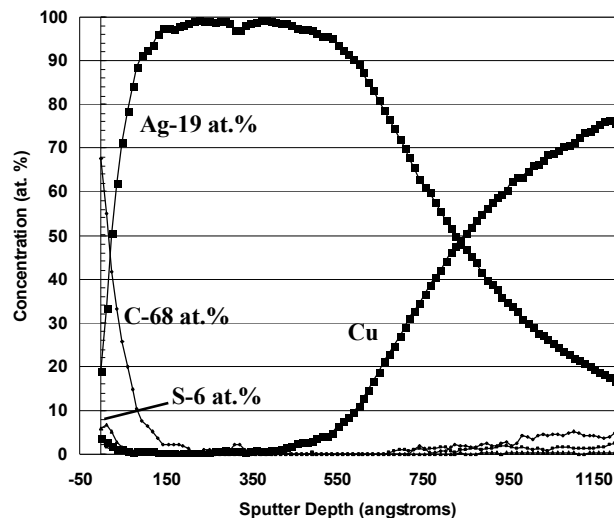


On the other hand, the 38 at.% C surface concentration on the non-inhibited coupon was a result of natural sources.

Furthermore, the non-inhibited coupon exhibited a greater degree of Cu diffusion towards the surface but not to the extent to affect solderability.

Auger Electron Spectroscopy – ImAg Depth Profile Battelle Class 2 Environment

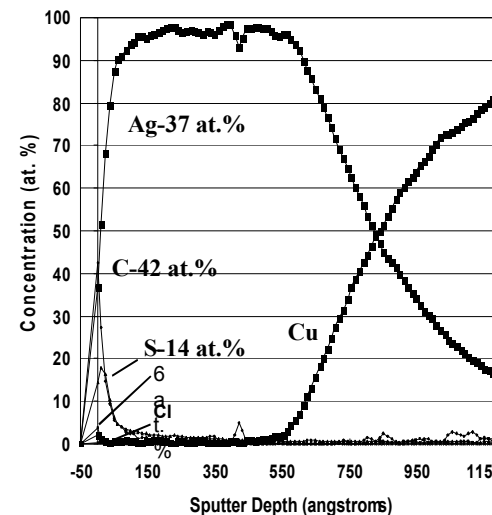
ImAg Auger depth profile (without inhibitor)
after 3 month simulated storage.



The 8 hour exposed surface exhibited more carbon
at the surface than the 6 month exposed surface.

The surface carbon concentrations did
not correlate with the contact angles.

ImAg Auger depth profile (without inhibitor)
after 6 month simulated storage.

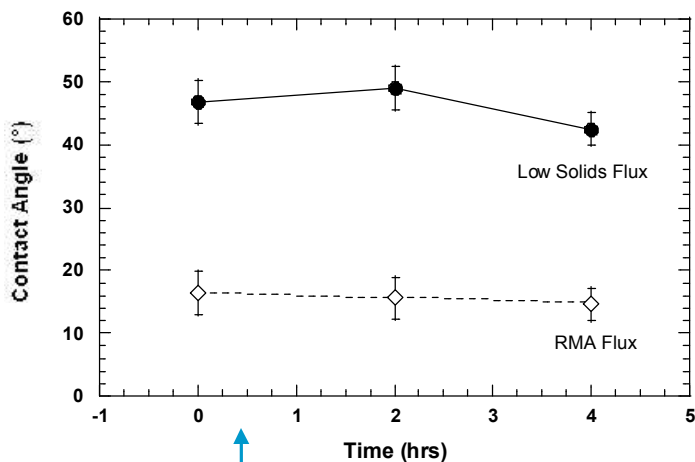


The change in solderability could
not be correlated to Cu diffusion.

An significant increase in S (tarnish) likely
contributed to non-wetting after 16 hrs. exposure.

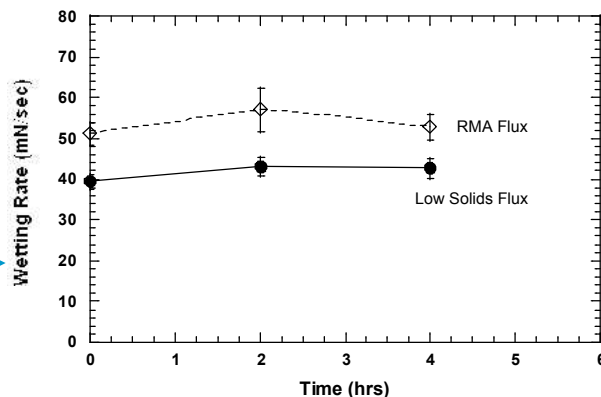
Contact Angle/Wetting Rate 2 and 4 hours Exposures (In Air) at 72°C and 93°C Using 63Sn-37Pb

Contact Angle at 72°C

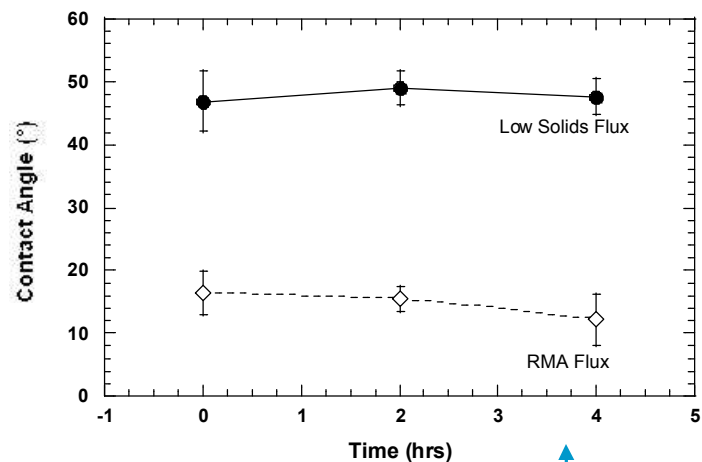


As expected, the LS flux had higher CA's than those Exhibited by the RMA flux.

W_R at 72°C were slower for LS flux



Contact Angle at 93°C

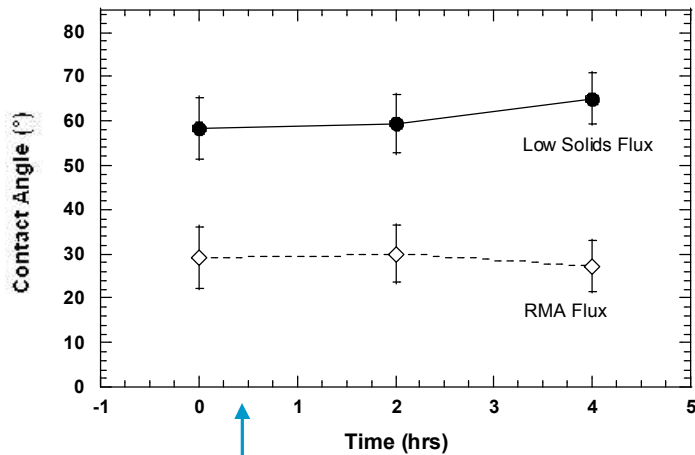


The pre-conditioning treatments can be performed in air on circuit boards having an ImAg coating plus inhibitor without loss of solderability.

Contact Angle/Wetting Rate

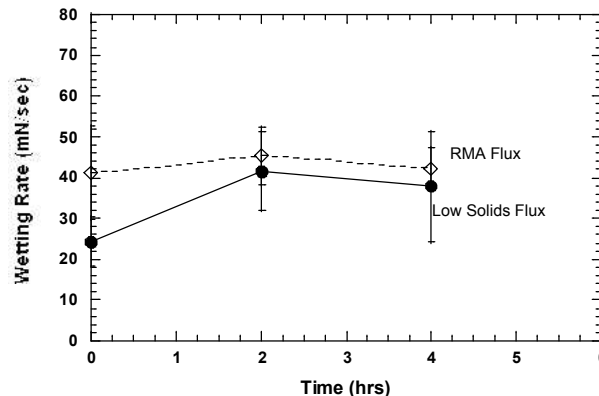
2 or 4 hours Exposures (In Air) at 72°C and 93°C Using 95.5Sn-3.9Ag-0.6Cu

Contact Angles at 72°C

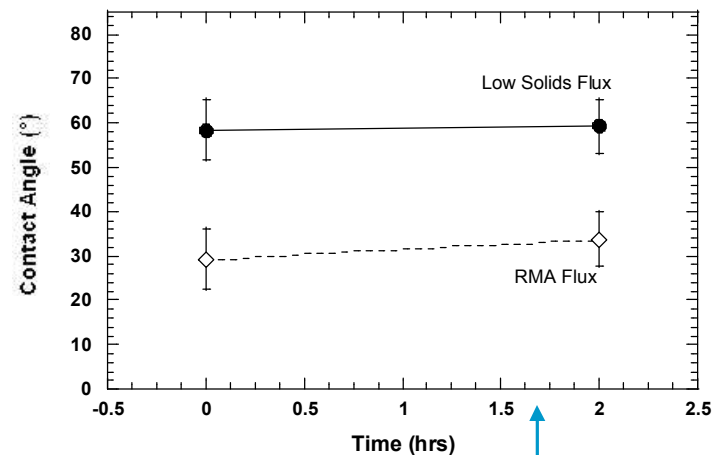


Same trend, the LS flux had higher CA's than were exhibited by the RMA flux.

W_R at 72°C using were slower with LS flux.



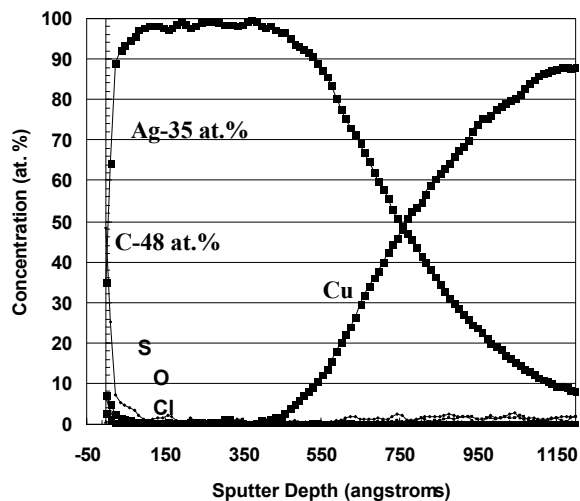
Contact Angles at 93°C



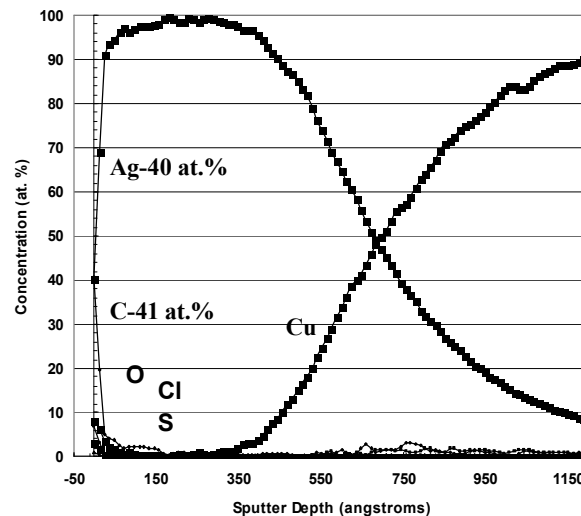
Pre-conditioning treatments can be performed on circuit boards having an ImAg coating-plus-inhibitor without loss of solderability.

Auger Depth Profile Pre-assembly

72°C – 2 hr. exposure – Inhibited



93°C – 4 hr. exposure – Inhibited



There is no significant difference between surface C, O, S, or Cl concentrations.

The absence of a substantial change to the C signal suggests that the preconditioning did not degrade the inhibitor material.



Summary

- **Solderability tests were performed on Cu coupons coated with an ImAg finish (inhibited and non-inhibited).**
- **Exposure to Battelle Class 2 Environment**
 - The contact angle and wetting rate demonstrated the requirement to have an inhibitor to realize an adequate shelf life performance.
 - The loss of solderability by the non-inhibitor containing finish was due to a combination of oxidation and sulfidation (tarnish) of the Ag surface.
 - Longer exposures times (~24 hrs.) are required to generate sufficient Cu diffusion thereby degrading solderability.
 - Weaker fluxes are more sensitive to even modest changes in the solderability of ImAg finishes, as expected.



Summary

- Solderability tests were performed on Cu coupons coated **with** an ImAg finish (inhibited).
- Exposure to pre-assembly circuit board pre-conditioning treatments (2 or 4 hrs exposure at 72°C and 93°C).
 - For both the 63Sn-37Pb alloy and 95.5Sn-3.9Ag-0.6Cu solder, the contact angles and wetting rates were not degraded by the pre-conditioning treatments.
 - Similar trends were observed for both the RMA and low-solids fluxes.
 - These results suggested that the driving force for Cu diffusion could be narrowed down to the Cl and S contents of the environment rather than simply oxidation.



Acknowledgements

- **Sandia Labs Support**
 - **Sam Lucero – FACT Operation**
 - **Wayne Buttry – AES Analysis**
 - **Carly George – Compilation of the data**
- **MAHALO!**