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COMPARISON OF THE SOLDERABILITY PERFORMANCES OF INHIBITOR CONTAINING AND INHIBITOR-FREE IMMERSION SILVER COATINGS[1]

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ABSTRACT

Solderability tests were performed on Cu coupons coated with an immersion Ag finish. The immersion Ag coatings were either with or without a co-deposited, organic inhibitor. The effect of inhibitor presence was investigated with 63Sn-37Pb (wt.%) solder. Test temperatures were 245°C and 260°C. The flux was a rosin-based mildly activated (RMA) solution. Solderability tests were performed on coatings in the as-fabricated condition as well as after exposure for 8 hours and 16 hours in a Battelle Class 2 environment. The contact angle and wetting rate data demonstrated the requirement that the immersion Ag coating have an inhibitor in order to assure adequate shelf life performance. The loss of solderability by the non-inhibitor containing finishes was due to a combination of oxidation, chlorination, and sulfidation (tarnish) of the Ag surface. Weaker fluxes are sensitive to even modest changes in the solderability of immersion Ag finishes. The solderability of inhibitor-containing immersion Ag coatings was evaluated for a matrix of aging times (2 or 4 hours) and temperatures (72°C or 93°C) representing potential, pre-assembly circuit board pre-conditioning treatments. For both the 63Sn-37Pb and 95.5Sn-3.9Ag-0.6Cu Pb-free solders, the contact angles and wetting rates were not degraded by the pre-conditioning treatments. Similar trends were observed between 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.

Key words: Solderability, immersion Ag, storage environments, inhibitors.

INTRODUCTION

Alternative finishes, in particular, immersion silver (Ag), have generated significant interest in the printed circuit board industry. There are several attributes as well as performance limitations associated with immersion Ag finishes [1,2]. The advantages of immersion Ag are that it is less expensive than Au or Pd and has excellent wire bondability. In addition, immersion Ag rapidly dissolves into molten Sn-based solder, a pre-requisite for a protective finish. The intermetallic compound layer that forms between Ag and Sn, Ag_3Sn, is not particularly brittle. Moreover, high electrical conductivity allows Ag to be an excellent finish for radio frequency (RF) circuits.

There are several limitations to the immersion Ag finish. For example, Ag tarnishes by reacting with sulfur (S) in the air. Silver also reacts with airborne chlorine (Cl) to form an Ag-Cl layer on the surface. Finally, like nearly all common metals and alloys, Ag develops an oxide layer on its surface (Ag_2O). Each of these reaction layers can impede solderability performance. However, immersion Ag coatings now contain co-deposited organic inhibitors that prevent or significantly limit the extent of these reactions on the Ag surface.

Strictly speaking, immersion Ag is a protective finish. During the soldering process, the molten alloy initially wets-and-spreads on the surface of the Ag coating. Subsequently, the Ag is dissolved into the molten solder. The Ag coating cannot melt during a soldering process because it has too high a melting temperature (962°C). After the Ag has been completely dissolved, the molten solder wets the underlying substrate material, which is the Cu pad. As such, the Cu pad surface must be equally solderable; otherwise, dewetting of the solder will take place.

Immersion Ag requirements are described in the IPC-4553 “Specification for Immersion Ag Plating for Printed Circuit Boards.” There are two ranges of recommended thickness: (1) the thin range of 0.07 – 0.15 μm that can be used for general-purpose applications and (2) the thick range of 0.20 – 0.30 μm. While the thicker layer is suitable for soldering operations as well, it is typically called out when wire bonding must be performed to the layer. Immersion Ag coatings are exempt from electromigration tests as required by the Underwriters Laboratories for Ag conductors [3].

A number of recent studies have examined the performance of immersion Ag as a printed circuit board finish [4, 5]. Those investigations, which involved the evaluation of printed wiring assembly test vehicles, have established a number of properties of the immersion Ag finish. For example, high temperature aging has indicated that Ag coatings can meet a minimum 6 month shelf life requirement (of Class III hardware per J-STD-003), but more than likely, remain solderable for up to 12 months prior to assembly. The Ag finish exhibits excellent

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solderability retention after multiple reflow steps that are often required for double-sided printed wiring assemblies. Finally, longer-term investigations have not uncovered any reliability concerns that can be attributed to the use of the immersion Ag coating.

Those studies provided valuable information on the performance of immersion Ag in applications-related cases. However, it is also necessary to establish a resource of well-controlled, laboratory data, particularly in terms of the effects of shelf life on solderability. Such an effort was undertaken at Sandia National Laboratories with the expressed goal of using immersion Ag coatings on circuit boards for high reliability applications.

Solderability testing at Sandia National Laboratories is based upon determining the contact angle, θ_C, formed between the molten solder meniscus, the substrate material, and the flux overcoat [6]. The smaller the contact angle (θ_C), the better the solderability performance. Under thermodynamic equilibrium, the contact angle is determined by the balance of three interfacial tensions as expressed by Young's equation:

$$\gamma_{SF} - \gamma_{SL} = \gamma_{LF} \cos\theta_C$$

Equation 1

where γ_{SF} is the solid (substrate)-flux interfacial tension; γ_{SL} is the solid-liquid (solder) interfacial tension, and γ_{LF} is the liquid (solder)-flux interfacial tension. The schematic diagram in Figure 1 illustrates the direction of the surface tension forces and the location of the contact angle for the two cases of horizontal and vertical substrate surfaces. All else being equal, a lower interfacial tension, γ_{LF}, reduces the contact angle per Young's equation (1). It remains to be determined whether the dissolved Ag from an immersion coating has an effect in this regard. A lower contact angle is also realized with a larger value of γ_{SF}, which is sensitive to the substrate material or, as in the current case, the surface condition of the immersion Ag coating.

The solderability test is based upon the meniscometer/wetting balance methodology [6]. This technique uses the height (H) and weight (W) of a solder meniscus, which has risen up the surface of a vertically-oriented coupon, to calculate the value of θ_C. A schematic diagram illustrating those parameters is provided in Figure 2. The value of θ_C is calculated from H and W using equation (2) below:

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

where ρ is the solder density (gm/cm^3), g is the acceleration due to gravity (cm/sec^2), and P is the sample perimeter (cm). The solder flux interfacial tension, γ_{LF}, can also be independently determined from the experimental data using equation (3):

$$\gamma_{LF} = \frac{\rho g}{4}\left\{\frac{4w^2}{(\rho g P H)^2} + H^2\right\}$$

Equation 3

In addition to the equilibrium parameters comprising Young's equation (1), the wetting balance test also provides wetting rate and wetting time data. Shown in Figure 3 is a general representation of meniscus weight versus time. The wetting rate and time to maximum wetting force parameters are shown on the plot. This test procedure has been used to determine the solderability behavior of a 95.5Sn-3.9Ag-0.6Cu solder on both Cu and Au-Ni coated Fe-Ni alloy sheet, using several fluxes and solder temperatures [7].

The first of two prior studies evaluated immersion Ag on copper Cu coupons using this solderability test methodology [8]. The coatings had an inhibitor. The effects of aging in a Battelle Class 2 environment were investigated for immersion Ag coatings having the co-deposited inhibitor. The Battelle Class 2 conditions were established to accelerate the aging of surfaces in what would constitute, a light, industrial storage environment. The first of two critical findings was that Cu diffusion through the thin Ag layer was the primary solderability degradation mode for the immersion Ag coating. The second finding was that steam aging for 8, 16, or 24 hours did not sufficiently degrade the solderability of an immersion Ag surface so that it could discriminate between good and poor coating performance.

The second study examined immersion Ag coatings also having an inhibitor, but this time, deposited on printed circuit boards [9]. The circuit boards were exposed to different storage environments [9]. Again, the Battelle Class 2 environment provided the accelerated aging conditions. The results of these studies revealed that, in fact, the Class 2 environment was the driving force for Cu diffusion into the Ag layer. Without that environment at the immersion Ag surface, such as when the circuit boards are stored in vapor-phase corrosion inhibitor paper, thermal activation was insufficient to provide the driving force for Cu diffusion. Thermal degradation of the inhibitor coating, which was solely a function of the temperature environment, was a contributing mechanism to a loss of solderability. However, the degradation required an extended aging time – 336 hours – in order for it to affect solderability.

The aforementioned studies brought to light two concerns. The first issue was to determine, quantitatively, the role of the inhibitor coating on protecting the solderability of the immersion Ag coating. Testing was performed on Cu coupons having two brands of immersion Ag finishes, one with an inhibitor and the second without. The Battelle Class 2 environment was used. These experiments were based on the performance of 63Sn-37Pb (wt.%) solder.

The second concern addressed the fact that printed circuit boards are traditionally pre-conditioned by being exposed to a heating cycle prior to assembly. The purpose of that heat treatment is to drive off water that may have become absorbed into the laminate as well as to remove other volatile solvents that can potentially become entrapped in the circuit board as a result of fabrication. Therefore, experiments were established to determine the effects of an air environment, preconditioning heat treatment parameter "space" on the solderability of the immersion Ag surface. These tests evaluated the performance characteristics of both the Sn-Pb alloy as well as a 95.5Sn-3.9Ag-0.6Cu (Sn-Ag-Cu) Pb-free solder.

EXPERIMENTAL

Substrate Preparation

The test sample substrates were copper coupons with nominal dimensions of 2.54 x 2.54 x 0.0254 cm. The coupons were sheared from rolled sheet stock and flattened to remove residual curvature. Two immersion Ag coating methods were evaluated; one that contained co-deposited inhibitors and another that did not offer any protection. Coupons were plated in a single batch at each commercial vendor. The plating thickness was within the "thin" range as designated in IPC-4553, being from 0.08µm to 0.16µm. Prior to exposure to one of the accelerated aging environments, the plated coupons were degreased with trichloroethylene (TCE) and isopropyl alcohol (IPOH). The coupons were then stored in clean covered Petri dishes in a nitrogen cabinet prior to testing.

Environmental Exposure – Aging Process

The immersion Ag coated coupons were exposed to the Battelle Class 2 accelerated storage condition. That environment, which was reproduced in the Facility for Atmospheric Corrosion Test (FACT) located at Sandia National Laboratories, has the following conditions: 10 ppb H_2S, 200 ppb NO_2, 10 ppb Cl_2, 70% relative humidity (RH), and a 30ºC temperature [10]. The exposure times were 8 or 16 hours, which were approximately equivalent to shelf lives of 3 months and 6 months, respectively.

The second experiment addressed the effects of pre-conditioning treatments on immersion Ag solderability. Only coupons having the immersion Ag coating with an inhibitor were used in this effort. The coated coupons were exposed in air to aging conditions of 2 hours or 4 hours and 72ºC or 93ºC. These four conditions bracket those typically used to pre-condition circuit boards prior to the assembly process.

Solders and Fluxes

The eutectic 63Sn-37Pb (Sn-Pb) solder, having a melting temperature equal to 183ºC, was used in both studies. The solder pot test temperatures were 245ºC and 260ºC. A rosin (R) flux and a rosin-based mildly activated (RMA) flux were evaluated. The RMA flux was diluted one-to-one by volume with IPOH.

For the experiments used to evaluate the effects of the pre-conditioning heat treatments, both the 63Sn-37Pb solder and the 95.5Sn-3.9Ag-0.6Cu Pb-free solder alloy were utilized. The melting temperature of this solder latter is 217°C. The fluxes included a (diluted) RMA material and a low solids flux (undiluted). A single solder pot temperature was used, 245ºC.

Solderability Testing

The meniscus height, H, was determined by a meniscometer, which tracks the vertical movement of a solder meniscus up the face of a coupon that is immersed edge-on into the molten solder bath. The details of this procedure are available in Reference 8. Five replicates were performed per each test condition. A mean value and standard deviation for H were determined.

The meniscus weight, W, was measured using a wetting balance test apparatus. A similar sequence of steps was performed – applying flux, drying, etc. Five separate tests were performed with this technique. The meniscus weight was described by the mean of those five values and one standard deviation. The wetting rate was also determined from the wetting balance test. The wetting rate was measured from the slope of the wetting curve prior to the latter reaching the maximum weight as shown in Figure 3. Also, the time to maximum meniscus weight was recorded from the wetting curve. In the interest of brevity, the discussion below will be limited to only the wetting rate performance. Generally, the two parameters behave in a largely reciprocal manner so that omitting the time to maximum meniscus weight data does not compromise the analyses. The five wetting rate measurements were described by the mean ± one standard deviation of those data.

The contact angle, θ_C, was calculated via equation (2). An error term for θ_C was computed, based upon maximum and minimum values of H and W as described in Reference 8. A qualitative solderability guideline has been provided in Table 1 [11]. Generally speaking, contact angles less than 50º measured by this solderability test have predicted the successful use of Pb-free and Pb-bearing solders on printed wiring assemblies [12 – 15].

Auger Electron Spectroscopy

Auger Electron Spectroscopy was used to determine the chemical changes to the surface and near-surface regions of the immersion Ag coating that resulted from the aging exposures. Full elemental surveys were performed to identify chemical species. The elements Cu, Ag, S, C, O, and Cl were specifically targeted in the analyses. Sputtering was used to obtain a near-surface depth profile of elements in the immersion Ag coating. The objective of the surface analyses was to correlate solderability performance with changes to the condition of the immersion Ag coatings.

RESULTS AND DISCUSSION

Role of Inhibitors – 63Sn-37Pb Solder and RMA Flux

Solderability Performance

Shown in Figure 4 is a plot of the contact angle θ_C as a function of temperature for both inhibitor and non-inhibitor containing immersion Ag coatings. The as-received contact angles of the combination of 63Sn-37Pb solder and RMA flux for the non-inhibitor coatings tested at 245ºC and 260ºC were 9º ±2 and 8º ±4 respectively. After aging in the Battelle Class 2 environment for 8 hours (3 months equivalent storage time), the contact angles increased to 19º ±7 at 245ºC and 23º ±4 at 260ºC, which indicate acceptable solderability performances. When the coupons were exposed for 16 hours (approximately 6 months equivalent), non-wetting occurred at both temperatures for the non-inhibitor coating. (These data points are not present in the figure.)

On the other hand, when the current samples were tested with the immersion Ag layer having an inhibitor, 8 hours in the Class 2 environment resulted in reasonable contact angle of 21º ±2 for the 260°C test temperature. At this point, reference was made to data obtained from the study cited in Reference 8. It was observed in that prior work that immersion Ag coatings (with an inhibitor) exhibited low contact angles for exposures of up to 66 hours (approximate equivalent of 24 months storage per Figure 5). In addition, the contact angle was not sensitive to the solder temperature for these aging periods, at least to any consistent trend. When the aging times exceeded 66 hours, however, non-wetting was observed at 245ºC. Although wetting was observed at 260ºC beyond 66 hours, there was an unacceptable degree of scatter, indicating an imminent loss of solderability. Then, non-wetting occurred after a 336 hour exposure (120 months). These results were used to infer that, at 245°C, the 16 hour aging treatment would not have degraded the solderability of the inhibitor-containing finish.

The wetting rate data obtained when using the RMA flux are shown in Figure 6. The wetting rate was much slower for both coupon types after exposure to the Class 2 conditions. After 16 hours, the non-wetting condition of the immersion Ag coating without an inhibitor resulted in zero wetting rate. In the case of the inhibitor-containing finish, the trend of the wetting rate extended beyond the 16 hour treatment in a manner similar to that of the contact angle in Figure 5. That is, the wetting rates at 245°C would not have been significantly degraded.

The contact angle and wetting rate data clearly demonstrated the improvement in the shelf life provided by the co-deposition of an inhibitor with the immersion Ag finish. At these relatively short exposure times, there was no observable degradation to the inhibitor material, itself.

Auger Depth Profile Analysis

Auger surface analysis and depth profiles were taken of both immersion Ag coatings in the as-fabricated condition. The Auger profiles for the inhibitor-containing and non-inhibitor containing layers are represented in Figures 7 and 8, respectively. The coating with inhibitor, which is shown in Figure 7, has a higher C concentration (48 at.%) and lower Ag concentration (36at.%) at the surface. (The remaining components at the surface were S, O, and Cl from the natural environment.) The higher C content reflects the inhibitor material plus C from the natural environment. Since the immersion Ag coating in Figure 8 did not have an inhibitor, it can be presumed that the 36 at.% surface concentration represent natural sources.

The non-inhibitor containing finish exhibited a greater degree of Cu diffusion towards the surface, resulting from the driving force created by exposure of the coating to the air (S, Cl, O, etc.) environment. Yet, the diffused Cu had not reacted significantly with S, O, or Cl in the atmosphere; hence, solderability remained good (Figures 5 and 4). Therefore, these C levels at the surface do not substantially affect solderability.

Auger analysis was performed on coupons exposed to the Battelle Class 2 environment. The 8 hour and 16 hour exposures of the immersion Ag coating having an inhibitor increased the surface concentration of C in the former case, but not so in the latter case as shown in Figures 9 and 10, respectively. This anomalous behavior is not unexpected, given the complicating factor of possible oxidation of the inhibitor surface as the explicit degradation mode. More importantly, however, was the fact that the aging treatments had little effect on Cu diffusion profile vis-à-vis the as-fabricated condition. In fact, the higher S concentration on the surface of the immersion Ag coating did not have Cu available to form the detrimental sulfide compound because of the role of the inhibitor. Therefore, all of these factors caused little degradation to the good solderability performance of the inhibitor-containing finish.

Auger analysis was also performed on the immersion Ag coating without an inhibitor. After the 16 hour exposure to the Battelle Class 2 conditions, the extent of Cu diffusion was still very limited. However, there was a significant concentration of sulfur (S) and/or oxygen (O) on the surface.

These results indicate that the loss of solderability by the non-inhibitor containing finishes is due to a combination of oxidation and sulfidation (tarnish) of the Ag surface. Longer times – it appears to be 24 hours of aging – are required to generate sufficient Cu diffusion for the latter element to appear at the surface and, likewise, contributed to a loss of solderability.

Role of Inhibitors – 63Sn-37Pb Solder and R Flux

Solderability Performance

The contact angles, θ_C, for the 63Sn-37Pb solder and R flux are shown in Figure 11 for the immersion Ag coating without a co-deposited inhibitor. The as-received contact angle at 245ºC was 22º ±5 and 15º ±6 for 260ºC. As expected, these contact angles are higher than those observed with the RMA flux. When immersion Ag coupons were exposed to the Battelle Class 2 environment for 8 hours (simulated 3 months), the contact angles were 79º ±31 at 245ºC and 29º ±5 at 260ºC. This trend differed from that of the RMA flux because the latter resulted in acceptable solderability at both temperatures. Therefore, a flux with reduced activity will be more sensitive to the changes brought about by the aging of an immersion Ag coating that does not have an inhibitor. When the coupons were exposed for 16 hours (simulated 6 months) to the Class 2 environment, the coupons exhibited non-wetting at both temperatures as was similarly observed with the RMA flux.

The wetting rate performance was also evaluated for the 63Sn-37Pb solder and R type flux. The data are shown in Figure 12 and are limited to the non-inhibitor finish. It was interesting that the wetting rate values were very similar between the two fluxes for corresponding test conditions, particularly at 245°C where a considerably higher contact angle was observed with the R flux. It has been observed that wetting rate does not always correlate exactly with contact angle [6]. Lastly, after the 16 hour exposure, the wetting rates were zero for either temperature, corroborating the non-wetting condition indicated by the contact angle data.

The solderability behavior can be correlated with the Auger analysis described earlier in reference to the RMA flux. The trends identified between the Auger (surface and depth profile) analyses versus solderability performance were similar for the R flux.

Role of Pre-Conditioning Treatments

Solderability Performance

Immersion Ag coupons, which had the co-deposited inhibitor, were exposed to aging for 2 or 4 hours at 72ºC or 93ºC. All aging treatments were performed in air. The coated coupons were tested at a solder temperature of 245ºC, only. The fluxes were the RMA material and a low-solids solution. Shown in Figure 13 is a plot of the contact angle for the 63Sn-37Pb solder as a function of aging time at 72°C. As expected, the low-solids flux had higher contact angles than were exhibited by the RMA flux. Nevertheless, the contact angles resulting from either flux did not show a significant dependence on the pre-conditioning time at 72°C. Moreover, the very same trends were observed when the pre-conditioning treatment temperature was increased to 93°C as is illustrated in Figure 14. These results indicate that pre-conditioning treatments can be performed in air, on circuit boards having an immersion Ag coating-plus-inhibitor, without a loss of solderability.

The same solderability analysis was performed as described above, but with the 95.5Sn-3.9Ag-0.6Cu Pb-free solder alloy (245°C, only). The contact angle data corresponding to the 72°C and 93°C pre-conditioning temperatures are shown in Figures 15 and 16, respectively. The solderability tests were restricted to the 2 hour treatment at 93°C for the Pb-free solder due to a limited availability of samples. The contact angle values are higher than those of the 63Sn-37Pb solder. Also, the two fluxes exhibited the same relative difference of contact angles. The important observation is that, like the 63Sn-37Pb solder, the pre-conditioning step had no significant effect on the solderability performance over the range of conditions used.

The wetting rate data were also analyzed for both the 63Sn-37Pb and 95.5Sn-3.9ag-0.6Cu solders. Those results appear in Figures 17 and 18, respectively for the 72°C pre-conditioning temperature. In the case of the 63Sn-37Pb solder (Figure 17), the trends corroborated those observed for the contact angle (Figure 13). The wetting rate was slower for the low-solids flux. More importantly, however, the pre-conditioning time caused no significant change to the wetting rates of either flux. The same summary applied to the 95.5Sn-3.9Ag-0.6Cu solder with the exception that the pre-conditioning treatments appeared to have improved the wetting rate realized with the low-solids flux. (Again, as noted earlier, the trends observed between wetting rate and contact angle do not always exactly correlate.) It can only be surmised at this point that the pre-conditioning treatment altered the chemistry of the immersion Ag coating that allowed the low-solids flux to more quickly activate the surface – not more effectively as indicated by the unchanged contact angle – than was possible with the as-fabricated condition. As expected, the wetting rates of the low solids flux were slower than that of the RMA flux at all conditions. The same trend was observed at 93ºC.

The wetting rate data for the 95.5Sn-3.9Ag-0.6Cu solder using the RMA and low-solids flux at 72ºC are shown in Figure 18. The wetting rates of the low-solids flux were slower than those with the RMA flux. Similar trends were observed with the wetting rate data of both solders for coupons pre-conditioned at 93ºC.

Auger Depth Profile Analysis

The Auger surface and depth profile analyses were performed on coupons used in the pre-conditioning experiments. (Again, the immersion Ag coatings for these tests had a co-deposited inhibitor.) The Auger profile for the as-fabricated sample appears in Figure 7. The two extreme cases that will be discussed here were 72ºC, 2 hours and 93ºC, 4 hours. The corresponding plots appear in Figures 19 and 20, respectively. Between all three plots – Figures 7, 19, and 20 – 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 pre-conditioning did not degrade the inhibitor material. In addition, the exposure of coupons to these treatments did not cause a noticeable diffusion of Cu to the surface. Both of these observations corroborate the fact that the treatments did not degrade the solderability of the coupons.

A final note is made regarding the lack of significant Cu diffusion observed in Figures 19 and 20 following the respective pre-conditioning treatments. In the continuing effort to understand the diffusion of Cu in immersion Ag coatings, the latter phenomenon was considered further in light of these two graphs. In the study cited in Reference 8, Cu diffusion was observed after 20 hours in the Class 2 environment, which included the 30°C temperature and listed gaseous concentrations. If the pre-conditioning environment with its oxygen content, offered the same driving force for Cu diffusion, then the higher 93°C temperature would be calculated to cause Cu diffusion in a little over 5 minutes! Clearly, the Auger analysis in Figure 20 does not corroborate this prediction. Therefore, it can be further discerned that the oxygen content of the environment was not the driving force for Cu diffusion in the immersion Ag film. Explicitly, the driving force appears to be associated with the S and Cl contents of the atmosphere, which can form Cu-S and Cu-Cl compounds on the immersion Ag surface.

SUMMARY

1. Solderability tests were performed on Cu coupons coated with an immersion Ag finish. The immersion Ag coatings were with or without a co-deposited, organic inhibitor. The effects of inhibitor were investigated with the 63Sn-37Pb (wt.%) solder. Test temperatures were 245ºC and 260ºC. The flux was a rosin-based mildly activated (RMA) solution. Solderability tests were performed on coatings in the as-fabricated condition as well as after exposure for 8 hours and 16 hours (simulated approximately 3 month and 6 month storage life times) in a Battelle Class 2 environment. The contact angle and wetting rate were evaluated as solderability metrics. Auger surface and depth profile analyses were used to examine the composition profiles of the immersion Ag coatings.
2. The contact angle and wetting rate data clearly demonstrated the requirement of the immersion Ag coating to have an inhibitor to realize an adequate shelf life performance. The loss of solderability by the non-inhibitor containing finishes was due to a combination of oxidation and sulfidation (tarnish) of the Ag surface. Longer times – it appears to be 24 hours of aging – are required to generate sufficient Cu diffusion for the latter element to appear at the surface, then sulfidize or chloridize, thereby degrading solderability. Weaker fluxes are more sensitive to even modest changes in the solderability of immersion Ag finishes, as expected.
3. The solderability of inhibitor-containing immersion Ag coatings was evaluated for a matrix of aging times (2 or 4 hours) and temperatures (72°C or 93°C) representing potential, pre-assembly circuit board pre-conditioning treatments. For both the 63Sn-37Pb alloy and 95.5Sn-3.9Ag-0.6Cu Pb-free solder, the contact angles and wetting rates were not degraded by the pre-conditioning treatments. Similar trends were observed for both 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.

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Table 1 - "Relative Wettability Guideline" Using Contact Angle (θ_C) As The Metric

Contact Angle (θ_C) Range	Relative Wettability
0º < 0 < 10º	**Perfect**
10º < 0 < 20º	**Excellent**
20º < 0 < 30º	**Very Good**
30º < 0 < 40º	**Good**
40º < 0 < 50º	**Adequate**
55º < 0 < 70º	**Poor**

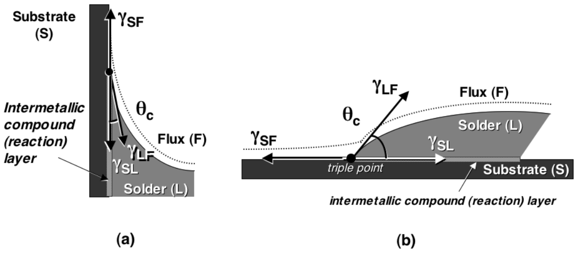

Figure 1 – Equilibrium balance of the three interfacial tensions, γ_{SF}, γ_{SL}, and γ_{LF}, as related by Young's equation (1) for the two generalized geometries: (a) vertical surface and (b) horizontal surface.

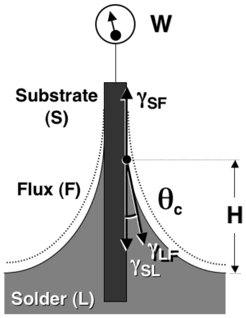

Figure 2 – Meniscometer/wetting balance test configuration.

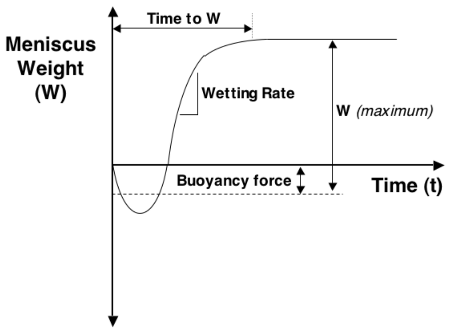

Figure 3 – Wetting balance output of meniscus weight as a function of test time.

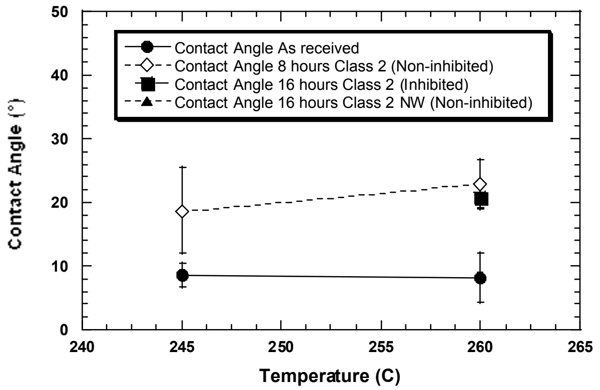

Figure 4 – Contact angle (θ_C) as a function of solder bath temperature (Battelle Class 2 environment) for immersion Ag coated coupons with inhibitor and without inhibitor, using 63Sn-37Pb solder and RMA flux.

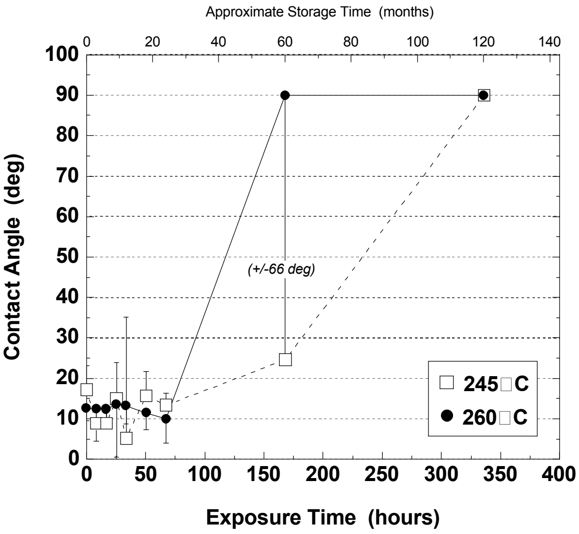

Figure 5 – Contact angle (θ_C) as a function of simulated aging time (Battelle Class 2 environment) for immersion Ag coated coupons with an inhibitor, using 63Sn-37Pb solder and RMA flux.

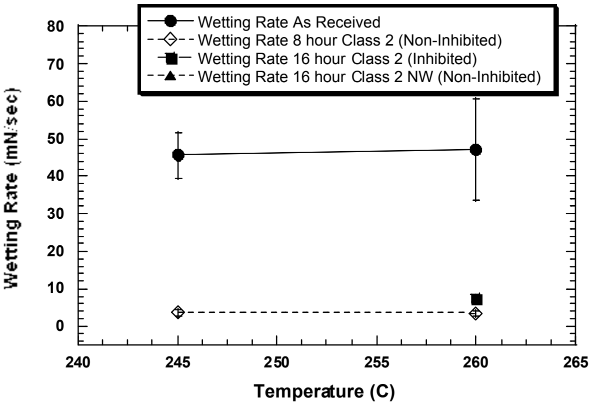

Figure 6 – Wetting rates as a function of as a function of solder temperature for immersion Ag coats with and without a co-deposited inhibitor. The samples were exposed to the Battelle Class 2 environment (FACT) as noted. The solder was 63Sn-37Pb solder and the flux, an RMA material.

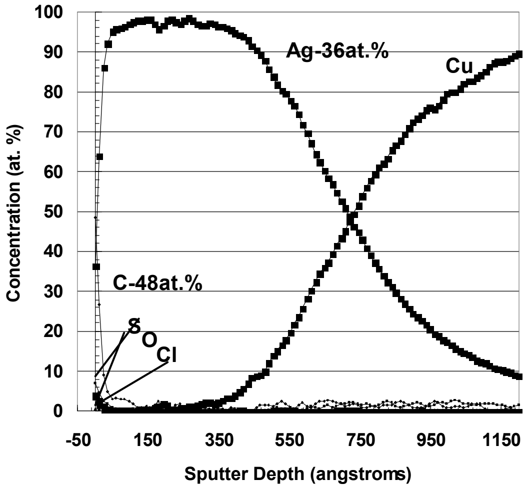

Figure 7 - Auger depth profile of the immersion Ag coating (with inhibitor) in the as-fabricated condition.

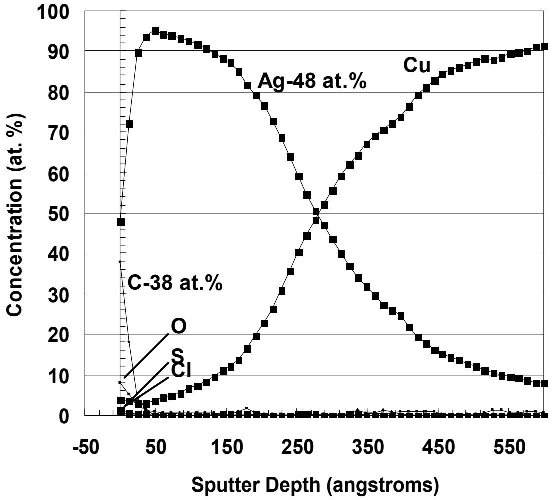

Figure 8 – Auger depth profile of the immersion Ag coating (without inhibitor) in the as-fabricated condition.

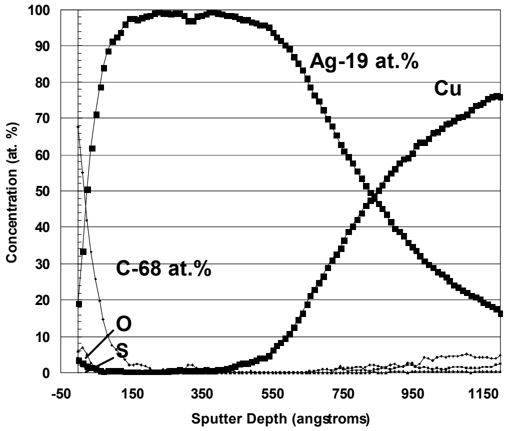

Figure 9 – Auger depth profile of the immersion Ag coating (with inhibitor) after 3 months of simulated storage per the Battelle Class 2 environment.

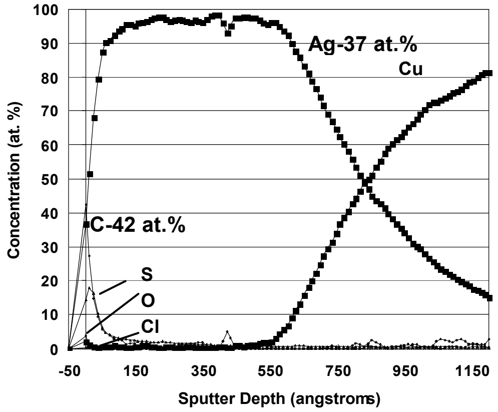

Figure 10 – Auger depth profile of the immersion Ag coating (with inhibitor) after 6 months of simulated storage per the Battelle Class 2 environment.

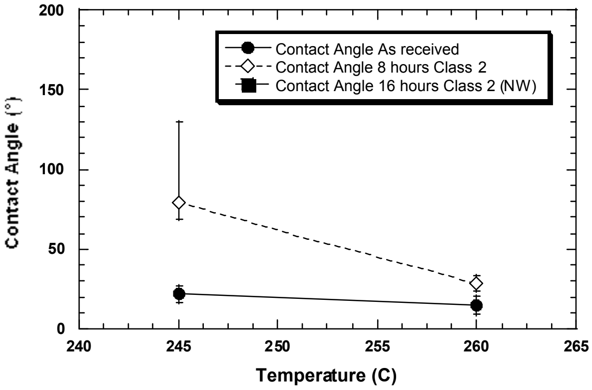

Figure 11 – Contact angle (θ_C) as a function of solder temperature for immersion Ag coats without a co-deposited inhibitor. The samples were exposed to the Battelle Class 2 environment (FACT) for 8 hours and 16 hours. The solder was 63Sn-37 Pb solder and the flux, a rosin (R) material.

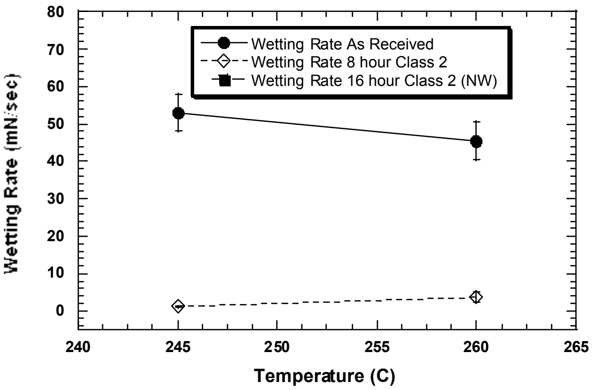

Figure 12 - Wetting rate as a function of solder temperature for immersion Ag coats without a co-deposited inhibitor. The samples were exposed to the Battelle Class 2 environment (FACT) for 8 hours and 16 hours. The solder was 63Sn-37 Pb solder and the flux, a rosin (R) material.

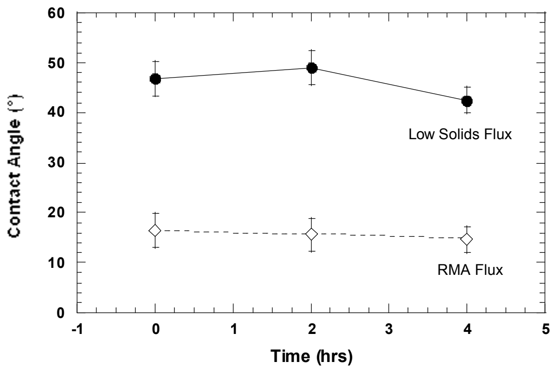

Figure 13 – Contact angles as a function of pre-conditioning time at 72°C. The immersion Ag coating had an inhibitor and was not exposed to a Battelle Class 2 environment. The solder was the 63Sn-37Pb alloy used at 245ºC.

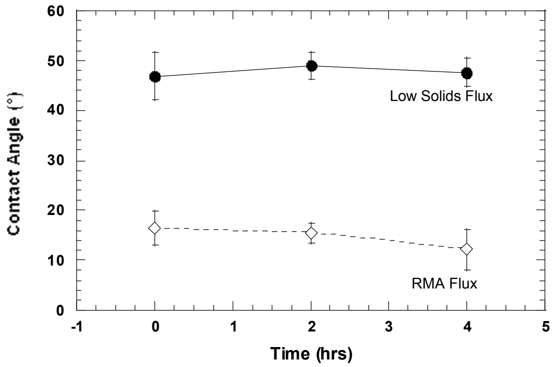

Figure 14 – Contact angles as a function of pre-conditioning time at 93°C. The immersion Ag coating had an inhibitor and was not exposed to a Battelle Class 2 environment. The solder was the 63Sn-37Pb alloy used at 245ºC.

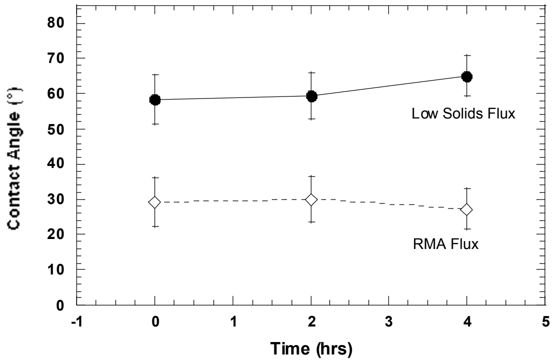

Figure 15 – Contact angles as a function of pre-conditioning time at 72°C. The immersion Ag coating had an inhibitor and was not exposed to a Battelle Class 2 environment. The solder was the 95.5Sn-3.9Ag-0.6Cu alloy used at 245ºC.

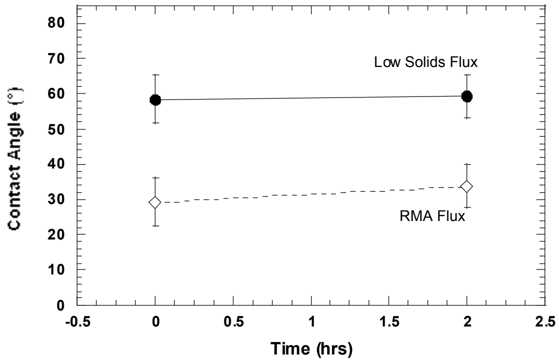

Figure 16 – Contact angles as a function of pre-conditioning time at 93°C. The immersion Ag coating had an inhibitor and was not exposed to a Battelle Class 2 environment. The solder was the 95.5Sn-3.9Ag-0.6Cu alloy used at 245ºC.

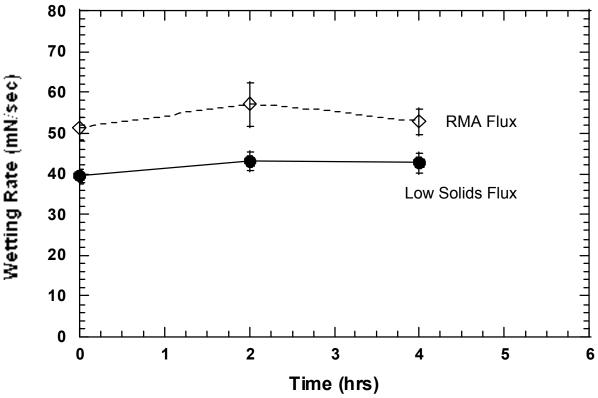

Figure 17 – Wetting rate as a function of pre-conditioning time at 72°C. The immersion Ag coating had an inhibitor and was not exposed to a Battelle Class 2 environment. The solder was the 63Sn-37Pb alloy used at 245ºC.

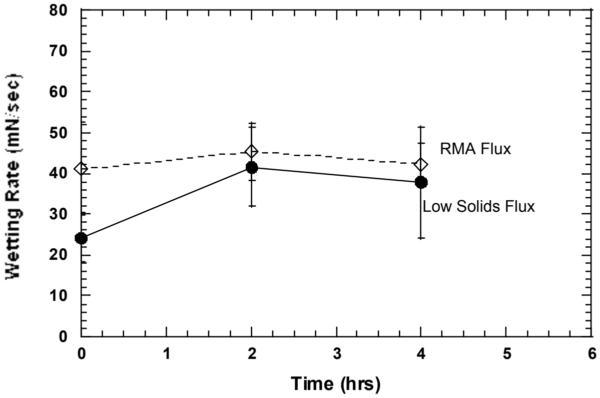

Figure 18 – Wetting rate as a function of pre-conditioning time at 72°C. The immersion Ag coating had an inhibitor and was not exposed to a Battelle Class 2 environment. The solder was the 95.5Sn-3.9Ag-0.6Cu alloy used at 245ºC.

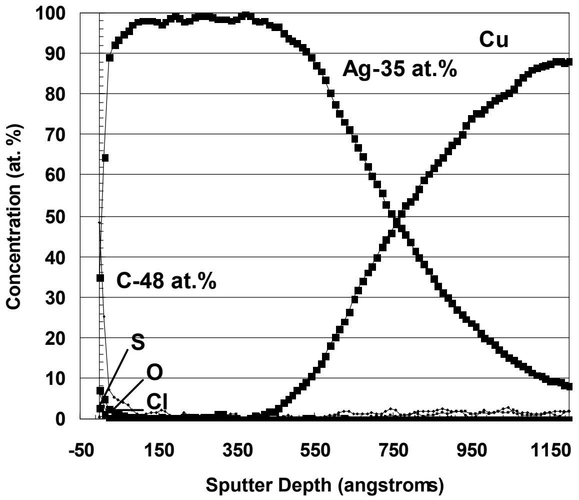

Figure 19 – Auger depth profile of an immersion Ag coating after a 2 hour exposure at 72ºC. The coating had an inhibitor.

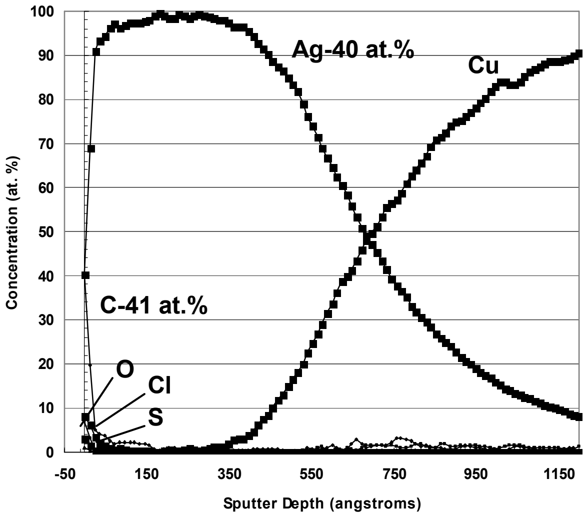

Figure 20 – Auger depth profile of an immersion Ag coating after a 4 hour exposure at 93ºC. The coating had an inhibitor.