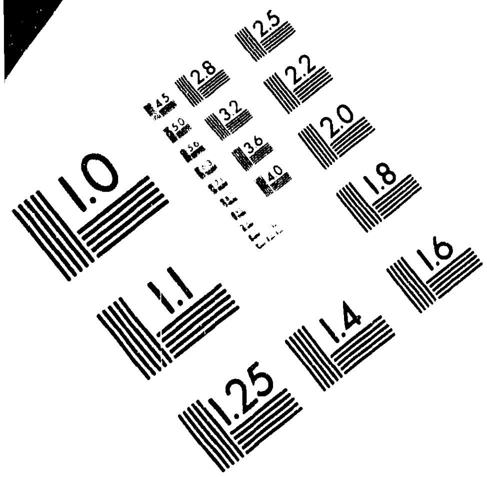

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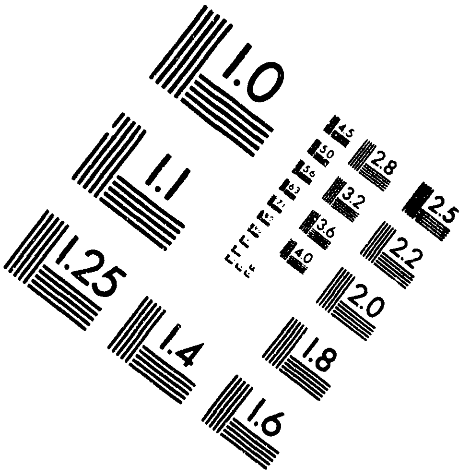

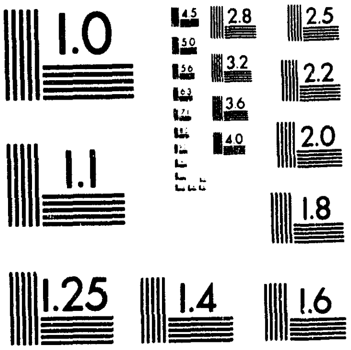

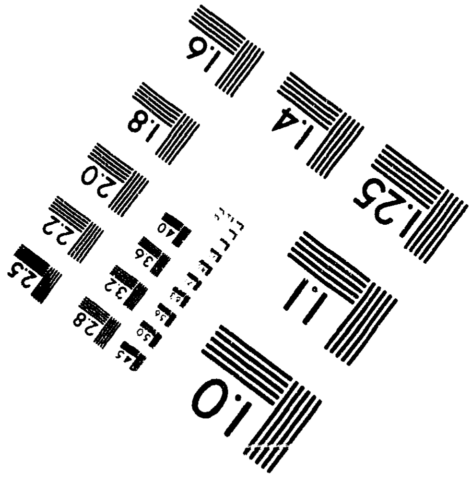

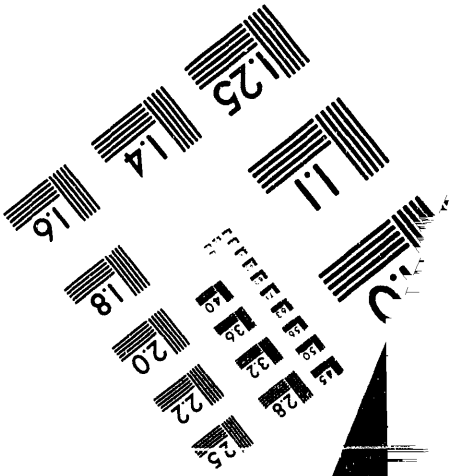

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Solderability Preservative Coatings: Electroless Tin vs. Organic Azoles

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1. ABSTRACT

Substitution of lead-free solders in electronic assemblies requires changes in the conventional Sn:Pb finishes on substrates and component leads to prevent contamination of the candidate solder. Options for solderability preservative coatings on the printed wiring board include organic (azole or rosin/resin based) films and tin-based plated metallic coatings.

This paper compares the solderability performance and corrosion protection effectiveness of electroless tin coatings versus organic azole films after exposure to a series of humidity and thermal cycling conditions. The solderability of immersion tin is directly related to the tin oxide growth on the surface and is not affected by the formation of Sn-Cu intermetallic phases as long as the intermetallic phase is protected by a Sn layer. For a nominal tin thickness of 60μinches, the typical thermal excursions associated with assembly are not sufficient to cause the intermetallic phase to consume the entire tin layer. Exposure to humidity at moderate to elevated temperatures promotes heavy tin oxide formation which leads to solderability loss. In contrast, thin azole films are more robust to humidity exposure; however upon heating in the presence of oxygen, they decompose and lead to severe solderability degradation.

Evaluations of lead-free solder pastes for surface mount assembly applications indicate that immersion tin significantly improves the spreading of Sn:Ag and Sn:Bi alloys as compared to azole surface finishes.

2. INTRODUCTION

In response to potential legislation and environmental regulation restricting lead use in manufactured products, the electronics community has begun a broad investigation of alternative lead-free attachment technologies. Replacement of the existing Sn:Pb solder requires not only the selection of a lead-free attachment material (whether a non-lead bearing solder or a conductive adhesive material), but also the replacement of the traditional Sn:Pb finish on the component leads and printed wiring boards.

Surface finishes provide solderability protection to the conductor features prior to device attachment. Popular circuit board finishes include hot air levelled or electroplated Sn:Pb coatings. Device lead finishes are generally plated or hot dipped eutectic or near-eutectic Sn:Pb. Replacement of the traditional Sn:Pb finishes is required not only

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from an environmental aspect but also because they are incompatible with the vast majority of conductive adhesive materials[1] and lead-free solder alloys.[2] [3] [4] Lead produces low melting tin-lead phases in tin-based lead-free alloys, resulting in depression of the solder melting temperature.[3] [4]

100% tin coatings are the leading choice for package leads and terminations, particularly since most of the viable lead-free solders are tin based. Options for solderability preservative coatings on the printed wiring board include organic (azole or rosin/resin based) films and tin-based plated metallic coatings.

This paper compares the solderability performance and corrosion protection effectiveness of electroless tin coatings versus organic azole films. The electroless tin coatings have been characterized relative to intermetallic growth and tin oxide formation after exposure to a series of humidity and thermal cycling conditions. Corresponding analyses of azole organic coatings are described elsewhere.[5] The advantages of each type of solderability preservative coating in typical lead-free surface mount assembly applications will be briefly discussed.

3. SURFACE FINISHES

The two types of surface finishes investigated are: (1) Azole based organic films and (2) Electroless tin coatings. The organic azole selected for this study is imidazole. The imidazole film is applied according to a patented procedure[6] involving pretreatment of the cleaned substrate with an ethylene glycol/phosphoric acid solution followed by immersion in a dilute aqueous imidazole solution. The electroless (immersion) tin coating is a commercial formulation (Shipley LT34) and is applied according to the supplier's recommended procedure.

Imidazole films range in thickness from ~20-50Å. The thickness of the immersion tin coatings (as measured by X-Ray Fluorescence) can range from 15 to 70 μinches, depending on the immersion time and bath temperature. For example, 1 hour immersion at 50°C can result in a tin coating approximately 60μinch thick.

4. SOLDERABILITY CHARACTERIZATION

The two principal performance criteria for circuit board surface finishes are corrosion protection and solderability. Solderability can be influenced by a series of processing parameters, including choice of soldering flux, thermal excursions prior to soldering and the configuration of the soldering process itself. Loss of corrosion protection during storage and aging can also impact on solderability performance. Thus, solderability is a key element in the qualification of a surface finish material.

Solder wettability was measured in this study with a commercial wetting balance, the Multicore Universal Solderability Tester (MUST). Wetting force and wetting time were the parameters used to provide a semi-quantitative means for comparing the different surface finishes and their associated processing conditions. Effects due to thermal treatment, humidity exposure and aging were examined.

Thermal Effects

To simulate the conditions in a typical surface mount assembly process, imidazole and immersion tin coated copper substrates were exposed to the solder reflow furnace cycle once and repeated a second time. The furnace was purposely non-inerted to simulate worst-case conditions. The temperature profile was adjusted for standard Sn:Pb reflow soldering (consists of a preheat region where the temperature rises at a rate of approximately 0.5°c/second for about 5 minutes, peaks at 235°C over a 30-40 second interval and cools to ~80°C over a 2 minute time interval).

Figure 1 compares the wetting tension (F) at 2 seconds for immersion tin and imidazole finishes before and after one and two passes through the reflow furnace. Both an RMA (Alpha 611) and a low solids flux (Multicore X3304) were used. Due to the similarity in the trends observed, only the low solids flux measurements are reported. Aggressive fluxes, such as a water soluble flux, will enhance the solderability behavior of any surface finish. However, due to reliability concerns and stringent cleaning requirements, aggressive fluxes have not been considered in this study.

As documented in earlier studies[5] [7] [8] the imidazole finish suffers a significant loss of solderability after a single pass through the non-inerted reflow furnace. This effect can be eliminated to a large extent by inerting the reflow atmosphere.[5] [7] [8] [9] In comparison, the immersion tin coating exhibits no detectable loss of solderability even after a double exposure to the non-inerted furnace. To further examine the possibility or extent of solderability degradation induced by thermal treatment effects, imidazole and immersion tin coated specimens were subjected to 1 hour bakes at temperatures ranging from 75°C to 175°C. Figure 2 illustrates the wetting force measurements as a function of bake temperature.

As reported earlier,[5] [7] the imidazole complex decomposes into volatile products at temperatures above ~ 100°C to leave the unprotected copper substrate susceptible to oxidation. The level of copper oxidation naturally increases with increasing bake time and temperature. A low solids flux is not sufficiently active to effectively clean the oxidized copper surface. The combination of these two effects leads to a gradual decrease in wetting tension with increasing bake temperature (as seen in Figure 2). In contrast, the wetting tension of the immersion tin coating remains fairly constant throughout the temperature range examined. A slight reduction is detectable above 150°C, however whether any practical significance can be attached to this reduction (0.20 to 0.18 mN/mm) is unclear. It appears therefore that in contrast to imidazole, immersion tin is only slightly affected by thermal effects.

The baseline applied immersion tin coating thickness was maintained at approximately 60 +/- 7 µinches. (The standard deviation reflects the coating thickness variability over the 6"x9" PWB surface.) The obvious concern with any metallic finish, (and in particular tin), is formation and growth of intermetallic phases. If the intermetallic layer reaches the surface by consuming the tin layer and becomes subsequently oxidized in the presence of air, the wettability of the substrate will rapidly degrade. Figures 1 and 2 indicate that ~60µinch tin coatings retain solderability after being subjected to the typical thermal excursions encountered in assembly processes. To better understand whether coating thickness played a significant role, thinner coatings of 15 and 30µinches were applied by reducing the immersion time in the electroless bath from 60 minutes to 5 and 15 minutes respectively.

Figure 3 depicts the wetting behavior of three immersion tin coatings of 60, 30 and 15 µinches as a function of bake temperature (1 hour bake). The 15µinch coating suffers a severe loss of solderability with increasing bake temperature, while the 30µinch coating shows the first sign of solderability loss above 125°C. This behavior is consistent with the presence of intermetallic phases, as measured by Rutherford Back Scattering Spectroscopy (RBS) and reported elsewhere.[10] In fact, the 15µinch tin coating is entirely consumed by the intermetallic compound during the 125°C bake.[10] Based on these measurements, the recommended minimum immersion tin coating thickness is ~ 60-70µin., the self-limiting thickness achievable with the electroless chemistry used.

Temperature/Humidity/Aging Effects

From the discussion above, it is apparent that elevated temperatures can dramatically affect the wettability of azole films, but have negligible effect on immersion tin coatings, provided these coatings are sufficiently thick to compensate for inherent intermetallic compound growth. Exposure to harsh humidity conditions can potentially induce additional surface reactions and lead to loss of solderability.

Recent reports have shown that[9] imidazole finished printed wiring boards retained solderability after 1 year storage in a typical industrial indoor environment. Wettability measurements performed in our laboratory on 1 year old imidazole specimens concur with these results. The effect of increased humidity levels and simulated accelerated aging on the stability of azole films is under investigation in other laboratories.[11] Preliminary results in our laboratory indicate that exposure to 35°C/90% relative humidity (RH) for 3 weeks results in no reduction in the wetting tension. From the limited information available, it appears that azole films are generally robust relative to aging and humidity exposure. These studies are continuing.

To investigate the effect of humidity on the wettability of immersion tin coatings, specimens were exposed to the following conditions for time periods ranging from 8 hours to 4 weeks: ambient temperature and humidity, 35°C/90% RH, 65°C/85% RH and steam at 95°C. Figure 4 summarizes the wetting tension data.

Clearly, humidity plays a significant role and its effect is augmented at elevated temperatures. Immersion tin does not survive the standard 8 hour steam aging requirement and undergoes fairly rapid degradation under moderate temperature and high humidity conditions.

The wettability data suggests that no degradation has occurred under ambient conditions for up to 4 weeks of aging. However, recent wave soldering assembly trials with immersion tin circuit boards have resulted in a number of unfilled 30 mil holes for storage periods longer than 2 weeks: i.e. 3.5% and 12.5% unfilled 30 mil holes after 3 and 4 weeks storage, respectively. On the other hand, the same storage conditions produced no adverse effects in surface mount reflow assembly trials. These effects are under investigation. Limited reflow assembly results will be presented in the last section of this report.

5. COATING CHARACTERIZATION

Previous work[5] [7] had focussed on the thermal stability of imidazole and other thin organic coatings. A series of spectroscopic analyses had demonstrated that the imidazole coating was unstable at temperatures above 100°C. When subjected to temperatures above 100-125°C, these films volatilize, leaving the underlying copper substrate susceptible to oxidation. In the earlier section of this report we had demonstrated that the solderability of immersion tin does not suffer significant degradation at elevated temperatures. However, the presence of humidity has an adverse effect as seen from Fig. 4.

Thermal effects

The oxidative stability of tin coatings was studied using X-Ray Photoelectron Spectroscopy (XPS). A Surface Science Laboratories Model SSX-206 Spectrometer using a 600μ monochromatized Al kα X-ray photon beam (1486.6eV) was used for this analysis. All XPS experiments were performed under ultra-high-vacuum (1.5×10^{-9} torr). Figure 5 shows the XPS spectra of tin-coatings as a function of thermal treatment in the Sn 3d high resolution region. Fig 5 (a) is from a freshly deposited sample and (b) and (c) are from samples which have undergone one and two reflows in air respectively. It should be noted that the samples have undergone a "simulated" reflow operation, where no solder paste was actually printed. The samples only passed through the reflow oven operated under standard condition for Sn-Pb reflow to experience the thermal effects.

In Fig 5, the peaks at 486.6 and 495.0 eV are the $3d_{1/2}$ and $3d_{3/2}$ levels of metallic Sn. The peaks at 484.8 and 493.1, are the corresponding peaks for SnO_x. It is clear from Fig 5 that the freshly deposited sample shows a thin (~ 40Å) layer of SnO_x over the Sn metal. The intensity of the metallic Sn peak decreases at the expense of the SnO_x peak after the samples were subjected to reflow. However, even after two reflows in air, the entire surface is not oxidized, as is evident from the non-zero Sn peak in Fig 5(c). This indicates the thermal oxide is not much more than 50-60Ås after two passes through the reflow oven.

The affinity of Cu and Sn to form intermetallics is well documented in literature.[12] [13] The mobility of Cu atoms in Sn at room temperature is sufficiently high that the growth of Cu-Sn intermetallic phases occurs in the film even at room temperature. At elevated temperatures, the intermetallic growth rate is significantly higher. The intermetallic formation can lead to a degradation of solderability. RBS studies have been performed to follow the Cu-Sn reaction as a function of temperature. In Figure 6, two RBS spectra of immersion tin coatings are shown. The scan labeled (a) is from the as-deposited sample (no heat treatment), and the scan labeled (b) is from a sample subjected to two simulated reflow passes in air. The thickness of the Sn film at room temperature is approximately 60μin. The two arrows labelled Sn (channel #437) and Cu (channel #381) indicate the backscattered energy position of Sn and Cu if they appear on the surface of the sample. As can be seen from Fig 6 scan (a), the Cu signal has been displaced to lower energy due to the top Sn layer. The spectrum (b) taken after reflow shows significant changes. The Sn signal has lowered in intensity but broadened to lower energy, overlapping that of Cu due to the formation of the intermetallic phase. The intermetallic is possibly Cu_6Sn_5, although there might be some contribution from a small amount of Cu_3Sn. The identity of the exact intermetallic phase is beyond the scope of this study, but experiments using X-Ray diffraction techniques are being performed at this time. From the relative intensities, we can calculate the intermetallic to be approximately two-thirds of the original Sn deposited. That is, approximately 40μin of the Sn layer (originally 60 μin) has been converted into a Cu-Sn intermetallic phase after this thermal treatment. It should be pointed out that not all of the Sn is consumed, because the Cu signal has not reached channel #381, which indicates that Cu has not reached the surface.

What is the role of the Cu-Sn intermetallic on solderability? It is clear from Fig. 1 that the 60μinch immersion tin coating is solderable using a low solids flux even after two passes through a reflow oven. It appears then that a thick intermetallic layer might not adversely affect soldering performance provided that it has not consumed the entire tin layer. Generally, the thermal processes associated with mixed technology assembly are not sufficiently aggressive to cause the intermetallic phase to reach the surface. The complete set of RBS measurements are documented in a separate report.[10]

Temperature/Humidity/Aging Effects

In the earlier section, we had shown that continued exposure to temperature and humidity causes degradation of solderability of immersion tin surfaces. XPS studies were performed to analyze the change in surface composition on temperature/humidity exposure. Figure 7 shows the high resolution XPS spectra in the Sn 3d region. The top scan is from a sample which was exposed to 65°C, 85%RH for one week. The entire surface of this sample is oxidized as evidenced by the disappearance of the metallic Sn peak. Auger depth profile studies carried out also on the same sample indicate the oxide layer to be >250Å thick. Further studies are in progress to study the SnO_x growth kinetics as a function of temperature and humidity.

Therefore, it appears that the solderability of immersion tin coatings is directly related to the SnO_x growth on the surface; the thicker the oxide layer, the less solderable the surface. The combination of temperature and humidity significantly accelerates oxide growth. Formation of Cu-Sn intermetallic phases does not adversely affect the soldering performance as long as the intermetallic phase is underneath a protective Sn layer. For a nominal Sn thickness of 50-60μin, typical thermal treatment (i.e., moisture removal bake or reflow) is not sufficient to cause the intermetallic to consume the entire tin coating and hence the soldering performance is not significantly deteriorated.

6. SURFACE MOUNT ASSEMBLY EVALUATION

To establish the merits of each surface finish in a typical surface mount assembly process, 68I/O PLCC, 24I/O SOIC and 1206 capacitors were attached to the (imidazole or immersion tin finished) circuit boards using eutectic Sn:Ag, Sn:Bi and Sn:Pb RMA based solder pastes. Solder paste reflow was performed under both air and inert (N_2) atmosphere using a convection BTU turbo reflow solder furnace. Reflow profiles were generated for each solder paste according to their melting point range and reflow behavior. Component leads and terminations were plated with 100% tin.

Due to the reduced spreading of most lead-free alloys,[14] the most recurring defect was non-wetting of the circuit board pads. Non-wetting defects were typically less than 5% of the total pad area. The non-wetted area was in most cases the result of a uniform shift in the solder volume caused by the printing process. The non-wetted areas were largely at the sharp corners of the land pattern. This non-wetting defect was observed on boards assembled in both nitrogen and air. In contrast, Sn:Pb, due to its excellent spreading, compensated for any printing misalignment and wetted the entire pad.

Figure 8 compares the incidence of non-wetted pads on imidazole and immersion tin finished circuit boards after assembly with eutectic Sn:Ag, Sn:Bi and Sn:Pb solders. Incomplete wetting is due to a large extent to the intrinsic characteristics of the solder, namely its surface tension and its metallurgical reaction with the substrate. The results shown in Figure 8 indicate that coating the circuit board pads with thin, displaceable metal layers (i.e. immersion tin) visibly promotes solder wetting. Therefore the benefits of immersion tin are most obvious for assembly applications requiring solders with reduced spreading properties. For both Sn:Bi and Sn:Ag solders, the immersion tin finish outperformed the imidazole finish.

7. CONCLUSIONS

This report compared the the wettability of thin azole and electroless (immersion) tin circuit board surface finishes after exposure to a series of temperature and humidity conditions.

The solderability of immersion tin coatings was shown to be directly related to the SnO_x growth on the surface; the thicker the oxide layer, the less wettable the surface. The combination of temperature and humidity significantly accelerates oxide growth. The thermal oxidation of tin is reduced in the absence of humidity. Formation of Sn:Cu intermetallic phases does not adversely affect the soldering performance as long as the intermetallic phase is protected by a Sn surface layer. For a nominal Sn thickness of 60μinches, typical thermal excursions associated with assembly are not sufficient to cause the intermetallic to consume the entire tin coating and hence the soldering performance is not deteriorated due to temperature effects alone. On the other hand, exposure to temperature/humidity conditions of 35°C/90%RH and 65°C/85%RH for

1 week or less promotes heavy tin oxide growth which then leads to significant solderability loss.

In contrast, thin azole films are more robust to humidity exposure, however, upon heating in the presence of oxygen, they decompose into volatile products and leave the unprotected copper substrate susceptible to oxidation. This leads to solderability degradation.

Evaluations of lead-free solder pastes for surface mount assembly applications indicated that immersion tin PWB surface finishes significantly improved the spreading of Sn:Ag and Sn:Bi solder alloys as compared to azole based finishes.

8. ACKNOWLEDGEMENTS

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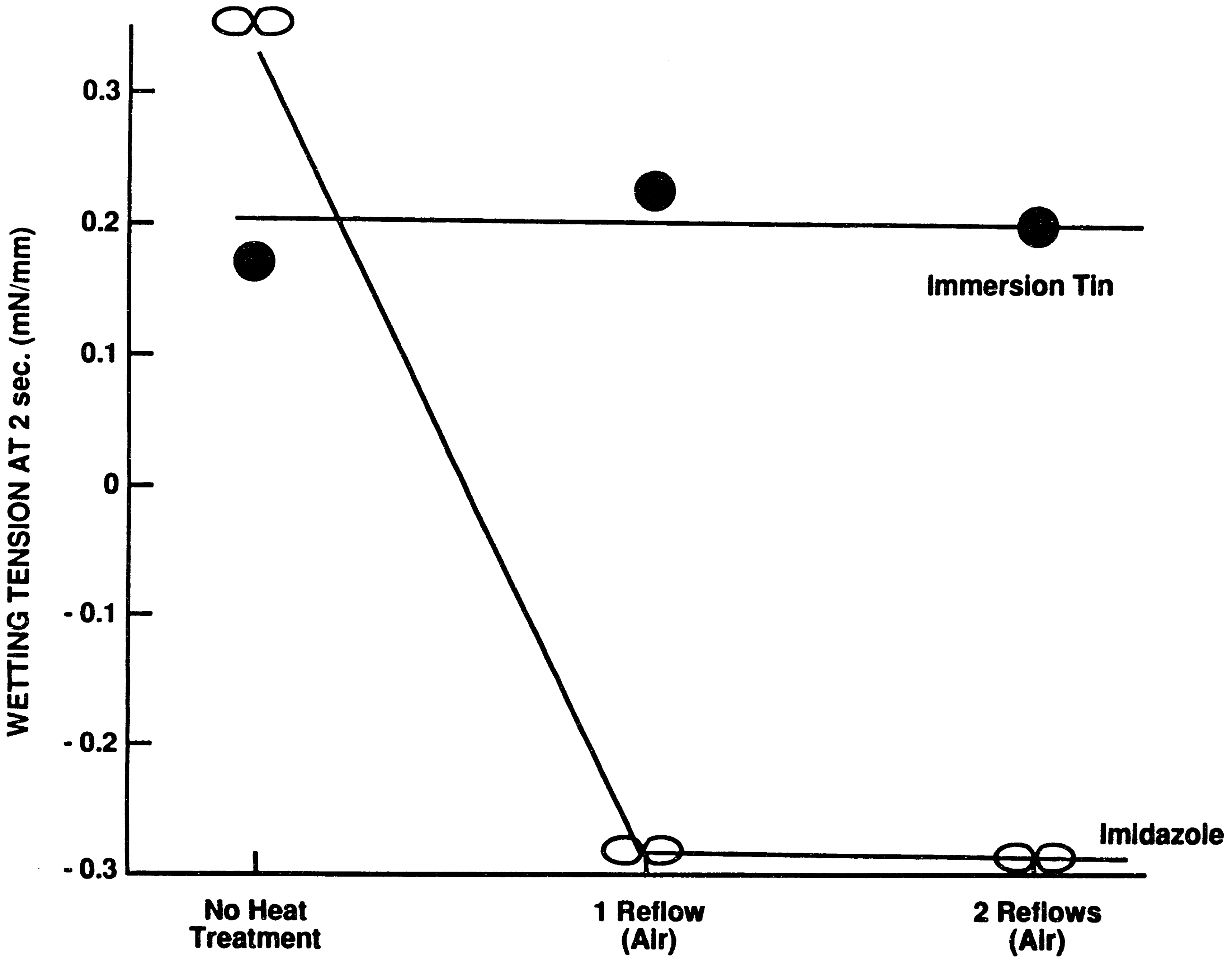
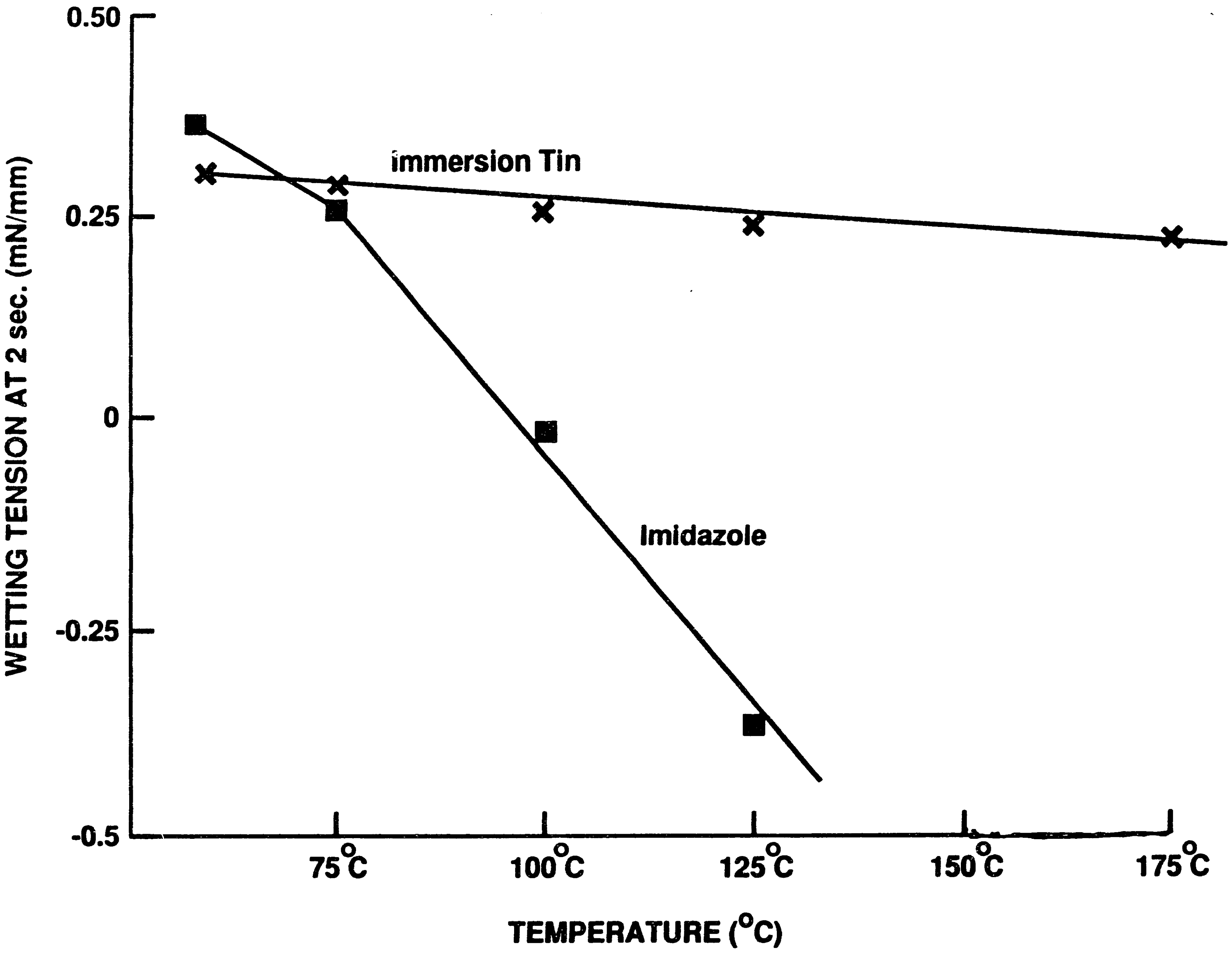


SOLDERABILITY PERFORMANCE COMPARISON OF IMIDAZOLE vs. IMMERSION TIN



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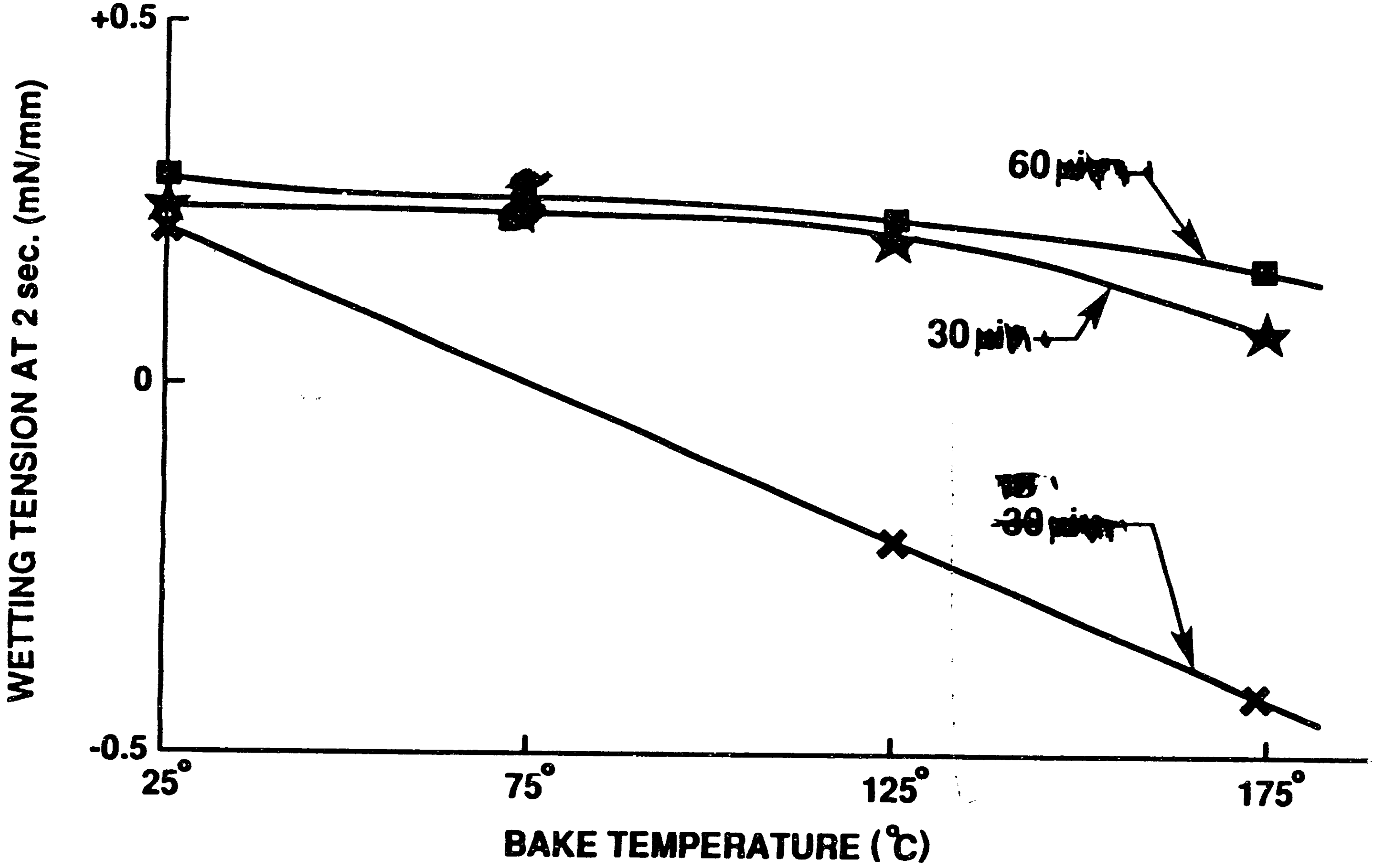
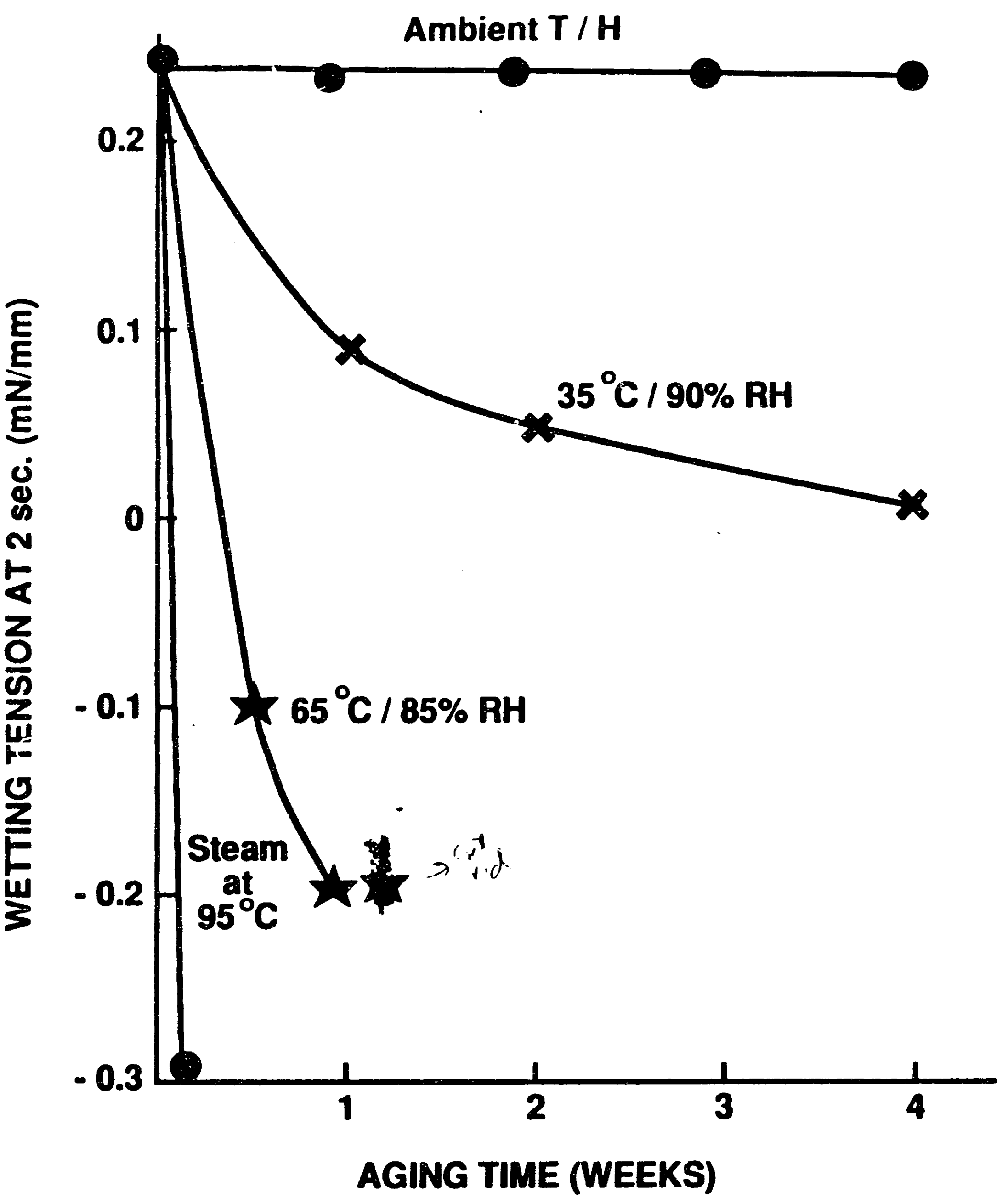
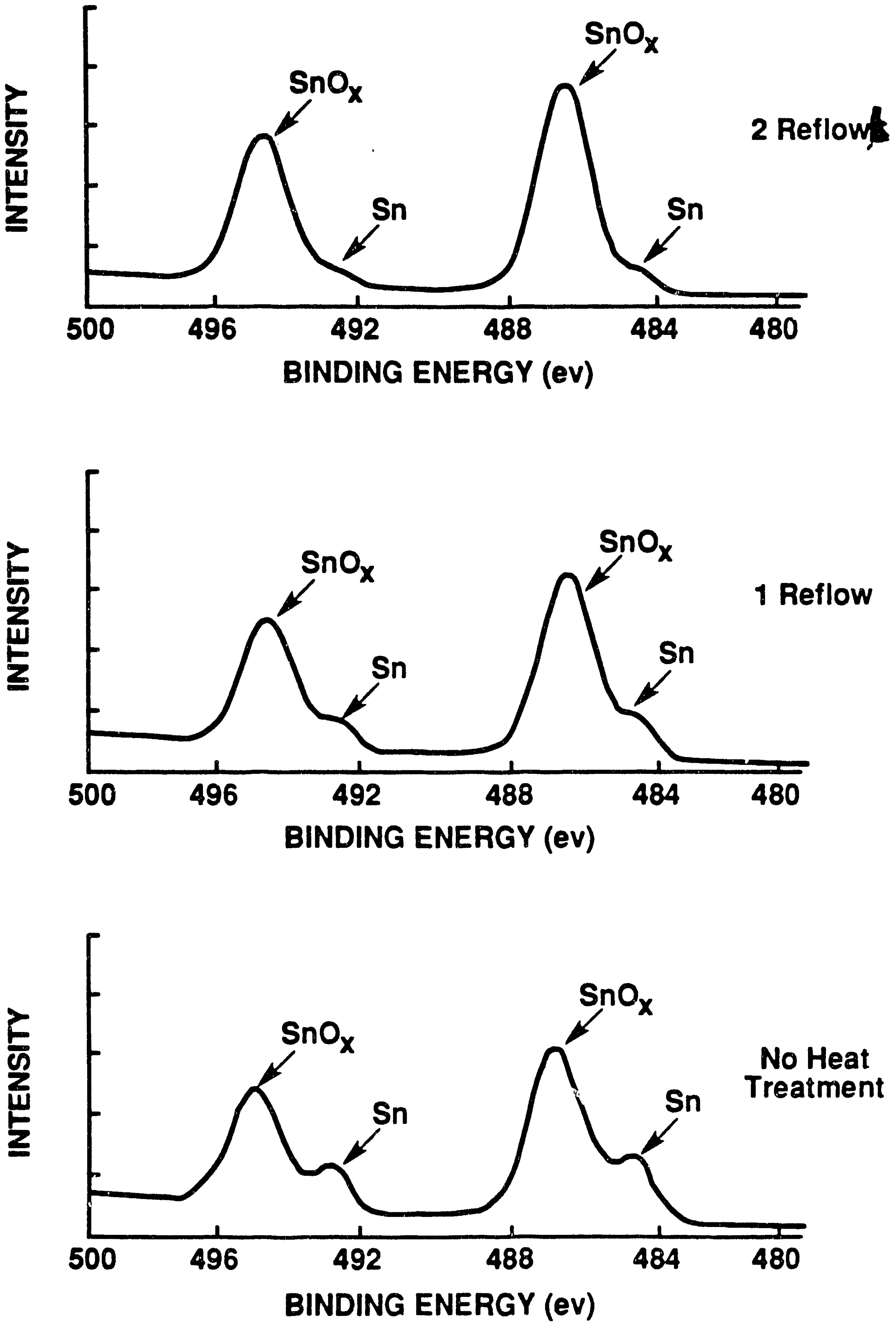


SOLDERABILITY OF IMMERSION TIN
AS A FUNCTION OF COATING THICKNESS



SOLDERABILITY PERFORMANCE OF IMMERSION TIN COATINGS AFTER TEMPERATURE / HUMIDITY AGING



Sn HIGH RESOLUTION SPECTRA XPS STUDIES OF IMMERSION TIN COATINGS

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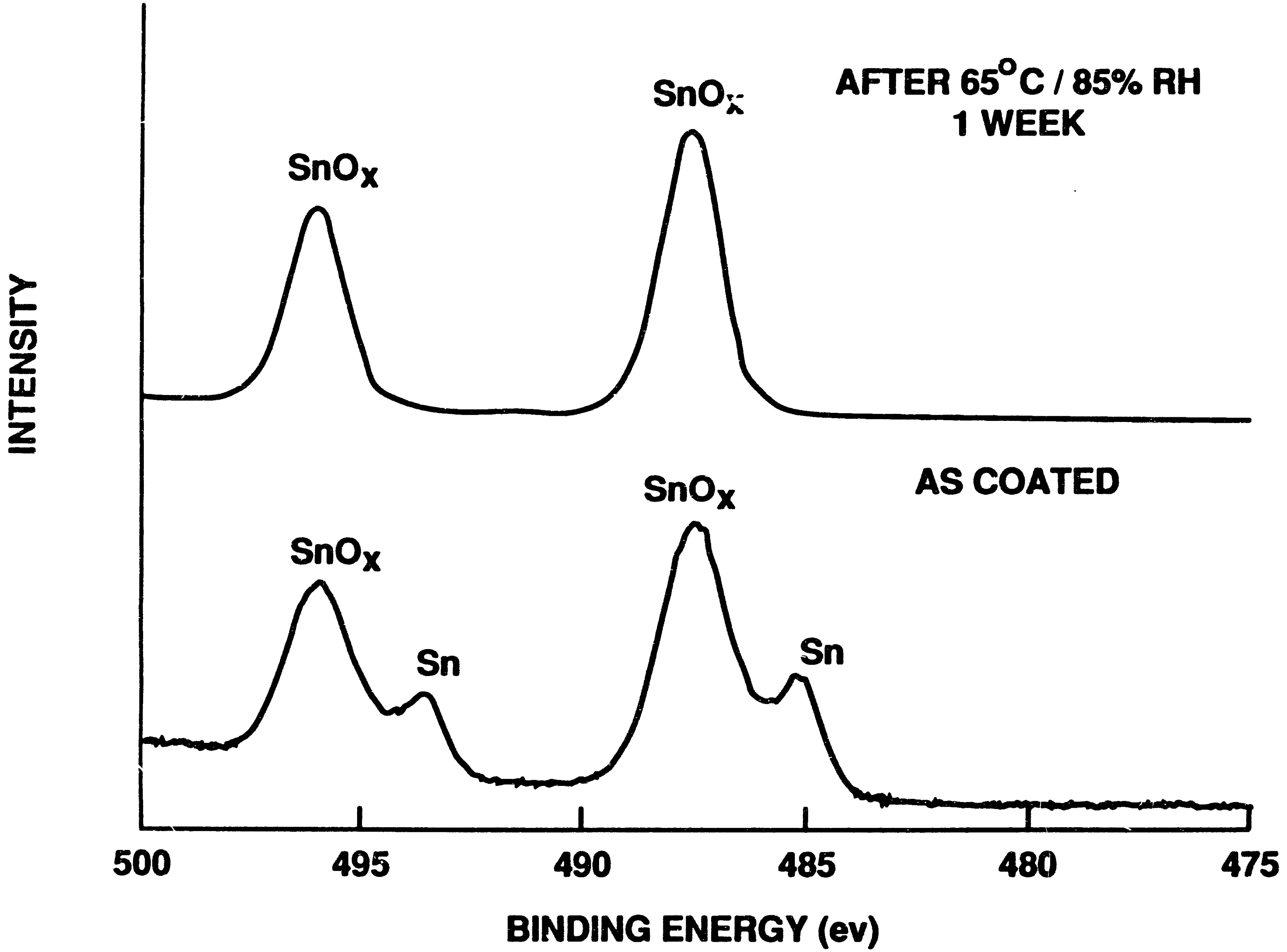
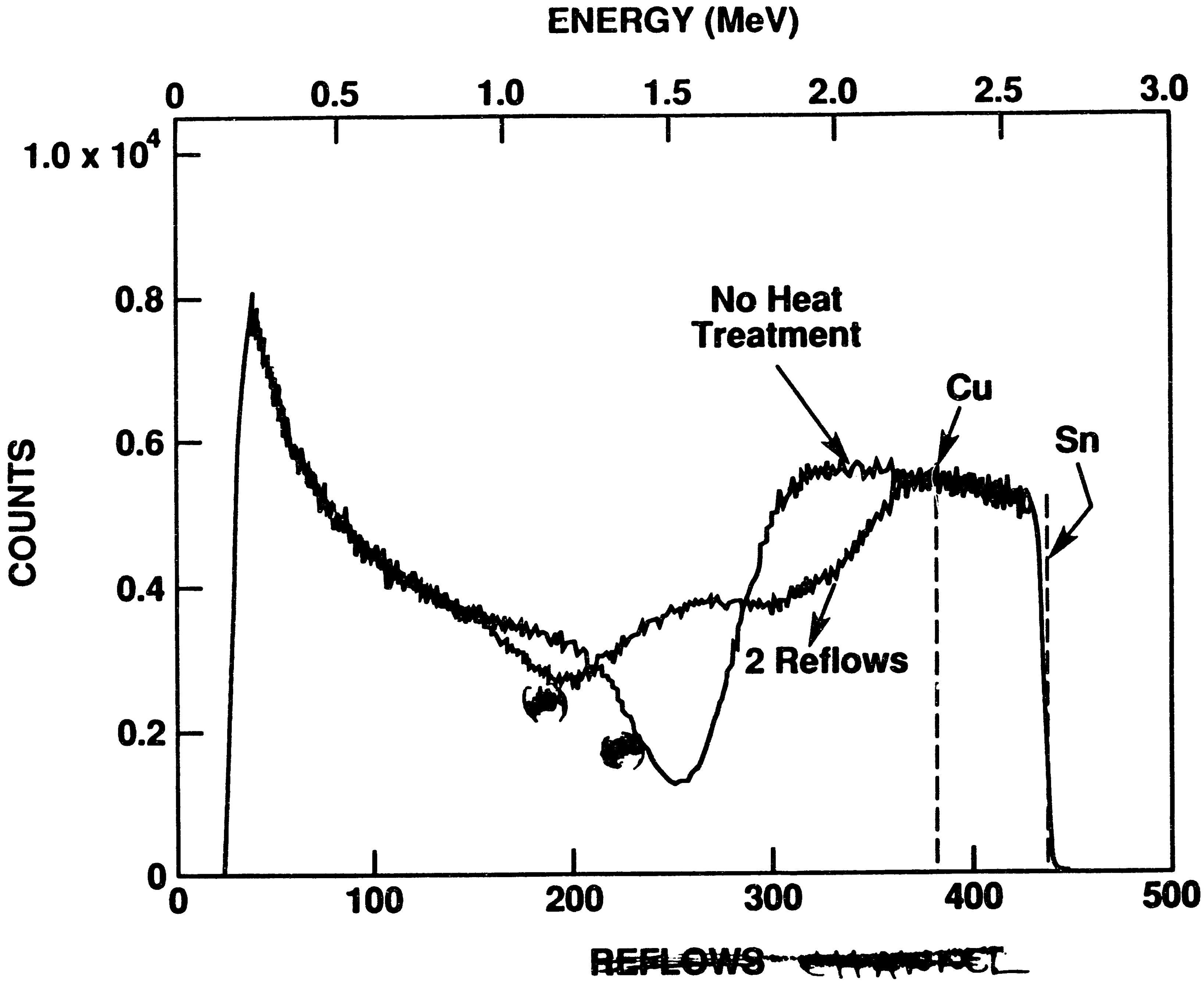


XPS STUDIES OF IMMERSION TIN COATINGS Sn HIGH RESOLUTION SPECTRA



RUTHERFORD BACK SCATTERING STUDIES
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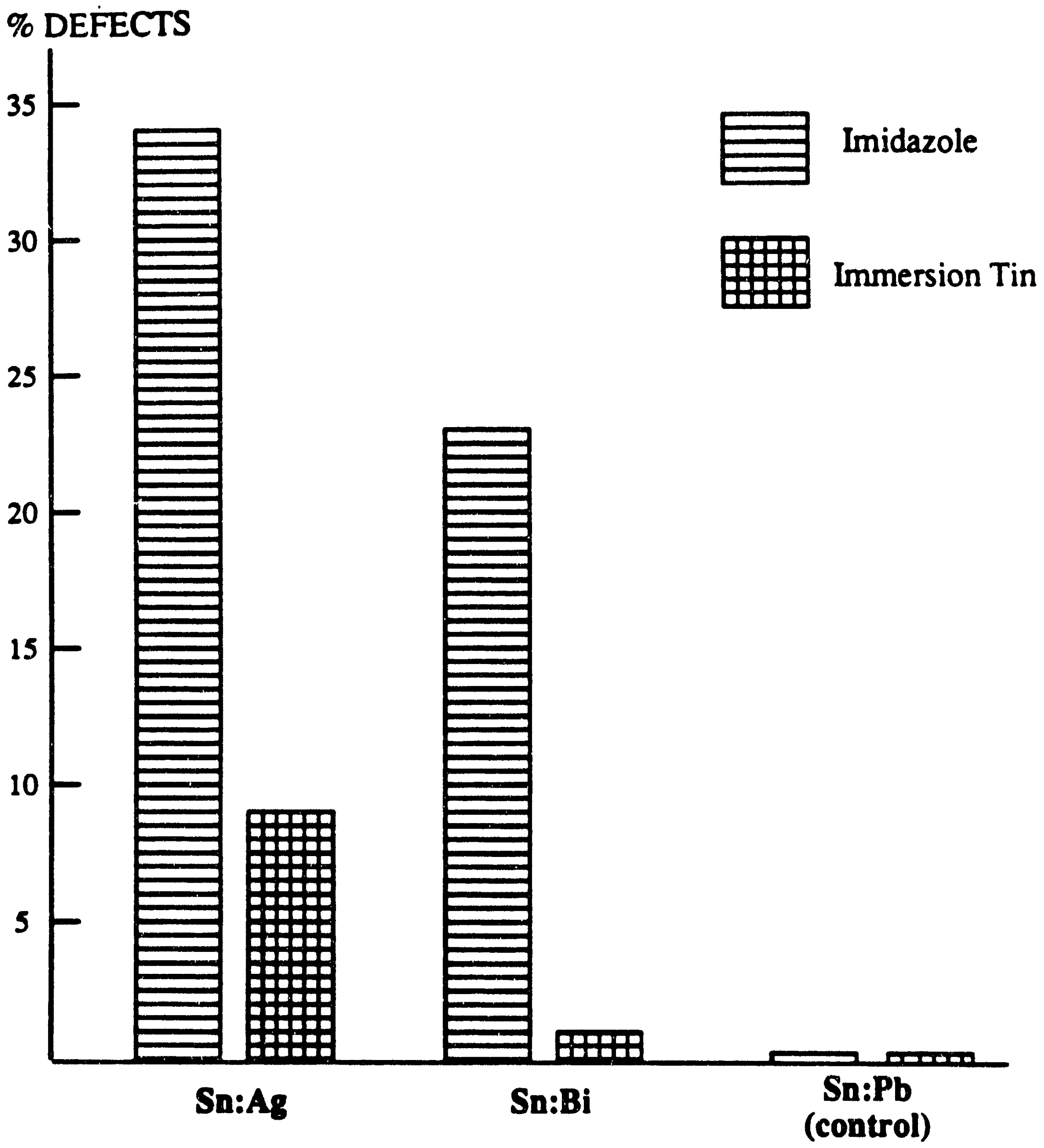

Wetting Defects of Immersion Tin vs. Imidazole Coated PWBs
After Surface Mount Assembly with Lead-Free Solder Pastes

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