Solderability Testing of Kovar with 60Sn-40Pb Solder and Organic Fluxes

Flux type, cleaning procedure and solder bath temperature were evaluated for their effects on solderability

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ABSTRACT. The solderability of 60Sn-40Pb solder on Kovar was examined as a function of surface cleaning procedure, flux and solder bath temperature. Organic acid fluxes were more effective than a mildly activated, rosin-based (RMA) flux on chemically etched Kovar with contact angles as low as 29 ± 5 deg as compared to 61 ± 11 deg, respectively. Varying the solder temperature through the range of 215° to 260°C (419° to 550° F) caused an insignificant change to the contact angle for the RMA flux and a decrease of the contact angle for a candidate water-based, organic acid flux. The dilution strength of the flux and the elapsed cleaning time significantly influenced the solder-flux interfacial tension, 7LF. T-peel strengths of Kovar 60Sn-40Pb oxygen-free, high-conductivity (OFHC) copper joints had a low correlation with the contact angle derived from the solderability experiments. The results of the solderability tests, T-peel mechanical tests and subsequent microanalysis of the as-soldered and T-peel samples revealed that with the use of an RMA flux, the best results were achieved with electropolishing and a 240° to 260°C (464° to 500°F) solder temperature range. A relatively low contact angle of 31 ± 2 deg was observed with no evidence of cracking or thick film intermetallic formation at the Kovar-solder interface. Furthermore, T-peel strengths were nominally 9.4 ± 0.5 X 10⁶ dyne/cm.

KEY WORDS
Solderability Testing
Kovar Solderability
60Sn-40Pb Solder
60Sn-40Pb on Kovar
Organic Acid Fluxes
Surface Cleaning
Rosin (RMA) Flux
Interfacial Tension
T-Peel Strength
Electropolishing

Introduction
The unique thermal expansion properties of Kovar have allowed this material to have many engineering applications, from glass-metal seals to conductor leads in microelectronic packages. In the latter case, the component is most often secured to the printed circuit board by soldering the Kovar leads to the conductive landing. Therefore, the wetting behavior of solder alloys on a Kovar substrate is of particular interest in the microelectronics industry. The goal of this investigation was to quantify and evaluate the wetting behavior of 60Sn-40Pb (wt-%) solder on Kovar as a function of flux, solder temperature and the procedure used to clean the Kovar surface prior to tinning. These results were then compared with wetting experiments performed on nickel-plated and gold-nickel-plated Kovar. In addition, T-peel strength measurements were made of Kovar oxygen-free, high-conductivity (OFHC) copper joints formed by the solder alloy to determine whether this data would correlate with the wettability of the Kovar.

The wetting behavior or solderability is quantified by the contact angle, \( \theta \), formed between the liquid solder and the substrate as defined in Fig. 1 (Ref. 1). The contact angle is dependent upon the equilibrium balance of the interfacial tensions as expressed by Young's equation:

\[ \gamma_{SL} - \gamma_{SF} = \gamma_{LFC} \cos \theta \]  

where \( \gamma_{SL} \) is the solid (substrate)-liquid (solder) interfacial tension, \( \gamma_{SF} \) is the solid (substrate)-flux interfacial tension, and \( \gamma_{LFC} \) is the liquid-flux interfacial tension. The smaller the value of \( \theta \), the better the wetting capability of the solder.

The calculation of \( \theta \) is based upon the measurement of two properties of the solder meniscus formed on the vertical coupon (Fig. 1) (Refs. 2, 3): the height to which it has risen, \( H \), and the weight of the solder contained in the meniscus, \( W \). An analytic expression for \( W \) is given by the following equation:

\[ W = \frac{pH}{2} \sqrt{\frac{4\gamma_{LFC}}{\rho g} - H^2} \]  

where \( p \) is the solder density; \( g \) is the acceleration due to gravity; and \( P \) is the perimeter of the coupon. The values of \( p \), \( g \) and \( P \) are known. Values of \( H \) and \( W \) are measured experimentally by the meniscometer and wetting balance, respectively. Therefore, Equation 2 is solved for the value of \( \gamma_{LFC} \), which is then introduced into the following expression that calculates the contact angle:

\[ \theta_c = \arcsin \left( \frac{1 - \rho g H^2}{2\gamma_{LFC}} \right) \]  

Two other parameters originating from the experimental analysis are the rate at which the solder wets the substrate, \( W \), and the time required for the meniscus to reach its maximum weight, \( t_w \).

Experimental
Materials
The Kovar (29Ni-17Co-0.2Mn-bal Fe, nominal wt-%) coupons measured 0.028 x 2.54 x 2.54 cm (0.1 x 1.0 x 1.0 in) and were exposed to the following heat treatment prior to testing in order to simulate an industrial glassing process: 1) chemical etch, 2) high-temperature oxidation, and 3) second chemical etch. A second set of samples was electroplated with 2.4 to 6.0 \( \mu m \) of nickel. A third group con-

Aside from ensuring uniform surface conditions on all of the samples, this process modeled the engineering application for which this study was conducted.
sisted of nickel-plated specimens that were subsequently electroplated with 0.43 to 0.57 \( \mu \)m of gold.

The solder used in the wettability experiments was a 60Sn-40Pb alloy.

The five candidate fluxes examined here are: (1) Flux A—RMA, (2) Flux B—OA-CHOH, (3) Flux C—OA-CHOH, (4) Flux D—OA-H\(_2\)O, and (5) Flux E—OA-H\(_2\)O. Flux A is a rosin-based, mildly activated (RMA) flux while the other four are halide-free, organic acids (OA). The solvent is alcohol (CHOH) for fluxes B and C and water (H\(_2\)O) for fluxes D and E. Unless otherwise stated, all fluxes were used in a dilution of one-to-one (1:1) by volume with isopropyl alcohol.

Cleaning Procedures

A brief description of the cleaning procedures is presented below. The details are found in the appendix. A set of plain Kovar samples was etched for 2 min in 300 mL of a commercially available chemical etchant composed of a mixture of nitric, hydrochloric and phosphoric acids that was held at 80° to 85°C (176° to 185°F). The remaining cleaning steps detailed in the appendix were included to rinse away the corrosive agents of the etchant. The samples were coated with flux immediately after cleaning to protect the freshly etched surface.

An electropolishing process was performed on some of the plain Kovar coupons using a 250 mL solution of 9 parts glacial acetic acid to 1 part perchloric acid (60%) (Ref. 4) held at 30°C (86°F). The coupon was the cathode, while the anode was made of AISI Type 347 stainless steel screen. The polishing time was 3 min and the current density was 0.124 A/cm\(^2\) (under current control). In addition, subsequent processing steps were designed to remove the corrosive electrolyte from the sample surface. As in the etching procedure, samples were flushed immediately after cleaning.

The nickel- and gold-nickel-plated samples were cleaned by an agitated rinse of trichloroethylene followed by a similar rinse in isopropyl alcohol to remove organic contaminants from the specimen surfaces.

Solderability Testing

The meniscus height, \( H \), was evaluated on the meniscometer, which is a traveling stage microscope capable of measuring the vertical movement of the meniscus. Each sample was allowed to preheat for 30 s at a distance of 1 cm (0.4 in.) above the solder before immersion into the pot at a rate of 1.3 cm/s to a depth of 0.375 cm (0.15 in.). The meniscus height was recorded after 20 s. Four samples were evaluated per test series.

The meniscus weight was measured by means of a microbalance. A schematic diagram illustrating the meniscus weight as a function of time is shown in Fig. 2. The physical behavior of the meniscus responsible for certain features of the wetting curve has been included at the figure bottom. To determine the correct value of \( W \), the buoyancy force acting on the coupon must be calculated. Referring to Fig. 3, which shows the geometry of the risen meniscus, the total immersion depth is \((H - V_0) + (ID)\) where (ID) is the depth to which the coupon extends below the solder surface and \((H - V_0)\) is the additional submersion due to the risen meniscus. Total buoyancy force is then given by:

\[
BF = \rho g w t [(H - V_0) + (ID)]
\]

Six sample coupons were evaluated per test series. The maximum meniscus weight was taken as the average value between 10 and 20 s of testing. With the average meniscus height determined from the meniscometer data and the average meniscus weight compiled from the wetting balance tests, the solder-flux interfacial tension and contact angle were calculated for each test. The absolute error on \( \gamma_{SF} \) and \( \theta_c \) was the maximum and minimum values based upon the range of values of the meniscus height and weight established by plus-or-minus one standard deviation about the sample mean.
Finally, the wetting rate was measured from the slope of the wetting balance curve starting at the point of zero meniscus height (point B in Fig. 2) to where the curve begins to deviate from a linear trend. Although taking the wetting rate directly from the recorder output does not account for the buoyancy force, the time-dependent contribution to the buoyancy force caused by the meniscus rise was confirmed to have had a negligible effect on wetting rate values.

T-Peel Mechanical Tests

T-peel pull tests were conducted on solder joints formed between the Kovar coupons and OFHC copper sheet using the 60Sn-40Pb alloy in order to model a prototype joint. A schematic diagram of the test specimen geometry and the load-displacement output appear in Fig. 4. The Kovar segment was cleaned similarly to the solderability coupons and then immediately coated with the particular flux of interest. The copper sheet that formed the other segment was degreased, etched in a 1:1 dilution of HCl and deionized water for 15 s, and then passed through several rinsing steps to remove any acid residue. The copper was coated with Flux A (RMA). The 60Sn-40Pb solder (0.025 cm thick) was cut to size and degreased in trichloroethylene and isopropyl alcohol.

**Results**

**Solderability as a Function of Flux**

Chemically Etched—Plain Kovar and Plated Coupons

The solderability data comprised of $\theta_C$, $\gamma_F$, $\gamma_S - \gamma_L$, $W$, and $t_W$ for plain Kovar coupons, which were chemically etched, are shown in Table 1. The solder temperature was 260°C. Similar results from tests on the nickel-plated and gold-nickel-plated coupons that were coated with Fluxes A (RMA) and D (OA+H2O) have been included in the table. For the case of plain Kovar, Flux D (OA+H2O) caused the lowest contact angle at 29 ± 5 deg, while the RMA Flux A had the highest value at 53 ± 5 deg.

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**Table 1—Solderability Parameters for Chemically Etched Plain Kovar and Plated Kovar**

<table>
<thead>
<tr>
<th>Flux</th>
<th>$\theta_C$ (deg)</th>
<th>$\gamma_F$ (dyne/cm)</th>
<th>$\gamma_S - \gamma_L$ (dyne/cm)</th>
<th>$W$ (dyne/s)</th>
<th>$t_W$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>29 ± 5</td>
<td>430 ± 30</td>
<td>380 ± 10</td>
<td>1290 ± 50</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>C</td>
<td>45 ± 6</td>
<td>510 ± 90</td>
<td>360 ± 20</td>
<td>1400 ± 100</td>
<td>2.5 ± 0.2</td>
</tr>
<tr>
<td>E</td>
<td>53 ± 5</td>
<td>540 ± 80</td>
<td>325 ± 15</td>
<td>1390 ± 150</td>
<td>2.8 ± 0.2</td>
</tr>
<tr>
<td>B</td>
<td>53 ± 11</td>
<td>290 ± 100</td>
<td>175 ± 50</td>
<td>600 ± 100</td>
<td>3.8 ± 0.5</td>
</tr>
<tr>
<td>A</td>
<td>61 ± 11</td>
<td>650 ± 200</td>
<td>315 ± 50</td>
<td>1230 ± 50</td>
<td>4.7 ± 0.3</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>24 ± 2</td>
<td>380 ± 20</td>
<td>350 ± 15</td>
<td>1300 ± 150</td>
<td>3.97 ± 0.06</td>
</tr>
<tr>
<td>D</td>
<td>24 ± 3</td>
<td>480 ± 30</td>
<td>440 ± 15</td>
<td>1330 ± 20</td>
<td>4.4 ± 0.9</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>11 ± 5</td>
<td>360 ± 30</td>
<td>350 ± 20</td>
<td>1490 ± 50</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>D</td>
<td>15 ± 3</td>
<td>460 ± 20</td>
<td>440 ± 10</td>
<td>1670 ± 200</td>
<td>2.3 ± 0.2</td>
</tr>
</tbody>
</table>

(a) Flux diluted 1:1 by volume with isopropyl alcohol.

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The three components were assembled, preloaded with a 20-g weight, and then placed on a heated copper platen being held at 268° ± 2°C (514°F). Observations determined that a dwell time of 45 s ensured complete reflow of the solder; after which the completed sample was removed from the heat source and allowed to cool.

Testing of the T-peel sample was performed on an Instron tensile tester at a displacement rate of 0.085 cm-s⁻¹. Four specimens were conducted per test condition. The strength, defined by Fig. 4B, was taken as the average of the four specimens. The absolute error was plus-or-minus one standard deviation of the four values.

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**Fig. 3** — Meniscus geometry describing the buoyancy force correction.

**Fig. 4** — A—Schematic diagram of the T-peel test specimen; B—force-displacement curve of the T-peel test.
61 ± 11 deg. The other fluxes resulted in contact angles between 45 and 53 deg. Fluxes C (OA-CHOH) and D (OA-H₂O₂) had the two largest values, of (γFS - γSL). The Fluxes A (RMA) and E (OA-H₂O) had slightly lower values, and Flux B (OA-CHOH) showed the poorest (γFS - γSL).

It is apparent in Table 1 that the solder-flux interfacial tension, γLF, was very sensitive to the particular flux and had a substantial influence on the value of tanθ. The surface tension (in vacuum) of 60Sn-40Pb solder is estimated at 510 dyne-cm⁻¹ (Ref. 8). The wetting rate, W, and time to maximum meniscus weight, tw, did not depend upon the behavior of tanθ. A linear least squares analysis between W and tanθ demonstrated a correlation coefficient (R²-value) of 0.06.

The gold-nickel- and nickel-plated coupons showed values of tanθ, which were well below those of the plain Kovar samples for comparable fluxes. In addition, the values of W were generally higher and those of tw, lower than for the gold-nickel-plated samples at the same parameters for the plain Kovar specimens. The nickel-plated samples had slightly higher values of tw and comparable wetting rates when compared to the plain Kovar results.

Shown in Fig. 5 are representative wetting curves of the chemically etched, plain Kovar coupons tested at 260°C as a function of flux: A — Flux C (OA-CHOH); B — Flux A (RMA).

Fig. 5 — Representative wetting curves of chemical etched, plain Kovar coupons tested at 260°C as a function of flux. A — Flux C (OA-CHOH); B — Flux A (RMA).

Also, Fig. 6 shows the meniscus weight reaching a maximum and then decreasing slightly with time. These phenomena can be caused by a time-dependent change to γSL (such as caused by high-temperature polymerization of the flux — Ref. 6), or changes in γSL due to alloying effects between the substrate and the solder. The decrease in W was not consistent for a given flux between the different samples so that volatilization of flux constituents was not a likely cause. The effect was greatest for the gold-nickel-plated coupons.

In several tests of plain Kovar fluxed with either A (RMA), B (OA-CHOH), or E (OA-H₂O), the solder did not wet some regions of the surface. A sample wetting balance curve of such a specimen that was coated with Flux A, is shown in Fig. 7. This phenomenon was not observed with the use of Fluxes C (OA-CHOH) or D (OA-H₂O₂).

Observations of the solder film on plain Kovar coated with the RMA Flux A indicated extensive dewetting after the coupon was removed from the solder bath. An optical micrograph of this phenomenon appears in Fig. 8.

As a consequence of the surface attack by the chemical etchant, preferred wetting of the grain boundaries was observed with use of the Fluxes C (OH-CHOH), D (OA-H₂O₂), and E (OA-H₂O). A sample scanning electron micrograph of this phenomenon is shown in Fig. 9. This behavior was not observed when Fluxes A and B were applied to the samples.

Scanning electron micrographs of the solder-Kovar interface revealed no evidence of cracking or separation between the two components. Chemical analysis along the Kovar-solder interface and in the bulk solder film by electron microprobe analysis did not detect iron, nickel or cobalt dissolved from the Kovar surface. On the solder film surface, porosity and residues were evident with the use of Fluxes C (OA-CHOH), D (OA-H₂O₂) and E (OA-H₂O); were sharply diminished with Flux B (OA-CHOH); and were absent with the RMA Flux A.

Fig. 6 — Representative wetting curve of the Au/Ni-plated Kovar specimens tested at 260°C with Flux A (RMA).

Fig. 7 — Wetting curve of a nonwetting sample (chemically etched, Flux A) tested at 260°C.
Table 2—Solderability Parameters vs. Chemical Etching Time (Flux D)

<table>
<thead>
<tr>
<th>Chemical Etching Time (min)</th>
<th>$\theta_C$ (deg)</th>
<th>$\gamma_F$ (dyne/cm)</th>
<th>$\gamma_F - \gamma_S$ (dyne/cm)</th>
<th>$W$ (dyne/s)</th>
<th>$t_w$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>180</td>
<td>530 ± 150</td>
<td>355 ± 150</td>
<td>1050 ± 50</td>
<td>3.9 ± 0.7</td>
</tr>
<tr>
<td>0.5</td>
<td>48 ± 10</td>
<td>450 ± 100</td>
<td>350 ± 150</td>
<td>900 ± 150</td>
<td>4 ± 1</td>
</tr>
<tr>
<td>1.0</td>
<td>39 ± 10</td>
<td>420 ± 40</td>
<td>360 ± 15</td>
<td>1260 ± 150</td>
<td>3.0 ± 0.6</td>
</tr>
<tr>
<td>2.0</td>
<td>32 ± 5</td>
<td>460 ± 30</td>
<td>380 ± 10</td>
<td>1250 ± 20</td>
<td>4.3 ± 0.3</td>
</tr>
<tr>
<td>4.0</td>
<td>34 ± 3</td>
<td>460 ± 30</td>
<td>380 ± 10</td>
<td>1250 ± 20</td>
<td>4.3 ± 0.3</td>
</tr>
</tbody>
</table>

For Flux D (OA-H$_2$O), the time period during which the plain Kovar coupons were exposed to the chemical etchant was varied between 0 and 4.0 min. The solderability results are outlined in Table 2. A new batch of test samples was used for the 2.0-min etch; hence, the slight variation from the D (OA-H$_2$O) data of Table 1. The data indicate that the behavior of $\theta_C$ was more sensitive to the interfacial tension, $\gamma_F$, than ($\gamma_F - \gamma_S$). The minimum value of $\theta_C$ was achieved with the 2.0 min etching time. As expected, no wetting took place on samples that received no surface etch treatment. The value of $W$ was a maximum and $t_w$ a minimum for the 2.0-min etch. Otherwise, the parameters $W$ and $t_w$ demonstrated no apparent trend with etching time nor with the other solderability parameters.

Similar analyses were performed on the nickel-plated and gold-nickel-plated specimens. Electron microprobe analysis revealed that some of the nickel coating had dissolved into the solder film. Shown in Fig. 10A is a scanning electron micrograph (backscattered electron image) of the solder film profile on a nickel-plated specimen. Figures 10B and 10C are the nickel and tin x-ray maps, respectively, of the region shown in Fig. 10A. The intermittent regions of coincident concentrations of tin and nickel were quantitatively determined to have the composition of the tin-nickel intermetallic, Ni$_3$Sn$_4$.

Dissolution of the gold layer on the gold-nickel-plated coupons was also investigated by the microprobe technique. As the thickness of the solder film increased (or the further away from the meniscus edge that one examined the film cross-section), the more complete was the dissolution of gold. Optical microscopy of the solder film surface revealed an extensive array of gold-tin intermetallic crystals and an overall solder film morphology that was dependent upon the flux in use.

Electropolishing Process—Plain Kovar

A comparison of solderability results between plain Kovar coupons that were chemically etched and those that were electropolished is made in Table 3. Changing to the electropolish treatment had little effect on the contact angle of samples fluxed with B (OA-CHOH), D (OA-H$_2$O) and E (OA-H$_2$O). For Flux D, this observation was caused by both $\gamma_F$ and ($\gamma_F - \gamma_S$) remaining unchanged. However, the other two fluxes, B and E, showed increases in both $\gamma_F$ and ($\gamma_F - \gamma_S$), which left $\theta_C$ unchanged. While a moderate decrease of $\theta_C$ was observed with the use of Flux C (OA-CHOH) between the two cleaning procedures, a large decline of $\theta_C$ from 61 ± 11 to 31 ± 2 deg was recorded for samples coated with the RMA Flux A. This substantial decrease of contact angle was due entirely to a drop in the value of the solder-flux interfacial tension, $\gamma_F$. Although some dewetting was observed, it was not as severe as that on the chemically etched coupons. Also, as with all of the other fluxes, Flux A on electropolished plain Kovar did not exhibit any nonwetting cases—Fig. 7.

For the fluxes, the electropolishing procedure caused a higher wetting rate as compared to the chemically etched samples. Yet, no obvious trend was observed between the pairs of values of $t_w$. Finally, no alterations in the generalized shape of the wetting curves between the two cleaning processes were noted for the fluxes.

Fig. 8 — Optical micrograph of a dewetted sample (chemically etched, plain Kovar, Flux A, 260°C).

Fig. 9 — SEM micrograph (secondary electron) of the meniscus front on chemically etched, plain Kovar coated with Flux E. Solder film is to the left; the Kovar surface to the right.
Effect of Flux Dilution

Flux D (OA-H2O) was selected to determine the effect of flux dilution. The plain Kovar coupons were chemically etched (after a 20 s diluted sulfuric acid etch to remove a heavier than normal oxide). Shown in Fig. 11 is a graph of the contact angle and solder-flux interfacial tension as a function of the degree of dilution of the flux. The behavior of $\theta_C$ followed closely that of $\gamma_F$ with a minimum at 50 to 60% dilution. The values of the parameter, ($\gamma_F - \gamma_S$), did not contribute to the overall trend of $\theta_C$. The wetting rate, W, and the value of $\gamma_W$ showed no significant dependence on the degree of dilution.

Effect of Solder Temperature

Contact angle as a function of the solder bath temperature for plain Kovar samples coated with Flux A (RMA) or Flux D (OH-H2O) is shown in Fig. 12. The specimens received the electropolishing treatment. A small decrease in contact angle with increasing temperature was observed for the samples fluxed with D. A slope of $-0.08 \text{ deg/°C}$ and a correlation coefficient ($R^2$) of 0.74 were measured by a linear least squares analysis of the data. For the RMA Flux A, a correlation coefficient ($R^2$) of 0.27 confirmed no statistical dependence of $\theta_C$ on temperature over the range tested. Samples of the wetting curves from tests using both fluxes and solder temperatures of 215° and 245°C are shown in Fig. 13. The solderability results are listed in Table 4. With the RMA Flux A, increasing the solder temperature caused a significant increase in the wetting
rate and a corresponding decrease in the value of $t_w$. Flux D (OA-H$_2$O) did not exhibit a temperature dependence to the wetting rate. However, the decrease of $t_w$ with increasing temperature corresponded to a diminishment of the negative meniscus weight observed at the start of the wetting curve for the lower temperature tests. The values of $\gamma_{LF}$ and ($\gamma_{SF} - \gamma_{SL}$) as a function of the solder temperature (Table 4) were generally the same in the temperature range of 215°C to 260°C (419°F to 500°F) for Flux A (RMA). However, both parameters dropped sharply at 288°C (550°F) causing a slight decrease in $\theta_C$. For the Flux D (OA-H$_2$O) data, the overall trend of the parameter ($\gamma_{SF} - \gamma_{SL}$) was found to increase with temperature and was chiefly responsible for the decreasing behavior of $\theta_C$. $\gamma_{LF}$ exhibited no particular trend over the temperature range for this flux.

Qualitative observations of the solder films showed that the amount of residues and the difficulty of their removal increased with increasing temperature for both fluxes. The same temperature dependence was recorded for the amount of solder film porosity generated by Flux D.

## T-Peel Strength Measurements

The T-peel strength data for the plain Kovar coupons that were chemically etched and coated with one of the five fluxes appear in Table 5 together with the contact angle determined by solderability testing. Also included are the data derived from the electropolished plain Kovar specimens and the gold-nickel-plated coupons; both having been coated with RMA Flux A. A rough correlation was observed between the nominal T-peel strengths and $\theta_C$ of the chemically etched Kovar data.

An optical micrograph of the Kovar side of a sample, which was chemically etched and coated with Flux E (OA-H$_2$O), is shown in Fig. 14. Voids that had formed during the reflow process are quite numerous. An analysis comparing the area fraction of voids and the T-peel strengths of five individual samples is shown in Table 6. No dependence was found between the void fraction and strength.

Observations of the fracture surfaces revealed two prevalent paths of crack propagation: 1) at the Kovar-solder interface (Fig. 15A), and 2) near the copper-tin solder interface (Fig. 15B). The topography of the latter case has isolated areas of large deformation originating from failure of the bulk solder film and a facetted surface layer incorporating minor fissures and cracks in the brittle, copper-tin intermetallic that had formed at the copper-solder interface.

### Table 3—Solderability Parameters for Electropolish vs. Chemical Etching Process

<table>
<thead>
<tr>
<th>Flux</th>
<th>Load (gf)</th>
<th>$\theta_C$ (deg)</th>
<th>$\gamma_{LF}$ (dyne/cm)</th>
<th>$\gamma_{SF} - \gamma_{SL}$ (dyne/cm)</th>
<th>$W$ (dyne/s)</th>
<th>$t_w$ (s)</th>
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<tbody>
<tr>
<td>A</td>
<td>11 ± 5</td>
<td>31 ± 5</td>
<td>30 ± 20</td>
<td>100 ± 10</td>
<td>400 ± 20</td>
<td>30 ± 2</td>
</tr>
<tr>
<td>B</td>
<td>16 ± 5</td>
<td>35 ± 5</td>
<td>35 ± 20</td>
<td>105 ± 10</td>
<td>350 ± 20</td>
<td>32 ± 2</td>
</tr>
<tr>
<td>C</td>
<td>18 ± 5</td>
<td>38 ± 5</td>
<td>38 ± 20</td>
<td>110 ± 10</td>
<td>300 ± 20</td>
<td>38 ± 2</td>
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<tr>
<td>D</td>
<td>20 ± 5</td>
<td>40 ± 5</td>
<td>40 ± 20</td>
<td>115 ± 10</td>
<td>270 ± 20</td>
<td>40 ± 2</td>
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<td>E</td>
<td>22 ± 5</td>
<td>42 ± 5</td>
<td>42 ± 20</td>
<td>120 ± 10</td>
<td>240 ± 20</td>
<td>42 ± 2</td>
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### Table 4—Solderability as a Function of Temperature for Flux A (RMA) and Flux D (OA-H$_2$O)

<table>
<thead>
<tr>
<th>Flux</th>
<th>$T$ (°C)</th>
<th>$\gamma_{LF}$ (dyne/cm)</th>
<th>$\gamma_{SF} - \gamma_{SL}$ (dyne/cm)</th>
<th>$W$ (dyne/s)</th>
<th>$t_w$ (s)</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>215</td>
<td>30 ± 20</td>
<td>10 ± 20</td>
<td>400 ± 20</td>
<td>30 ± 2</td>
</tr>
<tr>
<td>B</td>
<td>230</td>
<td>35 ± 10</td>
<td>15 ± 20</td>
<td>350 ± 20</td>
<td>32 ± 2</td>
</tr>
<tr>
<td>C</td>
<td>245</td>
<td>40 ± 15</td>
<td>20 ± 20</td>
<td>300 ± 20</td>
<td>38 ± 2</td>
</tr>
<tr>
<td>D</td>
<td>260</td>
<td>45 ± 20</td>
<td>25 ± 20</td>
<td>250 ± 20</td>
<td>40 ± 2</td>
</tr>
<tr>
<td>E</td>
<td>288</td>
<td>50 ± 20</td>
<td>30 ± 20</td>
<td>200 ± 20</td>
<td>42 ± 2</td>
</tr>
</tbody>
</table>

### Table 5—Contact Angle and T-Peel Strength

<table>
<thead>
<tr>
<th>Flux</th>
<th>$\theta_C$ (deg)</th>
<th>T-Peel Strength (10$^6$ dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>31 ± 2</td>
<td>9.4 ± 0.5</td>
</tr>
<tr>
<td>B</td>
<td>44 ± 2</td>
<td>10.4 ± 0.2</td>
</tr>
<tr>
<td>C</td>
<td>55 ± 3</td>
<td>11.0 ± 0.5</td>
</tr>
<tr>
<td>D</td>
<td>66 ± 4</td>
<td>11.6 ± 0.5</td>
</tr>
<tr>
<td>E</td>
<td>77 ± 5</td>
<td>12.2 ± 0.5</td>
</tr>
</tbody>
</table>

### Table 6—Void Formation and T-Peel Strength

<table>
<thead>
<tr>
<th>Flux/Sample</th>
<th>Area Fraction of Voids</th>
<th>T-Peel Strength (10$^6$ dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A/1-1, F</td>
<td>0.045</td>
<td>5.6</td>
</tr>
<tr>
<td>A/1-1, F</td>
<td>0.034</td>
<td>6.7</td>
</tr>
<tr>
<td>E/A-1</td>
<td>0.103</td>
<td>9.6</td>
</tr>
<tr>
<td>E/A-3</td>
<td>0.074</td>
<td>10.5</td>
</tr>
<tr>
<td>D/G</td>
<td>0.047</td>
<td>9.5</td>
</tr>
</tbody>
</table>
From a visual examination of the T-peel sample surfaces, a mixture of fracture paths was observed comprised of failures at both the Kovar-solder and copper-solder interfaces. When the percent of failure at the Kovar-solder interface was reviewed as a function of the T-peel strength of the specimens, an inverse relationship was observed between the two parameters. The data are listed in Table 7.

Discussion
Parameters Controlling the Contact Angle

The wetting behavior of 60Sn-40Pb solder on Kovar was quantitatively described by the contact angle, $\theta_c$. The smaller the value of $\theta_c$, the better is the wettability or solderability. The flux serves to decrease the value of $\theta_c$ by two processes: 1) by creating and protecting the freshly cleaned and deoxidized surface and 2) by lowering the solder-flux interfacial tension. With regards to the parameters in Young's Equation, the mechanism gives rise to a larger value of $(\gamma_S - \gamma_SL)$ by increasing $\gamma_SL$. It is assumed that the value of $\gamma_SL$ is constant where the solder has wet the substrate, irrespective of the prior condition of the substrate, since the surface contamination is displaced by the advancing liquid alloy. In

Fig. 13 - Representative wetting curves of electropolished, plain Kovar as a function of flux and temperature. A - Flux A, 215°C; B - Flux A, 245°C; C - Flux D, 215°C; D - Flux D, 245°C.

Fig. 14 - Optical micrograph of the T-peel fracture surface of the Kovar leg of the chemically etched, plain Kovar test sample coated with Flux E.
Table 7—T-Peel Strength as a Function of Fracture Morphology

<table>
<thead>
<tr>
<th>Flux</th>
<th>% of Failure at Kovar-Solder Interface (0.5%)</th>
<th>T-Peel Strength (10^6 dynes/cm)</th>
<th>Contact Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>80 ± 5</td>
<td>7 ± 2</td>
<td>61 ± 1</td>
</tr>
<tr>
<td>B</td>
<td>35 ± 5</td>
<td>9.5 ± 0.4</td>
<td>53 ± 7</td>
</tr>
<tr>
<td>C</td>
<td>15 ± 5</td>
<td>10.0 ± 0.7</td>
<td>45 ± 2</td>
</tr>
<tr>
<td>D</td>
<td>10 ± 5</td>
<td>11.0 ± 0.5</td>
<td>29 ± 1</td>
</tr>
<tr>
<td>E</td>
<td>7 ± 5</td>
<td>10.2 ± 0.5</td>
<td>53 ± 7</td>
</tr>
</tbody>
</table>

The dependence of γLF on the substrate surface condition is based upon the by-products generated through the corrosive action of the flux as it cleans the surface. The reaction products, which are carried away by the flux, may favorably segregate to the solder-flux interface, if the result is a decrease in the system's free energy. It has been observed experimentally (Ref. 7, 8) that the interfacial tension between two liquids can be extremely sensitive to such surface active contaminants present in either material. On the other hand, surface inactive solutes, by remaining dissolved in one of the liquids, may so change the bulk properties of the phase so as to also affect the interfacial tension. This hypothesis has some bearing on the results of this study.

The plain Kovar surface had a brighter appearance after the electropolish treatment, compared to that which was chemically etched. Therefore, the chemically etched surface should have more surface contaminants. Examining the data for Flux A (RMA) in Table 3, the value of (γSF - γSL) increased only slightly from the chemical etch to the electropolishing process. This observation suggests that the flux was capable of achieving nearly the same surface conditions after either one of the cleaning treatments. Therefore, the greater quantity of reaction by-products generated from the chemically cleaned samples and dissolved in the flux coating were responsible for the larger γLE values.

A similar relationship between the interfacial tension, γLE, and the substrate surface condition was observed in the data of Mayhew and Wicks (Ref. 2). Although the substrates were copper, the effect of surface condition on γLE is clearly demonstrated. Shown in Table 8 are the values of θC and γLE taken from the references. The value for (γSF - γSL) was calculated by the authors. For these experiments, the solder was 63Sn-37Pb at a temperature of 260°C. The flux was water white rosin-based with either 0.05, 0.50 or 1.00% activator. The surface oxidation of the copper samples increased in the order of A, B, C, and D. For the activator levels of 0.50 and 1.00%, as the degree of surface contamination increased, the value of γLE increased while (γSF - γSL) was constant. This is the same trend that was observed between the chemically etched and the electropolished data for Flux A (RMA) and Flux C (OA-CHOH).

For Flux D (OA-H2O), no significant change was recorded for the values of γLE and (γSF - γSL) between the two cleaning treatments. Table 3 illustrates tests in which the same flux was applied to differently cleaned surfaces. The result was significant changes in γLE, the characteristics of which were very dependent upon the particular flux in use.
processes. Therefore, the solder-flux interfacial tension was not sensitive to by-products contained in the flux layers that arose from these two test series. A comparison of $\gamma_F$ and $(\gamma_F - \gamma_{SL})$ between cleaning procedures for the other two fluxes, Bi-OA-CHOH) and E (OA-H2O), are slightly more ambiguous. In both cases, significant increases in $\gamma_F$ and $(\gamma_F - \gamma_{SL})$ were observed, while $\theta_c$ remained unchanged—Table 3. The increase in $(\gamma_F - \gamma_{SL})$ indicates that the cleaning capabilities of fluxes B and E were sensitive to the different surface conditions left by the two cleaning procedures.

Very little change in $\gamma_F$ and $(\gamma_F - \gamma_{SL})$ was noted for Flux D (OA-H2O) between the two cleaning procedures. However, increasing the chemical etching time prior to using Flux D from 0.5 to 2.0 min lowered the value of $\gamma_F$. It is hypothesized that as the cleaning process became more effective at removing surface contaminants with longer cleaning times, the value of $\gamma_F$ decreased as fewer corrosion products were entrapped in the flux film. This behavior was not observed between the (2.0 min) etched samples and those electropolished, because for Flux D, the difference in degree of surface contamination was probably not sufficient to cause a change between the two values of $\gamma_F$.

In summary, the interfacial tension, $\gamma_F$, had a significant impact on the contact angle data of the plain Kovar samples compiled for the five fluxes. Analysis of the solderability parameters $(\gamma_F - \gamma_{SL})$ and $\gamma_F$ as a function of the flux and substrate cleaning procedure indicates that aside from differences in $\gamma_F$ caused by the individual flux chemistries, the reaction by-products generated by the corrosive action of each flux also altered the value of $\gamma_F$.

**Effect of Surface Platings on Solderability**

The presence of surface plating had a pronounced effect on the interfacial tensions. The gold plating was almost completely dissolved by the solder, so that effectively the liquid alloy was wetting the nickel underlayer and the values of $\gamma_{SL}$ would be comparable between the gold-nickel plated and nickel-plated samples. Therefore, the values of $\gamma_{SL}$ were also similar for the gold-nickel and nickel-plated coupons since the quantity, $(\gamma_F - \gamma_{SL})$, was identical at a given flux. For a given plating layer, a larger disparity existed between the values of $(\gamma_F - \gamma_{SL})$ calculated for Flux D and those of Flux A than for a similar comparison between the same fluxes applied to the plain Kovar surface. This suggests that the plated surfaces were more sensitive to the different fluxes than were the electropolished Kovar surfaces.

The change of $\gamma_F$ when the gold-nickel and nickel plating were added to the Kovar was very sensitive to the flux in use.

The value of $\gamma_F$ caused by Flux A was lower and that from the use of Flux D higher than the respective values for plain Kovar. The lower contact angles for the gold-nickel-plated samples were caused by slightly lower $\gamma_F$ as compared to the nickel-plated samples.

The above analysis has been summarized for each flux in Table 9. With the use of Flux A (RMA), the lower contact angles achieved with either plating was predominantly the result of a lower value of $\gamma_F$. However, when Flux D (OA-H2O) was used, the lower contact angles were largely caused by the higher values of $(\gamma_F - \gamma_{SL})$; the Flux D achieved an improved surface condition on the plating rather than on the bare Kovar.

**Effect of the Flux Dilution**

In Fig. 11, the contact angle as a function of dilution of Flux D (OA-H2O) exhibited a minimum at approximately 50 to 60% concentration. The similar dependence on dilution strength exhibited by $\gamma_F$ was responsible for the overall trend of $\theta_c$. The values $\theta_c$ were not sensitive to $(\gamma_F - \gamma_{SL})$. It is suggested that the dilution dependence of $\gamma_F$ was caused by the simultaneous occurrence of two phenomena: one causing $\gamma_F$ to decrease with increasing flux concentration below 50 to 60% dilution, and the other increasing the value of $\gamma_F$ as the proportion of flux increased above the 60% level. The decrease of $\gamma_F$ as the flux concentration increased between 0 and 60% was caused by a transition from the solder surface tension (510 dyne-cm$^{-1}$) to 430 dyne-cm$^{-1}$). The slight increase of $\gamma_F$ beyond 60% resulted from an increased concentration of reaction by-products created by the greater corrosive action of the dilution.

**Effect of Solder Temperature**

The solder temperature affects the wetting behavior through two factors: first, the equilibrium conditions as determined by $\gamma_F$ and $(\gamma_F - \gamma_{SL})$ and secondly by the kinetics of wetting as described extrinsically by W and $\theta_c$.

For Flux A (RMA), no significant change in either $\gamma_F$ or $(\gamma_F - \gamma_{SL})$ was observed over the temperature range 215° to 260°C (Table 4). The decrease in $\theta_c$ at 288°C was caused by a drop in $\gamma_F$. The accompanying decrease of $(\gamma_F - \gamma_{SL})$ between 260° and 288°C is evidence that the fluxes' chemical activity had diminished slightly. The decrease of $(\gamma_F - \gamma_{SL})$ was not the result of increased oxidation of Kovar surface since the value of $\gamma_F$ would increase with the greater volume of reaction by-products. Rather, the decrease of $(\gamma_F - \gamma_{SL})$ and $\gamma_F$ was due to a temperature-sensitive change in the flux.

For the case of Flux D (OA-H2O), the decrease in $\theta_c$ with increasing temperature was due largely to a general increase in $(\gamma_F - \gamma_{SL})$. Therefore, the increasing temperatures improved the chemical activity of Flux D.

As for the effect of temperature on wetting kinetics of Flux A as measured by $W$ and $\theta_c$, an increase in $W$ and decrease in $\theta_c$ with increasing temperature was observed. Therefore, increasing solder temperature with use of the RMA Flux A increased the speed with which the flux reached a level of chemical activity, which itself was constant in the temperature range of 215° to 260°C as evidenced by the similar values of $(\gamma_F - \gamma_{SL})$ and no significant changes to the solder-flux interfacial tension.

For Flux D, the overall increase in chemical strength with temperature was not accompanied by an increase in the wetting rate. However, the value of $\theta_c$ did noticeably decrease upon raising the temperature and can be explained by the decrease of negative meniscus weight—Fig. 13. Therefore, $\theta_c$ was a more sensitive indicator of the speed of wetting (than $W$) as a function of solder temperature.

A qualitative analysis was made of the effect of the time-dependent temperature profile of the coupon on $W$. Hypothetically, if the temperature gradient along the coupon was the controlling parameter for the rate of meniscus rise, then the meniscus rise should be extremely fast since the coupon temperature at an infinitesimally small distance ahead of the solder front would be nearly the same temperature as that of the solder. The time lag due to heating the Kovar substrate just ahead of the solder was calculated to be negligibly small. Thus, if the temperature controlled the rate of meniscus rise, then the solder should have risen very quickly and shown similar behavior for the different fluxes.

The above hypothetical case was not observed in the present data. First, at simi-
ilar temperatures, the wetting rates (and \( t_w \)) were quite different between A and D fluxes. Secondly, the dependencies of W and \( t_w \) upon temperature were dissimilar between the fluxes. In conclusion, the temperature dependencies of W and \( t_w \) were a consequence of the chemical kinetics of surface conditioning by the individual fluxes and not explicitly the time-temperature profile of the Kovar coupon.

**T-Peel Data Analysis**

From the data in Table 5, the T-peel test results did not precisely follow the trend as recorded for the contact angles. This observation was not entirely unexpected due to the complexity associated with the mechanical behavior of a joint composed of two different substrates. The data summarized in Table 7 shows that the increase in T-peel strength corresponded to an increasing amount of failure taking place at the copper-solder interface. The Kovar-solder bond strength increased to that of the copper-solder interface, a larger percentage of failure took place at the copper-solder layer until the strength of the Kovar-solder interface exceeded that of the copper and nearly all of the failure took place at the latter region. The copper-solder bond strength can be approximated from the failure of the T-peel sample that was fluxed with E (OA-H \(_2\)) since nearly the entire failure took place at the copper-solder interface, that value being 10.2 \( \times 10^6 \) dyne-cm\(^{-1}\). Therefore, although it is not possible to compute the numerical strength of the Kovar-solder joints due to the mixed mode failure, a qualitative assessment of the fracture morphology suggests that the flux does affect the intrinsic mechanical strength of the joint.

**Conclusions**

1) Solderability testing of 60Sn-40Pb solder alloy on Kovar was evaluated as a function of flux, substrate surface preparation and solder temperature.

2) Etching the Kovar surface with an acid solution followed by application of either an RMA flux, A; one of two organic acid, alcohol-based fluxes, B or C; or one of the two water-based, organic acid fluxes, D or E, caused respective contact angles of 61, 53, 45, 29 and 53 deg. All fluxes were diluted one-to-one by volume with isopropyl alcohol.

3) Electropolishing the Kovar surface in a solution of acetic and perchloric acids improved the contact angles of Flux A to 31 deg and that of Flux C to 37 deg. The other fluxes exhibited little or no change.

4) The solder-flux interfacial tension, \( \gamma_{sL} \), had a significant effect on the contact angles measured for the different fluxes and surface cleaning treatments.

5) With the use of Fluxes A (RMA) and D (OA-H\(_2\)), solder temperatures from 215° to 288°C caused a corresponding decline in the contact angle of about 6 deg with Flux D, and an insignificant change for Flux A as determined by a linear least squares analysis. In both cases, the behaviors of \( t_w \) were not monotonic.

6) Microanalysis of the solder film cross-sections on plain Kovar showed no evidence of cracks at the solder-substrate interface or extensive intermetallic formation between the tin of the solder layer and the cobalt, iron or nickel constituents of the Kovar.

7) T-peel strength measurements were conducted on Kovar-OFHC copper joints bonded with 60Sn-40Pb solder in which the Kovar was coated with one of the five fluxes, and the copper, with Flux A. Only a rudimentary correlation was found between the solderability contact angles and the peel strength values for the surface-etched Kovar.

8) A qualitative evaluation of the sample fracture surfaces did reveal that the fluxes affected the Kovar-solder bond strength; irrespective of extrinsic characteristics such as void formation.

**Acknowledgments**

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**References**


**Appendix**

**Cleaning Procedures**

**Procedure for Chemical Etching of Kovar Substrates**

1. Immerses 2 min in 300 mL of agitated etching solution at 80 to 85°C (176° to 185°F). Five coupons cleaned per batch of etchant.

2. Immersed 4 min in agitated hot water. Repeat twice.

3. Immersed 75 s in agitated detergent solution.

4. Repeat Step 2.

5. Immersed 75 s in agitated deionized water. Repeat twice.

6. Immersed 75 s in agitated acetone. Repeat twice.

7. Dry with N\(_2\) gas.

**Procedure for Electropolishing of Kovar Substrates**

1. Samples are electropolished at constant current of 1.5 A for 5 min. Five coupons polished per 250 mL of electrolyte.

2. Rinse the sample in a jet of deionized water and store in agitated deionized water until a batch of five coupons exists.

3. Rinse (the batch) for 5 min in deionized water.

4. Immerse 2 min in detergent solution.

5. Rinse 2 min in agitated hot tap water. Repeat once.

6. Rinse 2 min in agitated deionized water. Repeat once.

7. Rinse 2 min in agitated acetone. Repeat once.

8. Dry with N\(_2\) gas.

**Degreasing Procedure for Plated Samples**

1. Immerse 3 min in agitated trichloroethylene.

2. Immerse 3 min in agitated isopropyl alcohol.

3. Dry with N\(_2\) gas.