Corrosive Effects of Solder Flux on Printed-Circuit Boards

AUBREY J. RAFFALOVICH

Abstract — A number of tactical radio sets have been reported inoperable as a result of lead breakage of transistor and crystal leads. The lead material was a Kovar®-type iron-nickel-cobalt glass sealing alloy (54 percent Fe-29 percent Ni-17 percent Co). The location and type of fractures indicated that these leads failed by stress-corrosion cracking. Such failures result from the combined effects of mechanical stress and a mildly corrosive atmosphere. The only source of specific corrosive ion for this type of failure was chloride ions found in residual flux on printed circuitry.

The corrosive effects of the residual flux was demonstrated by the identification of corrosion products found on the printed wiring. Careful selection of the solder flux, scrupulous cleaning of the printed circuit boards, and conformal coating is recommended for all similar applications.

BACKGROUND

A NUMBER of tactical radio sets were reported inoperable in Vietnam due to breakage of Kovar®-type iron-nickel-cobalt leads (54 percent Fe-29 percent Ni-17 percent Co) of such hermetically sealed components as quartz crystals and transistors (Figs. 3 and 4). The breakage was generally found to be very close to the point of egress from the component side of the printed-circuit board (Fig. 5). Breakage was also found at the sharpest bend of leads (Fig. 10). Also noted was the presence of some general corrosion on each module.

The breakage was initially attributed to stress-corrosion cracking. This destructive mechanism was believed to have occurred because the gold plating of the iron-nickel-cobalt alloy leads was insufficient to withstand the environmental condition encountered in Southeast Asia.

The purpose of the subject investigation was to confirm this early diagnosis and to recommend corrective action.

DEFINITION OF STRESS CORROSION CRACKING

Logan [1] defines stress-corrosion cracking as the "spontaneous failure of a metal resulting from the combined effects of corrosive and stress." Scully [2] calls it a "conjoint phenomenon." It is insidious because it may develop as fine intercrystalline or transcrystalline cracks with little or no evidence of telltale corrosion products. There is very little, if any, elongation of the material.

Such failure of metals usually occur under very mildly corrosive conditions.

The stress may be applied or residual, or a combination of the two. Residual stress is structural stress due to alloying constituents, heat treatment, cold rolling, drawing, welding, press and shrink fits, etc. Applied stress is externally applied in a tensile direction. In transistor and crystal can leads it is caused by assembly techniques. Moisture alone, without a specific corrosive ion, is seldom a cause of failure of stressed parts for any given alloy group. If corrosion is general over the surface of an alloy, stress corrosion is less likely to occur. Stress-corrosion cracking is generally normal to the applied tensile load and the two parts are mirror images.

Gold is cathodic to iron-nickel-cobalt alloys and, where pinholes are present in the plating, a chloride containing atmosphere will result in extensive corrosion at the plating pinhole, particularly as the cathodic area is large in relation to the anodic iron-nickel-cobalt alloy area. With porous gold plating over the entire lead surface, general corrosion will take place, thus obviating stress-corrosion cracking. Where the pores are concentrated at the stressed area, the stress corrosion cracking may be accelerated.

Baker and Mendizoa [3] have demonstrated that the iron-nickel-cobalt alloy used as lead wire in semiconductor devices is susceptible to stress-corrosion cracking. Elkind and Hughes [4] confirmed that this alloy stress cracks rapidly in the presence of both stress and condensed moisture. The stress is that resulting from normal device manufacture and/or conventional circuit installation procedures.

DISCUSSION OF TESTS

Physical Inspection of Modules Returned from the Field

The immediate problem presented was the cause of the breakage of the Fe-Ni-Co leads on transistor and crystal cases. Concomitantly, there was presented a secondary, albeit not unimportant problem of general corrosion of other components and parts on the same printed-circuit boards. Figs. 1 and 2 illustrate the open module, both obverse and reverse sides, containing the printed-circuit boards with the damaged parts. Omitted is the aluminum case.

Five modules were obtained from Vietnam and five modules were obtained from Germany. Three of the five modules from Vietnam had the leads of all of the transistors broken (9 leads, 3 transistors). The three modules also had 3-5 of the 14 crystal can leads broken. No breakage was reported from Germany. These had a scrubbed and buffed appearance.

Table 1 contains a list of criteria to determine the common
<table>
<thead>
<tr>
<th>Module</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Returned from Observations</td>
<td>SEA-1</td>
<td>SEA-2</td>
<td>SEA-3</td>
<td>SEA-4</td>
<td>SEA-5</td>
<td>G-2</td>
<td>G-3</td>
<td>G-4</td>
<td>G-5</td>
<td></td>
</tr>
<tr>
<td>Transistor leads (9)</td>
<td>good</td>
<td>9 broken leads</td>
<td>9 broken leads</td>
<td>good</td>
<td>9 broken leads</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>Flux in holes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>Solder appearance</td>
<td>good</td>
<td>finger corrosion</td>
<td>good</td>
<td>good</td>
<td>corrosion</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>Flux on board</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>Isolate some on posts</td>
<td>some smears</td>
<td></td>
</tr>
<tr>
<td>Solder droplets</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>General appearance</td>
<td>good</td>
<td>poor</td>
<td>poor</td>
<td>fair</td>
<td>poor</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>good</td>
<td></td>
</tr>
</tbody>
</table>

German (G).
Southeast Asia (SEA).

Fig. 1. Component side of board.

Fig. 2. Printed-circuit side of board.

The factor present in all modules with broken Fe-Ni-Co alloy leads. The common factor is extensive flux and dirt on both sides of each board making up the module. None of the ten had a conformal coating. Figs. 3-10 illustrate other conditions observed on the modules.

The cracking of the transistor leads was always observed at the rim of the hole on the obverse side. This is apparently the point of greatest stress resulting from the bend made prior to insertion into the hole. In addition to this stress inherent in the manufacturing processes, there appeared to be an applied stress resulting from the pressure of insulating washers at the base of the transistors. This pressure was attributed to thermally induced expansion. The thermal coefficients of expansion of the lead material and the plastic used for mounting the transistor on the printed-circuit boards differed by a ratio of 1:10.

Upon inspection it was also determined that the holes around the transistor leads were filled with flux but very little residual flux was noted over the rest of the leads. General corrosion was rare on all failed Fe-Ni-Co leads.

**Pull Tests on Transistor Leads**

Attempts made to break the soldered-in-place transistor lead on one of the boards by pulling vertically resulted in necking. Fracturing took a great deal of force and the appearance of the fracture surface was not the same as the stress-cracked break. It was uneven and random in location—that is, the leads did not break at any specific point but anywhere along the entire length of the lead. None of the broken leads returned from Vietnam showed necking or the type of a break resulting from a tensile pull indicating that the physical stress of the lead, without corrosion, did not cause failure.

The next step was to find a corrosive source in the affected modules.

**General Discussion of Corrosive Sources**

Whereas it has been reported by Baker and Mendizza and Elkind and Hughes [3], [4] that Fe-Ni-Co alloys will stress crack in a humid atmosphere alone, the presence of a specific
Fig. 1 Contaminated and corroded board

Fig. 2 Corroded transistor lead

Fig. 5 Mounted 2N2222 transistor

Fig. 6 Corrosion of printed wire interface
corrosion, such as a chloride (even if it is in the order of parts per million), is generally suspected in most realistic applications. It should be noted that the reported stress imparted to the leads in tests cited by Baker and Mendizza and Flanders and Hughes was much more intense than that found in practice.

Materials used in electronic equipment that are susceptible in causing stress cracking include: activated flux residues, polyvinyl chloride (hydrochloric acid is evolved), epoxy board and coatings that are cured with amines (such as diethylamine), RIV silicone conformal and potting compounds (that emit acetic acid fumes), and many other materials that emit ammonia, amines, hydrochloric acid, and other acids. (The presence of moisture is usually a requirement for stress-corrosion cracking.)

Accordingly, it was necessary to determine whether the organic materials used in the construction of the module were contributory towards FeNi-Co alloy lead breakage by emitting corrosive fumes.
TABLE II

Effect on Kovar of Organic Materials Found in Modules

<table>
<thead>
<tr>
<th>Flask</th>
<th>Exposure Medium</th>
<th>Observation After 9 Months Room Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control</td>
<td>No corrosion</td>
</tr>
<tr>
<td>2</td>
<td>Distilled water</td>
<td>Minor scattered rust spots</td>
</tr>
<tr>
<td>3</td>
<td>Ammonium hydroxide</td>
<td>Rusted in one week</td>
</tr>
<tr>
<td>4</td>
<td>10% hydrochloric acid</td>
<td>One lead had 3 rust spots, others no corrosion</td>
</tr>
<tr>
<td>5</td>
<td>Orange-dyed mylar film with tacky silicone resin adhesive</td>
<td>2 leads had 2-3 rust spots each</td>
</tr>
<tr>
<td>6</td>
<td>5 above with distilled water</td>
<td>No corrosion</td>
</tr>
<tr>
<td>7</td>
<td>5 above without adhesive</td>
<td>Scattering of rust spots more pronounced corrosion beneath thread</td>
</tr>
<tr>
<td>8</td>
<td>6 above without adhesive</td>
<td>No corrosion</td>
</tr>
<tr>
<td>9</td>
<td>Epoxy-glass laminate</td>
<td>No corrosion</td>
</tr>
<tr>
<td>10</td>
<td>9 above with distilled water</td>
<td>1-2 rust spots on each lead rust stain beneath thread</td>
</tr>
<tr>
<td>11</td>
<td>Teflon spaghetti wire insulation</td>
<td>No corrosion</td>
</tr>
<tr>
<td>12</td>
<td>11 above with distilled water</td>
<td>Rusted pit beneath each thread</td>
</tr>
<tr>
<td>13</td>
<td>Undyed mylar film with tacky silicone adhesive</td>
<td>No corrosion</td>
</tr>
<tr>
<td>14</td>
<td>13 above with distilled water</td>
<td>1 lead had 3 rust spots, others no corrosion</td>
</tr>
<tr>
<td>15</td>
<td>13 above without adhesive</td>
<td>No corrosion</td>
</tr>
<tr>
<td>16</td>
<td>15 above with distilled water</td>
<td>1-2 minute rust spots on each lead</td>
</tr>
<tr>
<td>17</td>
<td>Epoxy-glass laminate same as 9 but sanded</td>
<td>No corrosion</td>
</tr>
<tr>
<td>18</td>
<td>17 above with distilled water</td>
<td>1 lead had rust pit beneath thread, other no corrosion</td>
</tr>
<tr>
<td>19</td>
<td>Urethane sponge pad</td>
<td>No corrosion</td>
</tr>
<tr>
<td>20</td>
<td>19 above with distilled water</td>
<td>No corrosion</td>
</tr>
<tr>
<td>21</td>
<td>Ro-in core solder 60/40 from stock</td>
<td>No corrosion</td>
</tr>
<tr>
<td>22</td>
<td>21 above with distilled water</td>
<td>No corrosion</td>
</tr>
</tbody>
</table>

Note: Material in flasks 5-12 was obtained from module SEA-1. Material in flasks 13-20 was obtained from module G-1.

A 90° bend was chosen because it represented the severest bend found in the modules. Each flask contained organic material found in the module with and without water added, as listed in Table II.

None of the leads were immersed. They were suspended above the materials for nine months under room conditions. They were then examined both with a microscope (×100) and unaided eye. There were no signs of stress cracking.

Corrosion was observed at flaws in the gold plate. Except for the leads exposed to a 10 percent hydrochloric acid, there was no corrosion of the cut ends of the leads. No other significant corrosion took place.

Therefore, it was concluded that the materials used in module construction did not contribute towards lead breakage. Analysis of these materials had demonstrated that they were free of chloride ions.

However Reich [5] had previously conducted a series of experiments to determine the effect of various flux types on Fe-Ni-Co alloy leads. He concluded that the presence of a corrosive flux and humidity are the prime factors that contribute to failure of these leads.

Since the basic module materials did not seem to promote stress cracking, this study turned toward the effects of solder flux.

Printed Conductor Corrosion

Copper corrosion products were found on the edges of solder-dipped wiring adjacent to the epoxy board. Solder corrosion products were found adjacent to the copper corrosion products and rarely at any distance from the copper salts.
DISCUSSION OF CHEMICAL REACTIONS ASSOCIATED WITH CORROSION

Corrosion of Metals Induced by HCl

The following discussion on the corrosion of copper and tin illustrates the reactive nature of traces of hydrochloric acid (HCl). Since HCl is self-generating in the various reactions considered, a little goes a long way. Of the three metals under consideration (tin, lead, copper), tin is the most reactive to hydrochloric acid, copper and lead being relatively inert.

1) Copper: Cuprous oxide, which forms readily on copper in damp air, is a thin brown oxide that reacts with hydrochloric acid

\[
\text{Cu}_2\text{O} + 2\text{HCl} \rightarrow 2\text{CuCl} + \text{H}_2\text{O}.
\]

Cuprous chloride absorbs oxygen from the air spontaneously. At ordinary temperatures, in moist air, the formation of green atacamite is complete in several hours (see [6]).

\[
4\text{CuCl} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Cu}_2\text{(OH)}_2\text{Cl} + 2\text{HCl}.
\]

Cupric salts accelerate the corrosion rate of copper by hydrochloric acid, which is also obtained as a by-product of the above reaction.

2) Tin: Tin readily reacts with hydrochloric acid to form stannous chloride,

\[
\text{Sn} + 2\text{HCl} \rightarrow \text{SnCl}_2 + \text{H}_2.
\]

Stannous chloride dissolves in water and, with air, forms stannic oxychloride (see [7]).

\[
2\text{SnCl}_2 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{SnCl}_3(\text{OH})_2.
\]

On standing in water, the dissolved salt undergoes internal decomposition to form a basic salt by loss of hydrochloric acid [8]. According to Mellor [9], "Stannous hydroxide is converted into a crystalline stannous oxide by traces of any acid which is capable of forming stannous salt, which, in turn, is capable of being decomposed into free acid and oxide (Mellor specifies boiling water but extensive time and the internal heat of the operating equipment is considered to be equivalent). With hydrochloric acid, a little stannous chloride is formed; this reacts with the excess stannous hydroxide, forming an oxychloride which is decomposed by water into anhydrous stannous oxide less soluble in hydrochloric acid. The regenerated acid commences anew, and the cyclic reactions continue until the dehydration is complete."

\[
\text{Sn(OH)}_2 \rightarrow \text{SnCl}_2 + \text{H}_2\text{O}.
\]

3) Catalytic Effects of Copper: Copper salts are excellent catalysts in the autooxidation of stannous chloride when in the presence of hydrochloric acid; metallic tin dissolves in solutions of stannic chloride to form stannous chloride.

4) Lead: No lead salts were detected on the printed circuitry in the subject test. One reason for this is that metallic lead is inert to aqueous solutions of acids. Although lead oxide is attacked by hydrochloric acid to form lead chloride, the latter is not stable in a moist atmosphere.

Of the two metals used in solder, lead and tin, the latter is more readily attacked by hydrochloric acid. In addition, eutectic solder, being 63 percent tin and 37 percent lead by weight, or 72 percent tin and 28 percent lead atomic percent, contains 2½ times more tin than lead in its formulation.

Galvanic Effects and Their Relationship to Corrosion

Because the solder corrosion products were adjacent to the copper corrosion products on the boards examined in this test, it was postulated that the attack by hydrochloric acid was strongly affected by the solder-copper galvanic couple at the epoxy board interface. The basic reactions are the same as described in the preceding section with the additional drive of the galvanic voltage of 0.4 V.

It has been stated that copper and its alloys rarely corrode galvanically with solder because, copper being cathodic to solder, it is the solder that preferentially corrodes [10]. According to La Que and Copson [11], tin-lead solders are anodic to copper but this is usually of slight practical significance except in contact with solutions of high conductivity such as sea water.

In sea water, tin-lead alloys acquire corrosion products that are cathodic to copper. When they are used as a coating of copper, they can cause severe corrosion at bare spots. La Que and Copson state [11, p.566] that solutions of oxidizing salts such as ferric, cupric, and stannic are corrosive to copper.

They also demonstrate the following [11, Table 20.1].

<table>
<thead>
<tr>
<th></th>
<th>Industrial</th>
<th>Marine</th>
<th>Rural</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>None</td>
<td>Slight</td>
<td>Slight</td>
</tr>
<tr>
<td>Tin</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Slight</td>
</tr>
</tbody>
</table>
When juxtaposed in solder-plated copper, tin is preferentially corroded to either copper or lead; however, once stannic salts are formed there is a galvanic reversal and copper is corroded. Cupric salts accelerate the rate of corrosion of both tin and copper. The relatively surface exposed copper area compared with the solder area further increases the copper corrosion rate [12].

Discussion of Tin-Copper Corrosion

Burns and Bradley [13, p.267] give an explanation for the inertness of lead compared with the reactivity of tin and copper at the copper-solder interface. Molten lead does not wet copper surfaces as does tin. Instead of forming a thin surface film over the immersed part, the lead coalesces more or less into drops or rivulets when the copper alloy part is withdrawn from the lead bath. To form a bond some alloying element common to both (i.e., tin) must be used.

At the copper-tin interface a duplex layer consisting of Cu$_2$Sn and Cu$_4$Sn$_5$ is formed during the hot tinning of copper [13, p.199]. These compounds do not form as a result of electro-tin plating but do form if the plating is subsequently fused or reflowed, the characteristics depending on the temperature reached during reflowing and the time interval between fusion and quenching [13, p.203].

Cu$_4$Sn$_5$ is greater than 0.1 V, more noble than copper and, as formed during the soldering operation, has occasionally led to perforation of the copper from galvanic action [13, p.202].

CONCLUSIONS

The following was seen when reviewing the evidence yielded by this investigation.

1) The broken leads were in an environment suitable for stress-corrosion cracking. There was evidence of inherent and applied mechanical stress and of chemical corrosion on the affected boards.

2) Normal tensile lead fracturing tests did not cause fractures of the type observed in the defective modules.

3) Chemical tests appeared to eliminate the basic module materials as a source of corroden(s).

4) There was no evidence that general chemical corrosion alone could have caused these lead failures.

5) Chloride ions were detected in corrosion by-products on the boards that appeared to be related to the soldering operations.

It was therefore concluded that stress corrosion was, in fact, the cause of iron-nickel-cobalt alloy lead breakage. This was caused by the flux-filled hole in each instance. The flux not only prevented movement of the lead, but also was the source of chloride ions.

Hydrogen embrittlement was considered as a possible cause of failure because of the danger of hydrogen penetration into the metal as a result of cleaning and plating processes. Hydrogen embrittlement is difficult to differentiate from stress-corrosion cracking because hydrogen in the metal often migrates to the point of greatest stress. However, metals having a hardness of less than Rockwell C value of 25 are generally considered to be immune to hydrogen embrittlement and this phenomenon appears limited to medium and high-strength steels. The iron-nickel-cobalt lead alloy under investigation is a great deal softer than a Rockwell C value material.

The lack of corrosion products at or near the break, rules out other corrosion processes.

The presence of chloride containing corrosion products and chloride containing flux on the printed circuitry pointed to chloride containing flux, combined with a damp atmosphere, as a principal factor in the failure of these iron-nickel-cobalt alloy leads. Since it was a stress corrosion fracture, the breakage always occurred at the point of greatest stress, which was the point of egress from the component side of the printed circuit board.

The porous gold plating did not play a major role in stress-corrosion cracking but it may have accelerated it [3]. The common factor found that differentiated the units with broken leads from the same units with undamaged leads is extensive flux and dirt on both sides of each printed-circuit board.

Conformal coatings may have inhibited or prevented the corrosion problem on some modules despite the contamination present. However, these electrically insulating coatings are not effective if residues are not removed prior to coating [17].

RECOMMENDATIONS

It is recommended that solder fluxes be limited to the types specified in MIL-F-14256, "Flux, Soldering, Liquid (Rosin Base)" and QQ-S-571, "Solder, Tin Alloy, Lead-Tin Alloy; and Lead Alloy" flux-cored solder types R and RMA. Flux residues should be removed in accordance with requirement 5, paragraph 7.5 of MIL-Std-454, "Standard General Requirements for Electronic Equipment." It is further recommended that all printed-circuit boards be thoroughly cleaned and conformally coated in accordance with MIL-P-11268 titled "Parts, Materials, and Processes used in Electronic Equipment," paragraph 3.31 and 3.68.1.2.

The importance of thorough cleaning of printed-circuit boards and the removal of flux has been discussed at length by many authors. Coombs [14] enumerates possible sources of corrosion of printed circuitry. He concludes that traces of flux or flux residues indicate poor post-cleaning procedures [14, p.14-29]. This statement is repeated by Manko [15]. The importance of flux-residue removal is stressed [15, p.216]. Elsewhere, Manko stresses that flux residues be removed immediately and even rosin fluxes are difficult to remove after several hours of aging [16].

ACKNOWLEDGMENT

The valuable assistance of the following personnel of the Electronics Technology and Devices Laboratory is acknowledged and greatly appreciated: Dr. J.R. Schappis for identifying chloride ions in flux residues by electron beam microscopy techniques; D.W. Eckart for identifying the copper and tin corrosion products on the printed wiring by X-ray powder diffraction techniques; and W. Wade and Dr. E.E. Wells for
confirming the composition of the organic materials in the A-10 module.

REFERENCES

Aubrey J. Raffalovich was born in New York, N.Y., on December 26, 1916. He received the B.C.E. degree from the Polytechnic Institute of Brooklyn, Brooklyn, N.Y., in 1938.

From 1938 to 1939 he worked for Paragon Paint and Varnish Corporation and from 1939 to 1942 he was Research Chemist for Uvachron Emulsion Corporation working on photoengraving processes. Since 1942 he has been associated with the U.S. Army Electronics Command, Fort Monmouth, N.J., where he is a specialist in corrosion and protective coatings for prevention of deterioration of electronic components and equipment. He has published papers and holds patents in the fields of protective coatings and thin-film dielectrics. Currently, he is concerned with nonelectronic failure analysis of field equipment.

Mr. Raffalovich has received awards from the Federation of Societies for Paint Technology and from its predecessor organization the Federation of Paint and Varnish Production Clubs. In 1965 he received the Roy H. Kienle Award from the New York Society for Paint Technology. He is a member of the American Chemical Society, the Electrochemical Society, the American Electroplaters Society, and the American Society for Testing and Materials.

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