ELECTRICAL wire insulated with Teflon is an important material for a variety of modern engineering applications. In particular, this wire is widely specified for aerospace electronics packaging because of its superior electrical properties and high temperature characteristics of Teflon. Moreover, to use Teflon insulation over conventional stranded copper wire conductors, it is necessary to protect the copper from thermal degradation during the high temperature exposure and assembly operations involved in the application of Teflon. Wire manufacturers found that a thin coating of silver plate would adequately protect the copper and result in better physical properties and longevity. Although nickel or tin coatings also are used, silver-plated copper has been the standard conductor material for Teflon-insulated wire. Unfortunately, the silver-plated stranded copper conductors in Teflon insulated wire can be highly susceptible to corrosion. Among wire manufacturers and users, the term "red plague" has been adopted to describe the characteristic red appearance which appears. Although well known in the industry, this corrosion problem has not been exceptionally great in comparison to the vast quantities of Teflon insulated silver-plated copper wire that have been produced in the last nine or ten years. However, throughout this period, it has remained a persistent, uncontrolled, and unsolved problem. Wire manufacturers have represented an excellent quality control problem. To wire users, particularly those in the missile and aerospace fields, it has frequently posed a serious reliability question. The study reported here was undertaken as part of a study program to determine the cause and mechanism of corrosion in Teflon wire. A method for initiating and sustaining "red plague" corrosion is described which along with other laboratory work enable a clarification of the conditions for the corrosive process to be made; a supplemental study of the galvanic cell properties of the copper-silver couple is included.

Summary

Describes "red plague" corrosion on silver-plated copper electrical wire insulated with Teflon. Although a quantitative problem, this corrosion causes serious reliability problems in aerospace electronics and similar applications. Gives details of program to determine cause and mechanism of corrosion. Describes methods for initiating and sustaining corrosion plus lab tests which clarify conditions necessary for the corrosion process, includes study of the galvanic cell properties of the copper-silver couple.
As can be seen in Figure 3, a high percentage of the strands are affected and, in many, corrosion of the copper has progressed sufficiently to seriously impair the electrical conductivity and mechanical strength. Figure 4 illustrates the copper corrosion under the silver plate. A break in the silver plate such as was invariably found to be associated with each region of underlying copper corrosion can also be seen in Figure 4, as well as indications of corrosion products which have appear- ently "leapt" outward from the break over the surface of the strand.

Analysis of Corrosion Products and Wire Materials

There are two basic types of Teflon material currently used for wire insulation: polytetrafluoroethylene (PTFE) and fluorinated polyethylene (FEP). Also, there are two different grades of copper commonly used in wire conductors: electrolytic tough pitch (ETP) and oxygen-free high conductivity (OFHC). OFHC copper is an alloy of copper with 0.03 to 0.05 percent oxygen. In ETP copper, the oxygen is concentrated at the grain boundaries as cuprous oxide. Wire samples examined and tested in this work were from several manufacturers and included examples of both types of Teflon in combination with both grades of copper. With respect to the analytical results and corrosion experiments, there were no pertinent differences between the several varieties of Teflon insulated silver-plated copper stranded wire.

Samples of the corrosion products from a large number of corroded wire sections were subjected to chemical, spectrographic, and X-ray diffraction analyses. The qualitative results were the same in all cases. The red corrosion products were identified as cuprous oxide (Cu₂O) containing traces of copric oxide (Cu₂O). The black corrosion products were cupric oxide with traces of cuprous oxide. Small amounts of copper sulfates were detected in some samples. The only other substance found were traces of elemental silver and copper. In no case was there any evidence of silver corrosion products.

Various chemical and metallurgical tests were conducted on both corroded and uncorroded wire sections to determine if any anomalies in the conductor or insulation materials existed which
could be related to the corrosion phenomenon. Induced and spectrographic analysis of Teflon insulation material indicated no propagating in the Teflon composite and no contaminants. Metallographic examination of conductors revealed the absence of the grain structure growth such as is usually associated with heat promoted corrosion and which might have been initiated during the high temperature Teflon gifting. There were no visible indications of silver migration in the samples.

Breaks in the silver plating were observed in both corroded and uncorroded wire sections. Corroded areas in the copper core were invariably coincident with a break in the overlying silver. Although frequently breaks were found in the plating without accompanying corrosion, there were no cases of corrosion in regions near the silver plate that was entirely intact.

Quantitative chemical analyses for silver metal, where made on pre-weighted wire sections to determine the average plating thickness on the conductor strands. A minimum of 40 micrograms of silver plating is required by wire specifications. In all wire samples analyzed, sufficient silver was present to provide the minimum plating thickness. More importantly, there was almost the same amount of silver per unit conductor surface area in all cases, and therefore no apparent correlation between average plating thickness and wire conductivity. The amount of water soluble fluoride ion which could be extracted ranged from 34 to 410 micrograms per foot of wire, or the equivalent of only 6 to 10 parts per million. Again, it was significant that the amounts of fluoride ion detected in the various samples did not correlate with the degree of corrosion.

Several preliminary conclusions were reached, based on the analytical results and investigations into the history of the corroded wire specimens. First, it seemed to be in no inherent chemical or metallurgical condition of Teflon wire which could be shown to predetermine a "red plaque" type corrosion. Second, the red corrosion, although not as severe, factor consistently associated with corroded regions of the wire conductors was a mechanical discontinuity or break in the silver coating. Third, several spots in which corrosion was later observed were found to have been previously exposed to severe mechanical forcing storage and handling. This last factor is complicated by the fact that...
Adaptation of Corrosion Test for Wire Substrates

Wire manufacturers and users need a rapid method for routine inspection of Teflon wire for susceptibility to "red plague" corrosion. The vapor diffusion corrosion test offers one approach to such a method, particularly if conditions are modified to accommodate established processes so that the test period can be reduced and if the corrosion products are quantitatively analyzed for copper to provide a numerical indication of the corrosion. A considerable increase in the corrosion rate can be obtained by raising the temperature and introducing nitrogen under slight pressure to the flask as described above. As a standard corrosion susceptibility test, a zero wt. % of Cu (.001 C), and an oxygen atmosphere, was found to exceed the actual amount of corrosion during the test.

Figure 5—Appearance of wire corrosion resulting from exposure to Teflon and silver-plated copper wire exposed to 100% humidity at 100°F for 24 hours.

In order to determine the factors essential to test the corrosive attack, several corrosion tests were performed, using the apparatus shown in Figure 6. The data indicate that the most effective protection against corrosion is provided by the use of silver-plated copper wire. This method is simple and inexpensive, and it can be readily adapted to large-scale production.
pressure of 1 to 5 psig were used. The temperature was maintained by placing the fluids in a water bath, and stirring was carried out as a rate to balance the flow out through the wire sample being tested. This combination of elevated temperature and forced flow of moist oxygen through the wire accelerated the process sufficiently to readily differentiate between the corro-

sivity of various wire specimens within the 24-hour exposure. The upgu-
vation for the corrosion susceptibility test is discussed in Figure 6.

A copper wire specimen was exposed to the standard corrosion susceptibility test, the insulation was removed and the corrosion products extracted from the conductor by treatment with a known volume of 6 normal HCl (hydrochloric acid). An aliquot of the HCl solution then was prepared for colorimetric analysis of the copper content as the ammonia complex.

Samples of wire from the same sec-

tion or roll of wire as specimens used for the corrosion susceptibility test were monitored under magnification for silver plating damage and then anal-

ized for copper compounds to estab-

lish a control level. Again, a correlation

between the amount of damage to the silver plating and wire corrosivity is indicated.

### Copper-Silver Galvanic Cell Experiments

To further clarify in chemical terms the wire corrosion phenomenon observed to occur naturally and in the vortex diffusion tests, a series of experiments was conducted with the copper-
silver galvanic cell. The galvanic be-

havior of the copper-silver couple was studied by conventional electrochemical cell techniques. The individual electrode solution potential relative to a satu-

rated calomel reference electrode, as well as the open circuit cell potentials, were measured in each electrolyte to provide an indication of the cell reaction mechanisms. The galvanic current in the cells was determined as a function of time with the ease retention ammeter circuits. A diagram of the circu-

it arrangement used is shown in Figure 7.

**TABLE 1—Typical Solution and Galvanic Cell Potentials of Copper and Silver in Chloride and Fluoride Electrolytes**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Copper, Cu+</th>
<th>Silver, Ag+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>0.55</td>
<td>0.80</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.45</td>
<td>0.75</td>
</tr>
</tbody>
</table>

### Typical Values for the solution poten-

Figure 7—Diagram of copper-silver cell with saturated calomel electrode (SCE) for silver as the anode and zinc-zinc sulfate electrode for gal-

vonic current measurements.

Typical values for the solution poten-


tiation of copper and silver electrodes are given in Table 1. The potential of the copper-silver couple in fluoride electrolyte was exceptional, that the potential was very unstable. The initial potential was 0.85 volt, but it dropped to 0.41 volt. Similarly, the "open copper" cell potential of the copper-silver couple in fluoride solution was found to be 0.85 volt, but it immediately dropped to less than 0.2 volt. Apparently, the silver electrode in fluoride ion set up a strong potential, possibly a passivating process. Although the solution potential of copper in a mer-

namic chloride was fluoride solution, the reactivity of the silver electrode caused the galvanic potential to be greater in fluoride solution. The measured silver solution poten-


tial was about 0.56 volt positive than the SCE in molar KCl but was 0.56 vol-


tage for the KCl solution, it was found that the two electrolytes are strikingly


different in nature. The galvanic corrosive current changes little even when a slight drop in the initial value, the current actually increases in the electrolyte conductivity, and if the cell control is not properly maintained, the current may increase to a larger extent. It is the electrolyte fluoride, how-


ever, the initial current, although sub-


ductive of the lower, drops rapidly to low levels. The steady state current of the copper-silver couple was about 30 times less in the fluoride solution, even though initial currents were about three times greater than in the chloride solution.

To determine the effect of a con-


tinuous oxygen supply, air was bubbled through the electrolyte. Similar cells were tested with both higher and lower than that of air, so that the effects of the agitation alone caused by the rising gas bubbles would be known. In KCl electrolyte, neither air nor hydrogen had much effect on the copper-silver galvanic current, while the smallest increase in the current when the gas
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Figure 8—Change of copper-silver galvanic current with time in potassium chloride and potassium ferrocyanide electrolytes.

However, in Teflon wire there is an additional factor since in the wire-exposed copper surface is equilibrated with a flux of chlorine during galvanic plating with silver. The cell reaction then involves the anodic oxidation of copper and concomitant reduction of silver on an adherent silver surface. To complete the circuit for the galvanic reaction the current in the wire conductors facilitates the metallic path through the copper and silver, and the electrolytic path through a film of water or another corrosive electrolyte, depending on whether oxygen or carbon dioxide is present in the environment.

In the presence of anodic attack, water and atmospheric oxygen, the galvanic process in silver plated copper:

\[ Cu + 2\text{Cl}^- \rightarrow CuCl_2 + 2e^- \]
\[ \text{O}_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]

which is analogous to the well known galvanic cell:
\[ \text{Cu} + 2\text{Cl}^- \rightarrow \text{CuCl}_2 + 2e^- \]

However, the galvanic reaction apparently does not cause the copper surface to be attacked by the copper ferricyanide solution which is made more anodic by the addition of ferricyanide to the solution. The anodic effects of copper ferricyanide solutions, such as silver, have been reported. In chloride solutions, such silver does not form from the insoluble CuCl but can be deposited from the soluble CuCl₂ by secondary oxidation or by cathodic reduction directly.

Mechanism of "Red Plague"

Wire Corrosion

The experimental results show that wire corrosion will occur simply by exposure to moisture and air. Tendence of moisture contamination does exist in Teflon insulated wire, but the "red plague" corrosion product is anodic relative to copper. Therefore, the corrosion product probably develops at a point on the insulation which is exposed to air and is not the result of a complete cell action between copper and oxygen present in the wire conductors. When exposed to water and oxygen, the galvanic circuit is complete, and the corrosion process occurs.
wire would proceed by the following mechanism:

Anodic reaction: \( 4CO + 4H_2O \rightarrow 4CO_2 + 4H_2 + 4e^- \), \( E = 0 \) volt

Cathodic reaction: \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \), \( E = -1.23 \) volt

Net cell reaction: \( 2CO + O_2 \rightarrow 2CO_2 \), \( E = -0.40 \) volt

By an analogous mechanism, potential for the reaction could arise while corrosion products 0.14 volt. In the rare cases where the oxide of iron products counteracted, the wire probably retained more substance treatment or the environmental conditions probably were not favorable.

It is significant that the mechanism water must be present in the environment. In principle, a given anode wire would corrode even if corrosion is not present. However, corrosion must be continuous to explain the corrosion to progress.

Conclusions

1. The "red plague" usually referred to in silver plated copper stranded wire is due to the formation of copper corrosion products which are red cuprous oxide. Result of etched copper oxide for the copper conductor core at a break in the silver plating.

2. Corrosion can occur whenever copper conductor is exposed at both silver plating and moisture or atmospheric air (oxygen) are present.

3. The rate of this type wire corrosion is dependent on the availability of oxygen to the corrosion sites in the wire.

A combination of microscopic examination of wire samples for breaks in the silver plating and varying dilution corrosion test are used to inspect wire for susceptibility to corrosion.

4. Increasing the thickness of the silver plating on the copper conductor and added precautions to minimize the possibility of damage to the copper during stripping and handling operations would probably reduce the incidence of corrosion considerably.

5. Substitution of nickel plate under silver plating for silver plating on copper conductor would eliminate red plague corrosion. These coatings, being stable to copper oxidation process, would effectively reduce it and protect the copper core from attack.

References