

Corrosion of Silver-Plated Copper Conductors

Abstract Silver-plated conductors, insulated, with fluorocarbon plastics or aromatic polyimide resin and used in aerospace applications, in both Europe and the United States, have been examined for evidence of red-plague corrosion. Extensive metallurgical investigations have shown that, in the worst cases, 3% of the strands making up the braid cross-section can have some degree of corrosion. Metallography revealed that it had initiated at isolated defects in the silver-plating.

A test method has been developed suitable for the acceptance testing of fabricated wires and cables. Its use has shown that the extent of corrosion is only marginally affected by the type of insulation, strand manufacturer, and wire and cable processors. Plating type and thickness and also the position of the strands in the cable do influence their corrosion behaviour.

The mechanisms of red-plague corrosion and the influence of such parameters as halides and moisture are discussed and recommendations made for its preclusion.

Résumé Des conducteurs à revêtement argent, isolés au plastique fluorocarboné ou à la résine polyimide et destinés à l'usage spatial, aussi bien en Europe qu'aux Etats-Unis, ont été examinés pour y déceler les traces éventuelles de corrosion due à la 'peste rouge'. Des études métallurgiques poussées ont montré que, dans les cas les plus défavorables 3% des fils sur l'épaisseur de la tresse peuvent présenter certain degré de corrosion. L'étude métallographique a révélé que cette érosion prend son origine dans des défauts localisés dans le revêtement argent.

On a mis au point une méthode d'essai qui convient aux essais de recette des fils et câbles. Son utilisation a montré que le degré de corrosion n'est affecté que de façon marginale par le type d'isolation, par la provenance des fils et les conditions d'élaboration des fils et câbles. Le type de revêtement son épaisseur ainsi que la position des fils à l'intérieur du câble influencent également la tenue à la corrosion.

On étudie les mécanismes de cette corrosion ainsi que les facteurs tels que la présence des halogènes et l'humidité, et on présente des recommandations en vue d'éviter une telle corrosion.

Introduction

Silver-plated conductors are generally specified when wires and cables must have a good resistance to high temperature. They are invariably insulated with fluorocarbon plastics or aromatic polyimide resin, which have high working temperatures and low out-gassing properties under vacuum. These wire and cable materials are those most commonly selected for use in ESA's satellite and manned spacecraft projects. Silver-plated copper wire is also used extensively for military and aerospace applications in both Europe and the United States.

The purpose of this paper is to detail the findings of the metallurgical examinations performed by ESA on cables discovered to have degraded by red plague corrosion. In addition, an extensive laboratory test programme was undertaken in an attempt to gain a more comprehensive understanding of the red plague phenomenon. The aims of this programme will be discussed, as will the results achieved to date. A test method based on the laboratory procedures of Anthony & Brown¹ has been developed into a draft ESA specification, which is thought suitable for the acceptance-testing of fabricated wires and cables.

Papers published in the literature¹⁻⁶ on red plague are limited to the 1965 – 70 period and no more recent articles have appeared. This paper will initially reiterate the current theories related to the mechanism of red-plague corrosion and, as a historical record, will include an account of the reasons for the selection of silver plated conductors for ESA projects.

Previous studies of red-plague corrosion

Two potential corrosion problems were recognised to be associated with the use of silver-plated copper conductors in the 1960s. Because of their characteristic corrosion products, they are referred to throughout the electronics industry as 'red-plague' and 'green plague'. Red plague is the cuprous-oxide (possibly with some black cupric oxide) corrosion product that forms when a galvanic cell is formed between copper and silver. Green plague is the reaction product of some resin-based solder fluxes with copper oxide; it has been found on tin- and silver-plated conductors and is considered to be an undesirable cosmetic defect.

A number of reports¹⁻⁶ were written in the late sixties which established that red plague originates at breaks in the silver plating of copper-wire strands in the presence of moisture and oxygen. Although some authors considered the problem to be persistent, uncontrolled and unsolved, others presented solutions thought likely to avoid the problem. A NEMA investigation reported⁶ that out of a total US production of 18 to 20 x 10⁹ ft of silver-plated copper wire, only 10⁵ ft (i.e. 0.003%) had a significant amount of red plague and that no malfunctions could be attributed to this phenomenon.

Several investigative activities were undertaken by ESA in the mid-seventies. These included laboratory evaluations, a European red-plague survey, and eventually the auditing of wire manufacturers' premises. It was concluded that silver-plated copper conductors would be suitable for general spacecraft usage, but essential that the platings be defect-free and of uniform thickness (at least 2mm, and preferably 4mm). It was considered that red plague could be avoided if the wire manufacturer and the user companies implemented certain mandatory controls. Also, extreme gauge sizes of stranded copper, such as large gauge AWG '0' and '4', should be nickel-plated copper, and very thin gauge AWG '26' and smaller must use high-strength copper alloy strands with a silver-plated finish. ESA and its contractors have experienced no practical problems during wire interconnection (e.g. soldering, crimping and wire wrapping), hardware integration or service operation with silver-plated wire cables and harnesses. The results of studies¹⁻⁵ performed in the 1960s can be summarised as follows:

- (i) Imperfections ranging from porosity to deep scrapes penetrate the silver plating and reveal the copper core of a wire strand. Such damage may result from the use of defective wire-drawing dies, wear action between strands during stranding and braiding operations or when conductor strands are wound and re-wound from reels to bobbins.

- (ii) Moisture may penetrate beneath the insulation of wires and cables either during the wire fabrication process, during insulation testing or from the humidity in air.
- (iii) The presence of moisture in the region of exposed copper can produce an electrolytic cell, the copper tending to corrode and protect its more noble silver plating. The following reactions were proposed:

At the anode (i.e. exposed copper):
 $4\text{Cu} + 4\text{OH}^- = 2\text{Cu}_2\text{O} + 2\text{H}_2\text{O} + 4\text{e}^-$

At the cathode (i.e. silver plating):
 $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$

The sum reaction is:
 $4\text{Cu} + \text{O}_2 + 4\text{H}^+ + 4\text{OH}^- = 2\text{Cu}_2\text{O} + 4\text{H}_2\text{O}$

Note that the water is not consumed and in the presence of oxygen the galvanic copper corrosion can proceed indefinitely.

- (iv) Copper hydroxides are soluble in water and will contaminate the water that surrounds the stranded wires. As the water dries out, the cuprous-oxide crystals, which have a characteristic red appearance, precipitate out onto the silver plating.
- (v) Excessive corrosion can impair the wire's fatigue life and electrical conductivity.

There is no wire conductor material that can be recommended as the panacea to all potential corrosion, processing and application problems. The suitability of various metallic finishes on copper wires for spacecraft applications was studied by ESA in 1975. The choice was finally limited to tin, silver and nickel. However, due to its low melting point, tin could not be considered for the insulation materials that require high-temperature processing, such as PTFE, FEP, Teflon, Tefzel and Kapton. A review of the literature, discussions with cable specialists and the results of ESA metallurgical test programmes indicated many advantages and disadvantages when choosing silver or nickel finishes.

Historical basis for selecting silver-plated copper conductors

Silver finishes (more than 2mm thick)

Advantages

- a. Exceptional electrical conductivity (essential for certain RF applications), so that smaller conductors may be employed than if nickel plated (i.e. possible weight saving).
- b. Good resistance to high temperature (200°C).
- c. Excellent solderability whether new or after many years' exposure to uncontrolled environments.
- d. Excellent crimpability and suitable for wire wrapping without cracking.
- e. Experience with this wire finish is very good in Europe and the USA (confirmed by spacecraft contractors).
- f. Least losses from skin effects for RF transmissions.

Disadvantages

- a. Poor plating and ingress of water into the wires causes a potential red-plague hazard.
- b. The silver surface may react with substances such as glycol to produce a potential flammability hazard (recent studies have also shown this reaction to occur with nickel and tin conductors).
- c. Slightly higher cost than other coatings.
- d. The larger gauge wires (AWG '0' and '4') cannot be used with this finish as cold welding at points of contact between the wire strands may increase wire rigidity.

Nickel finishes

Advantages

- a. No known potential conductor corrosion risks.
- b. Very high temperature rating (260°C).
- c. Minimal storage controls needed.
- d. Good flexibility after long-term aging at 200°C.

Disadvantages

- a. Impossible to solder with the non-activated fluxes prescribed by ESA⁹. With activated fluxes, it has a variable solderability, dependent on the type of nickel plating and thickness of nickel oxide. Active fluxes are undesirable for soldering hook-up wires as they are drawn under the insulation by capillary action of the strands and can cause corrosion, outgassing and corona problems under vacuum.
- b. Crimpability is fairly good, but more frequent adjustments have to be made to the crimping tool than with other finishes. Contact resistance is affected by the cleanliness of the surface. Ohmic resistance may be erratic for nickel platings (silver-plated copper connections exhibit negligible ohmic variations between similar joints).
- c. Nickel-plated conductors exhibit 7% to 10% more DC resistance with substantially greater power (I^2R) loss.
- d. Nickel has an unsuitable magnetic moment for certain spacecraft experiments.

Reliability

In assessing the reliability of a spacecraft system it is necessary to take into account individual materials, processes and their failure modes under various environmental conditions. In reviewing the above advantages and disadvantages of silver and nickel platings much emphasis was attributed to the red-plague question. From a total of nineteen replies to the ESA survey in 1975 of European aerospace users of silver-plated wires, only one company had experienced a problem (no details given), six companies had 'minor problems', but all before 1965 and none since. Eleven companies had never encountered problems, including one using 400 km of silver-plated cable per year.

These investigations showed that no functional failure had been reported under operational conditions. Consequently, the selection of wire and cable materials would have to be based on controlled processing and well-defined application considerations. A similar survey performed by NEMA⁶ supported the ESA findings.

Processing precautions

To minimise the occurrence of red plague, ESA has instigated a number of requirements via specification SLP/2110:

- a. Prior to silver plating, conductors shall be cleaned with a reverse current in an alkaline bath.
- b. To avoid scratches, all drawing and stranding dies shall be exchanged regularly and whenever necessary.
- c. Drawing, stranding and braiding of silver-plated copper wire and shields shall not be performed with the same dies and tools used for processing tin, nickel, or other plated conductors.
- d. No lubricants shall be used during stranding or braiding.
- e. Water quenching shall not be used in the production process.
- f. Hygroscopic cleaning agents shall not be applied in production or during testing (no water-tank testing).
- g. Strands, wires and cables shall be sealed such that the humidity environment for storage and shipment is less than 50% relative humidity.
- h. All open wire ends shall be sealed against water ingress.
- i. Silver-plating thickness of at least 2 mm (80 minch) is required for all strand sizes.
- j. Silver plating shall be uniform and concentric around the copper strand so

- that no area is covered with less than $1.5\mu\text{m}$ as determined by micro-sectioning.
- k. Silver plating shall be free from porosity.

In the latter half of 1983, ESA experienced the first case of red plague identified on a short length of 125Ω RF cable withdrawn from a contractor's store. On stripping the outer insulation, severe corrosion was noted to be present in small irregular patches along the newly exposed braid. To assess the origin and extent of this problem, and to define remedial actions, extensive efforts were made to locate and inspect all silver-plated copper wires and cables purchased and stored by ESA contractors from the same cable manufacturer. Finally, new wires and the remainders of wires and cables on reels from various silver-plated wire/cable suppliers were inspected by project contractors.

The following is a summary of the metallurgical examinations performed on the three cables noted to have suffered from red-plague corrosion. Extensive stripping operations have only revealed corrosion, in irregular patches, along the newly exposed lengths of braided shield. Insulation stripping has not revealed any corrosion damage to the inner wire conductors. The most severe attack was seen on the 125Ω RF cable, manufactured in 1978 (Inner conductors are $2\mu\text{m}$ silver-plated copper strands with insulation constructed of helically wound and sintered PTFE tape: the braiding is closely woven single copper braid of AWG '36' having a silver-plating of 2 the outer jacket is extruded FEP, black in colour). Figures 1 - 5 relate to the most severely attacked cable.

Experimental procedure

Visual inspection

The conductors and braided shields of the submitted cables were inspected with a stereo microscope under $\times 20$ magnification, the various insulations being removed with a scalpel blade before inspection. 6% of the 125Ω cable produced in 1978 has been visually inspected by ESA, cables users and cable suppliers.

SEM inspection

Corroded strands of braiding were cut from the cable and examined by scanning electron microscopy and X-ray spectrometry (EDAX).

Auger Analysis

The surface of the silver-plated areas was sputter-removed with an argon beam and the sub-surfaces reanalysed to assess the penetration of any surface contamination. Auger analysis was also applied to the ends of corroded and fractured strands.

Metallography

The cables and individual strands were mounted into a cold-setting plastic and micro-sectioned. The mounts were ground and polished to a $0.5\mu\text{m}$ diamond finish and examined both as-polished and etched. Polarised light could distinguish red cuprous oxide (Cu_2O) from black cupric oxide (CuO).

Summary of findings

No cracks or pinholes were observed in the outer jacket insulation materials.

After removal of the outer jackets, many local areas of discolouration could be seen on the silver strands; they had a red, black and green-blue appearance. Several individual strands were noted to have shattered in a brittle manner (Figs. 1 & 2).

Visual inspection of the 125Ω , 1978 cable identified the corrosion areas to have various sizes and an irregular distribution over the inspected cable lengths (no in depth inspections were made of the other cables as they were not integrated into flight hardware).

Examination of corroded cables withdrawn from storage

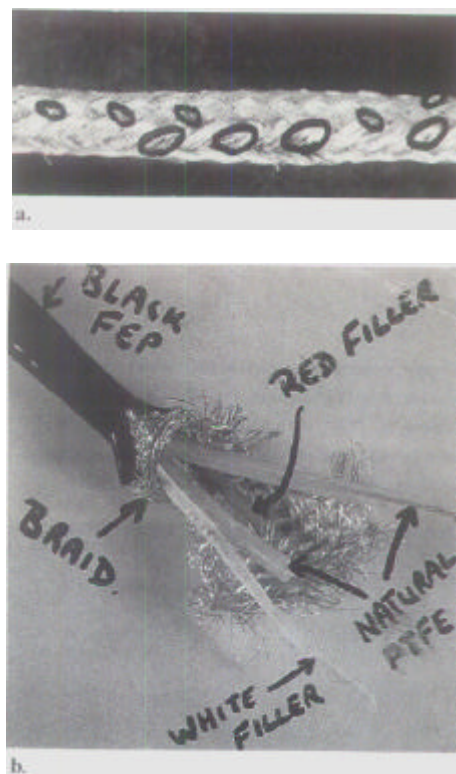


Figure 1. Appearance of the most severely corroded braid after approximately 5 years of storage. Despite the presence of many corrosion sites (circled in a), the braid is still mechanically intact and can be spread out (as in b)

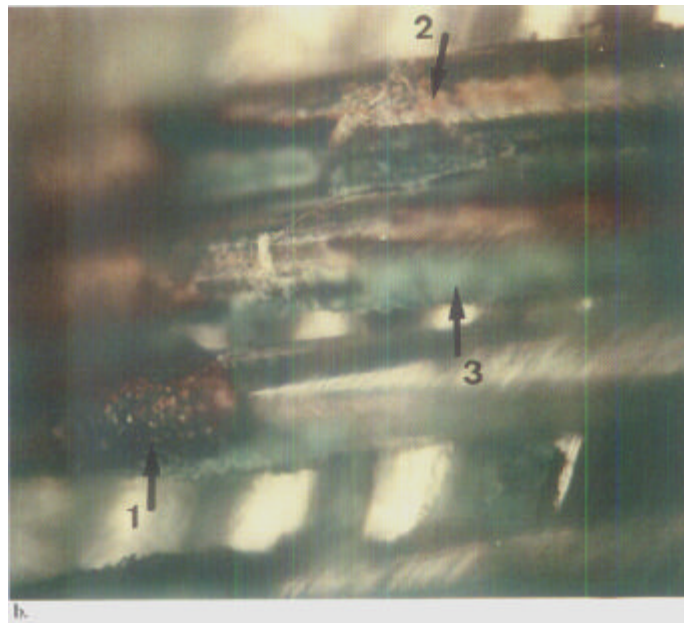


Figure 2. Colour photomicrographs of typical 'red-plague' corrosion areas on braiding, as circled in Figure 1.

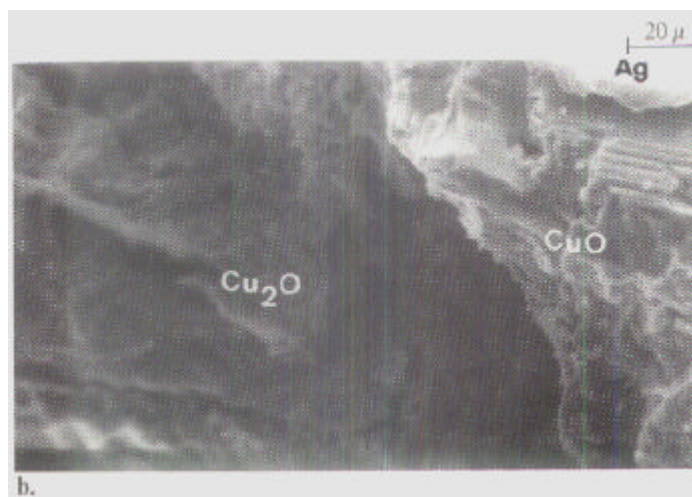
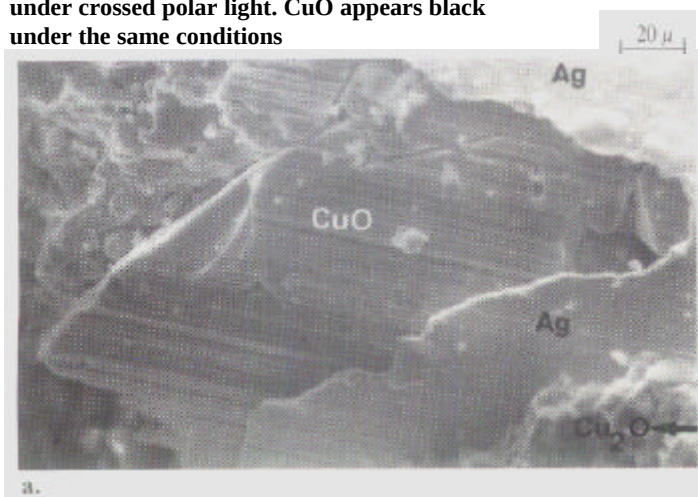
- a. Red and green corrosion products associated with two strands that have completely broken; the brittle fracture surfaces are arrowed (x 100);
- b. Corrosion products are black (1), red (2) and green-blue (3)

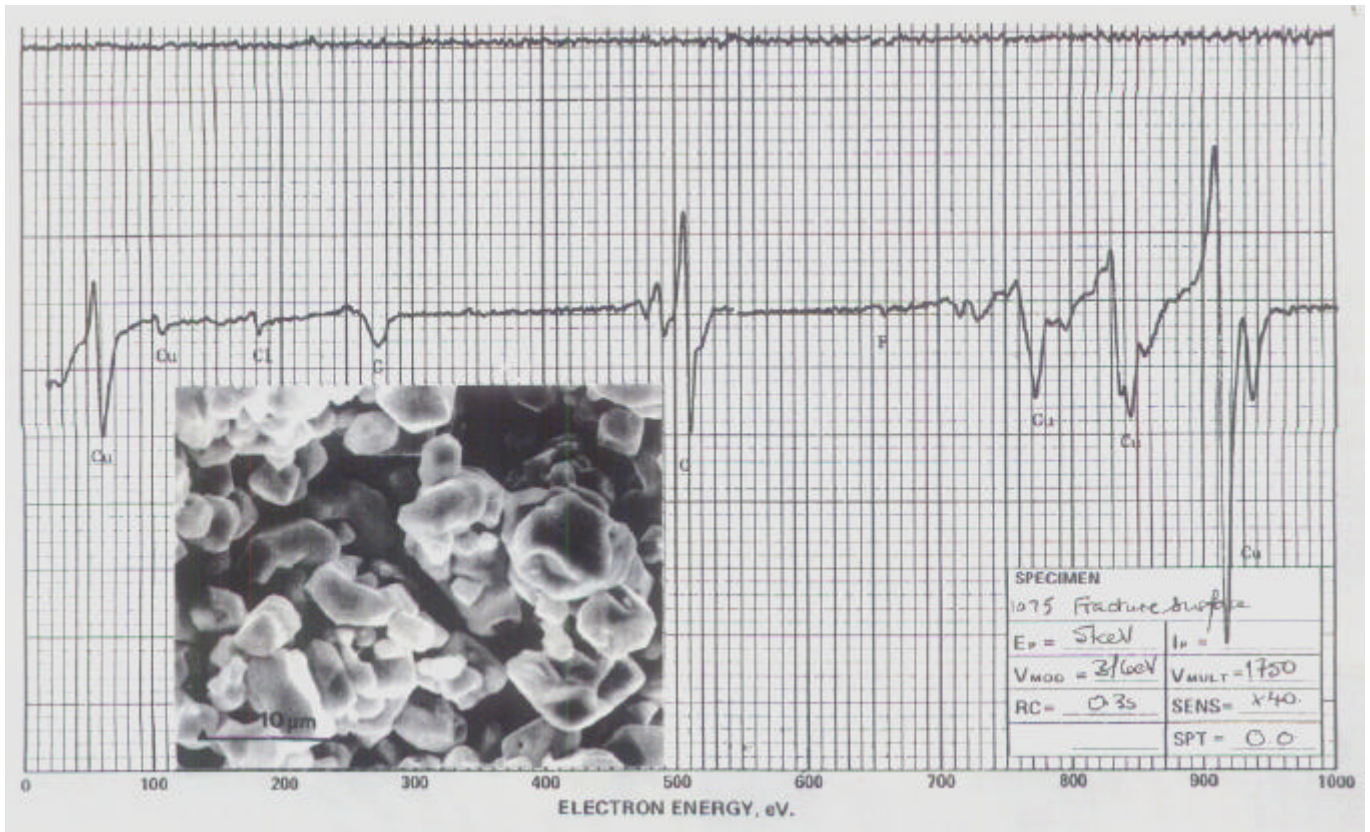
Examination of the corroded strands in the SEM showed them to consist entirely of brittle oxidised copper crystals. Adjacent strands supported crystals of cuprous oxide which were adherent to the silver platings (Fig. 3). Only the presence of copper, silver and a trace of chlorine were detected by EDAX analysis of the strand surfaces.

Auger examination revealed that both the silver surfaces, and the copper-oxide films were contaminated by chlorine and fluorine to a maximum of 5 at%. Depth profiles revealed fluorine in the silver plating to a depth of 40 Å. Further Auger analyses also detected the presence of chlorine and fluorine at the central area of the strand fracture surface. This area was composed entirely of copper-oxide crystals (Fig.4). Both chlorine and fluorine, when present as free ions, would tend to be an accelerating factor in any galvanic corrosion mechanism.

The micro-sections of the corroded 125Ω cable are described in Figures 5-9. Only a few (approximately 3%) of the 143 strands that make up the braid have corroded. The loose-fitting outer jacket has at some stage retained a liquid that promoted galvanic corrosion at minute locations of damaged silver. The average silver-plating thickness of these strands is 2 – 3µm. Copper oxides are present on the outside surfaces of silver strands at locations far from the corrosion sites. This is important as it gives the impression, from visual inspections, that the amount of corrosion and red plague is more extensive than initially apparent and illustrates that the braid must have been almost totally immersed in a liquid to enable the transfer of copper ions to these locations. On drying out, the liquid has precipitated at least three copper compounds: blue cupric hydroxide ($\text{Cu}(\text{OH})_2$), red-coloured cuprous-oxide crystals (Cu_2O) and black cupric-oxide layers (CuO), onto the silver surfaces. The red colouration on the braid is likened to a process of bleeding out of copper ions from occasionally corroding fissures. On drying, capillary forces tend to concentrate oxide precipitation at the braid cross-hatched turns.

Figure 3. Scanning electron photomicrographs of fractured ends of strands from braid shown in Figure 2a. The Cu_2O phases are characteristically seen as ruby-red crystals under crossed polar light. CuO appears black under the same conditions





Extensive insulation stripping, visual inspections and micro-sections have never revealed the oxidation or corrosion of any internal conductors from spacecraft wires and cables. These internal conductors, as seen in Figures 6 and 7, are tightly held within their insulation Jackets.

It is noticeable that the outer jackets are loose-fitting and particularly suitable for the ingress of moisture from unsealed cable ends. The volume of air that is contained within the 125 Ω cable has been derived from the transverse cross-section shown in Figure 7a.

The cross-sectional areas of the cable constituents are:

a. Complete cable	25.5090 mm ²
b. Each filler	1.4878
c. Each inner wire	4.1975
d. Outer insulation	7.3142
e. Individual braid	0.0182

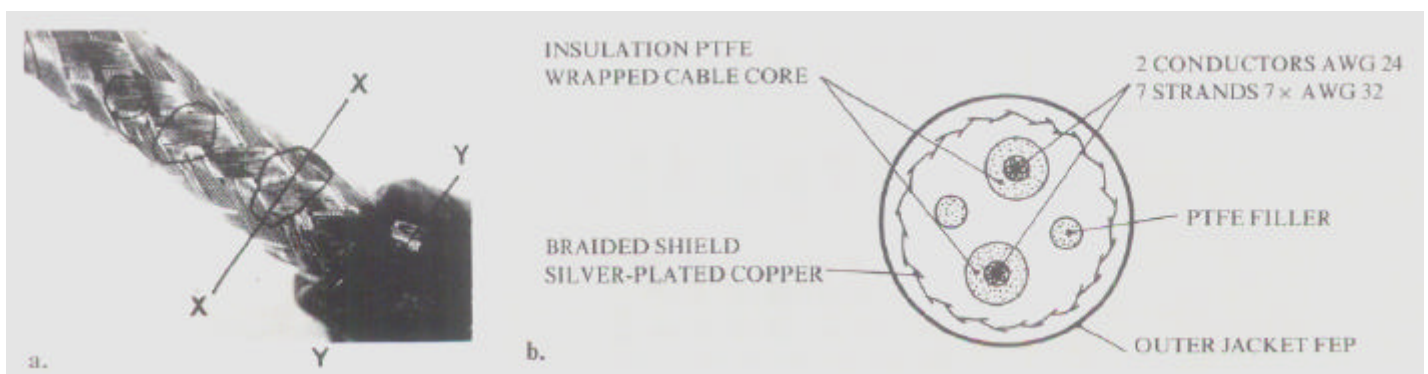
The 'area of voids' under the outer insulation was calculated by subtraction of each cable constituent from the total cable cross-sectional area, i.e.

$$\text{Area of voids} = a - 2b - 2c - d - 144e = 4.2034 \text{ mm}^2$$

In other words the amount of air retained beneath the Outer cable insulation accounts for 16.48% by volume of cable, or, each 1m of cable contains approximately 4 cm³ of air.

Figure 4. Secondary electron image of the copper-oxide crystals seen at the centre of a corroded and fractured strand. The SEM image is superimposed on the Auger analysis of this area (showing traces of chlorine and fluorine associated with copper oxides)

Figure 5. Detailed metallographic examination of the red-plagued cables. The most severely corroded cable (shown in a) was potted and micro-sections made through the severely corroded braid in the X-X plane. A second section was made in the Y-Y plane which is still covered in black FEP
a. Extensive red plague on braid;
b. General construction of cable examined



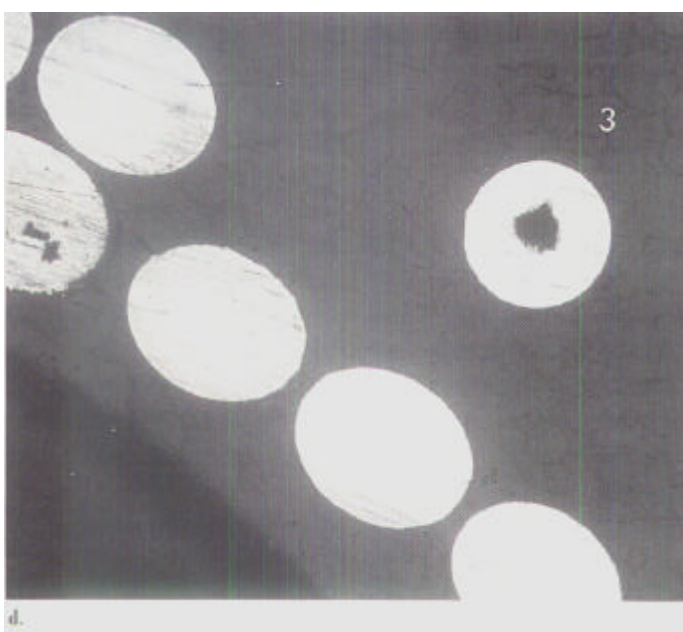
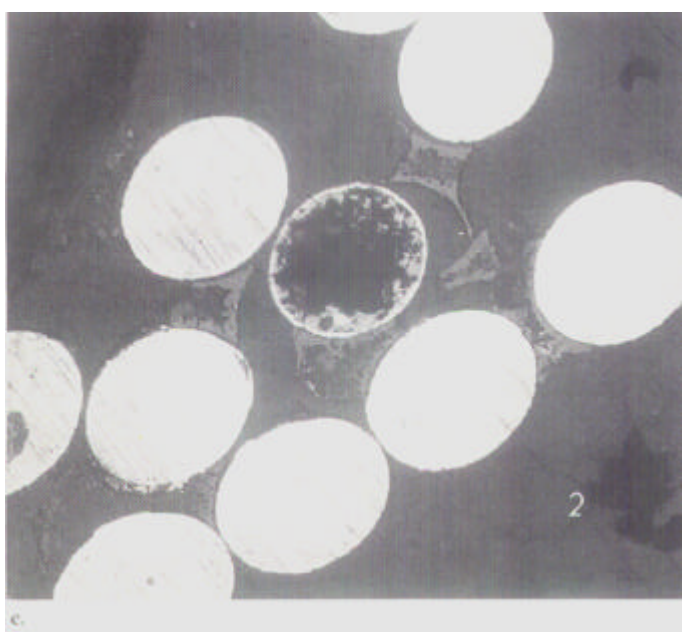
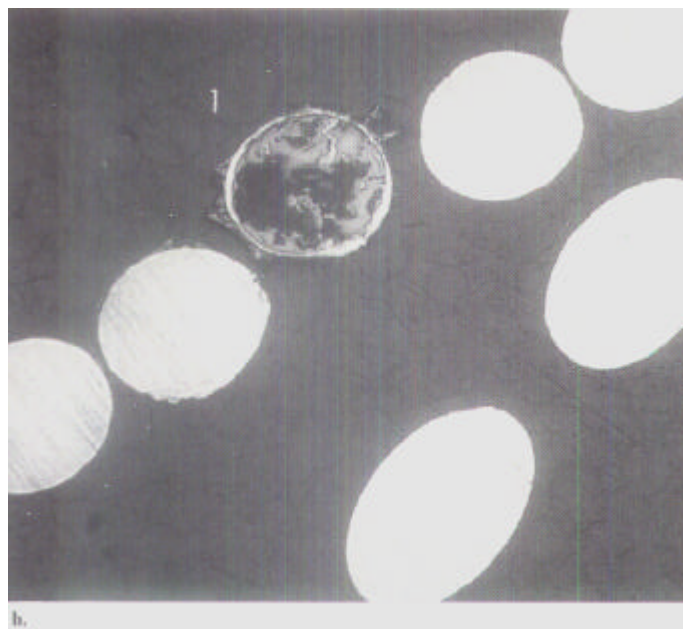
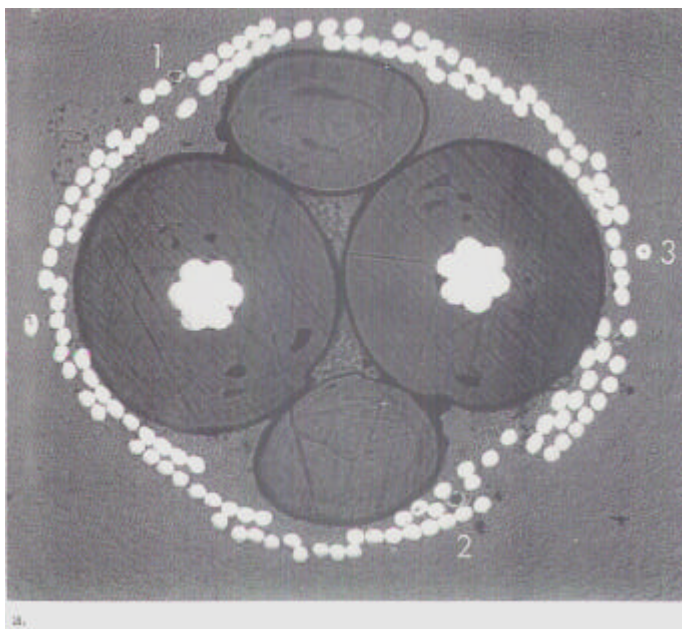


Figure 6a. Section through X -X (see Fig. 5), the superimposed numbers referring to corroded strands. Three of the 143 strands are corroded to some extent (2.1%)

Figure 6b. Detail of strand no. 1 from Figure 6a. Adjacent strands are uncorroded, but support crystals of cuprous oxide (x150)

Figure 6c. One strand in the centre of the braid has been totally transformed to a silver tube. Cuprous oxide (visible as bright red under polarised light) is located within the silver tube and within all the inter-strand spaces

Figure 6d. Tunnelling corrosion along strand no. 3 (x 150)

Conclusions

These laboratory examinations have confirmed the existence of red-plague corrosion, restricted to isolated areas, on the outer braid shield of three spacecraft cables. In the most severely affected area, 3% of the strands making up the braid cross-section have been affected. It is estimated that a maximum of 2% of the electrically conductive path has been degraded.

The silver-plating thickness on the braids is generally good, but corrosion has initiated at randomly spaced defects. The loose-fitting out jacket facilitates the ingress of humidity and chloride and fluoride contaminants may possibly have an accelerating effect on the galvanic corrosion mechanism.

The actual extent of red-plague corrosion is markedly less than would be expected from visual inspection alone. Corrosion has only taken place in isolated areas. These areas contain silver and copper oxides (both of which are electrically conductive).

The evidence of liquid on the braid suggests that in the past the <50% relative humidity requirement has not been strictly maintained during transportation and storage.

The mechanical behaviour and electrical conductivity of the braided screens are not severely affected.

Of the several hundred kilometres of wires and cables manufactured for ESA spacecraft, only three reels have been identified to possess a limited extent of red-

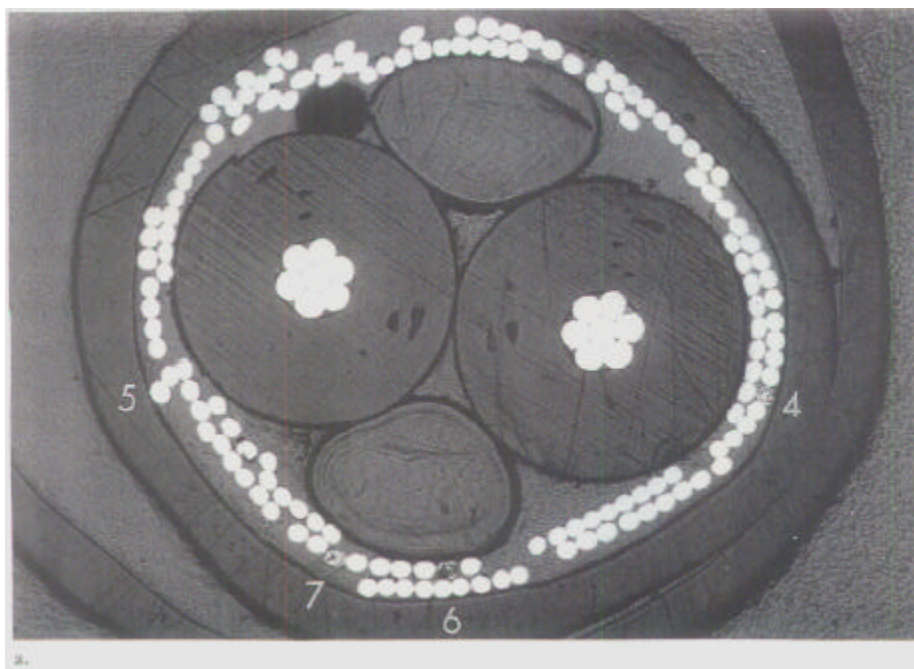
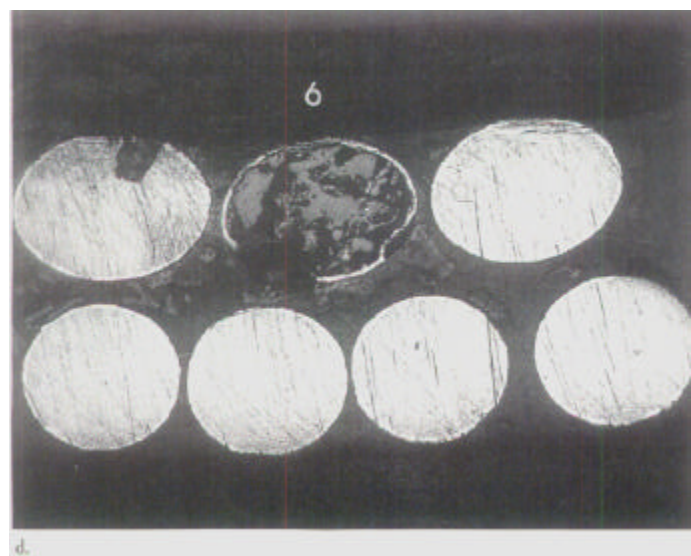
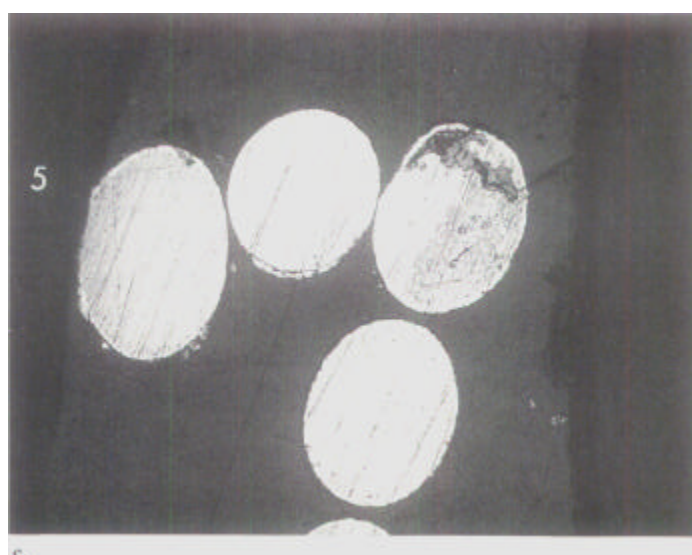
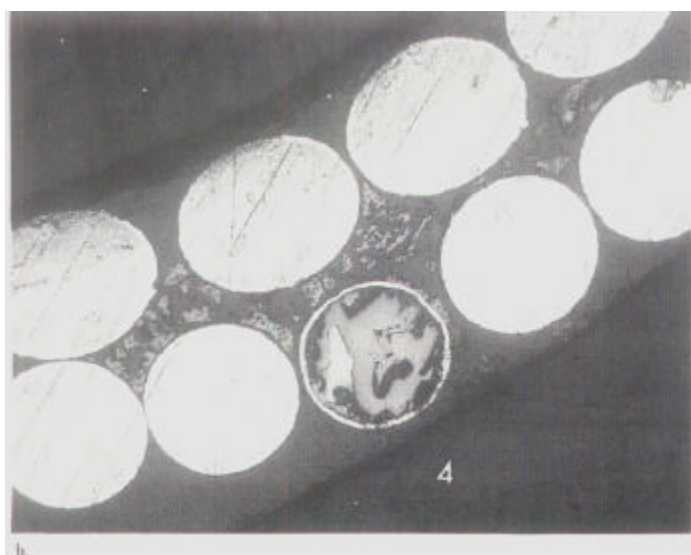


Figure 7a. Section made through Y-Y (see Fig. 5). Superimposed are numbers referring to corroded strands. Four of the 143 strands are to some extent corroded (2.8%) (outer FEP jacket has been peeled back and appears as two rings)

Figure 7b. One corroded strand is surrounded by non-corroded adjacent strands covered by cuprous-oxide crystals. Note large air gaps between outer FEP jacket and inner wire insulants (x 150)

Figures 7c-e. Remaining corroded strands in section Y-Y (x 150)



plague corrosion on their braided screens. The inner conductors of spacecraft cables and wires have never shown any form of corrosive attack.

The probability of wire/cable degradation due to copper corrosion of insulated silver-plated copper wire is concluded to be very small in view of the survey findings and the results of the laboratory examinations.

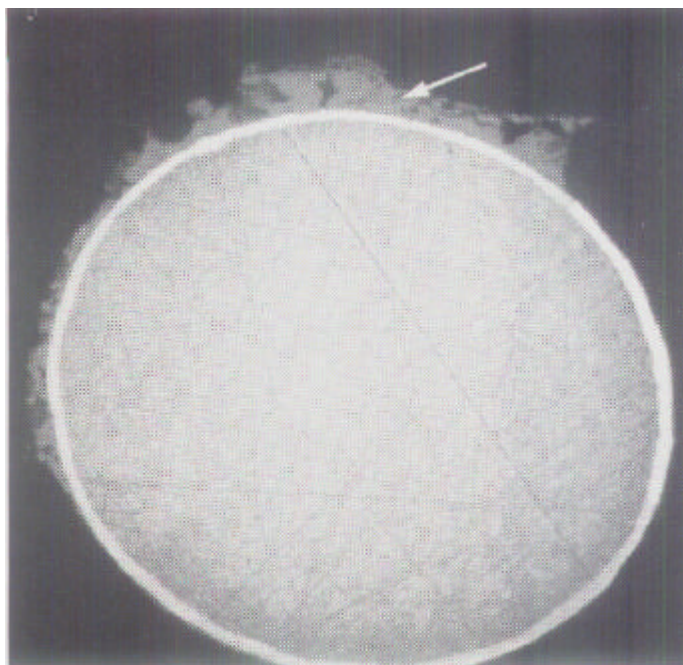


Figure 8. Section through red crystals on the intact 2 - 3 μm thick silver coating on strand from corroded braid (x 600)

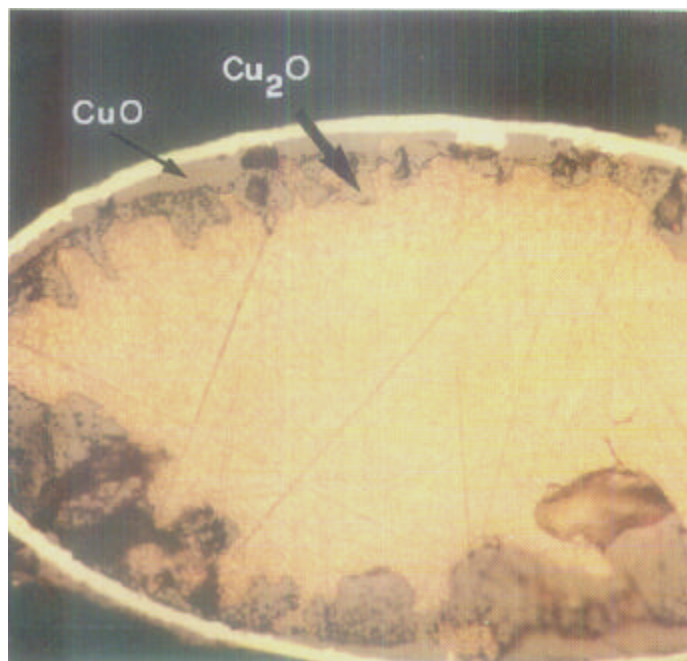


Figure 9. Colour micrograph clearly showing the various copper oxides to have 'tunnelled' beneath the silver coating. They are also present on the outer surface (x 600)

Programme to evaluate corrosion susceptibility of wires and cables

Objectives

A programme of work has been undertaken by ESA with the aim of understanding the phenomenon of red plague in greater detail. The basic mechanisms of corrosion presented in the literature have been described above, but a variety of factors still need to be resolved. The objectives of the programme include:

- To establish a database on the red-plague susceptibility of wire and cable products presently being supplied for ESA spacecraft projects.
- To develop and assess the test method described by Anthony & Brown¹⁻⁸ for the detection of susceptible products.
- To determine the origin and extent of contaminants on silver-plated strands – particularly chlorine and fluorine as were detected on the corroded braid and reported above. Also to assess their influence on the corrosion mechanism.
- To assess the quality and suitability of virgin silver-plated copper strands, supplied by two or three producers to the manufacturers of insulated wires and cables.
- To compare the red-plague susceptibility of different wire and cable manufacturers' products.
- To compare the effects of different insulation materials.
- To investigate alternative plated layers.

Several other lines of investigation are also being included and the work is still in progress. Seventy-five different wires and cables (from German, French, Swedish and US manufacturers and intended for spacecraft use as RF shielded cables, hook-up wires and coaxial cables) have been evaluated between November 1983 and March 1984, including the individual assessment of a total of 100 different braids and internal conductors. All were subjected to accelerated corrosion testing. For cost reasons, the number of samples forwarded for surface analysis has been restricted to 51.

Laboratory procedures

Visual inspection

The wires and cables were inspected with a binocular microscope under x20 magnification. The outer jacket was removed with a scalpel and the braid

inspected. This was repeated for the inner conductors. A polarised-light microscope was used to establish the presence of cuprous oxide (ruby-red under crossed polars). Areas of interest were photographed with a Reichert projection microscope onto colour film. Post-test inspection results were graded according to criteria listed below.

Surface analysis

The surfaces of conductor strands were analysed by Auger Electron Spectroscopy (AES) at the Surface Analysis Centre of Standard Telecommunication Laboratories Ltd. This method permits the characterisation of surface contaminant levels down to fractions of a mono-layer. AES makes use of discrete maxima in the secondary electron energy spectra obtained from less than a few Angstroms of the silver-plated surface's thickness during irradiation by X-rays degrade detection of these elements within a few seconds so that spectra must be recorded as soon as the analysis commences.

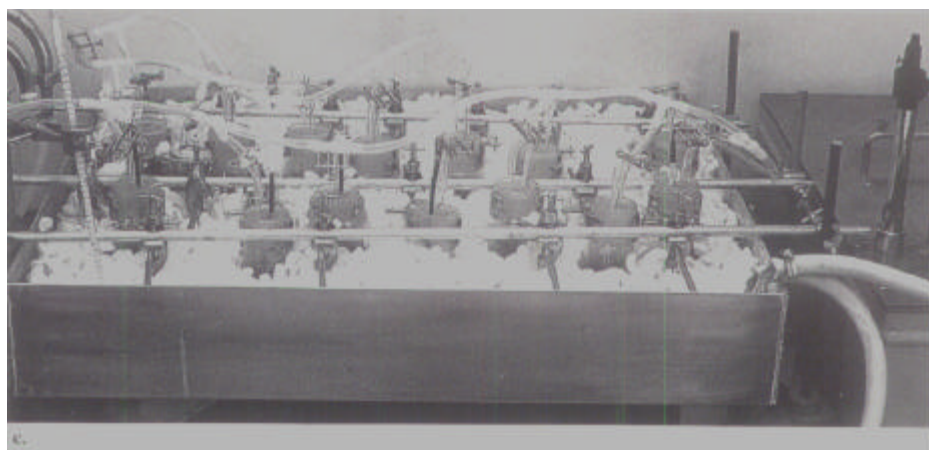
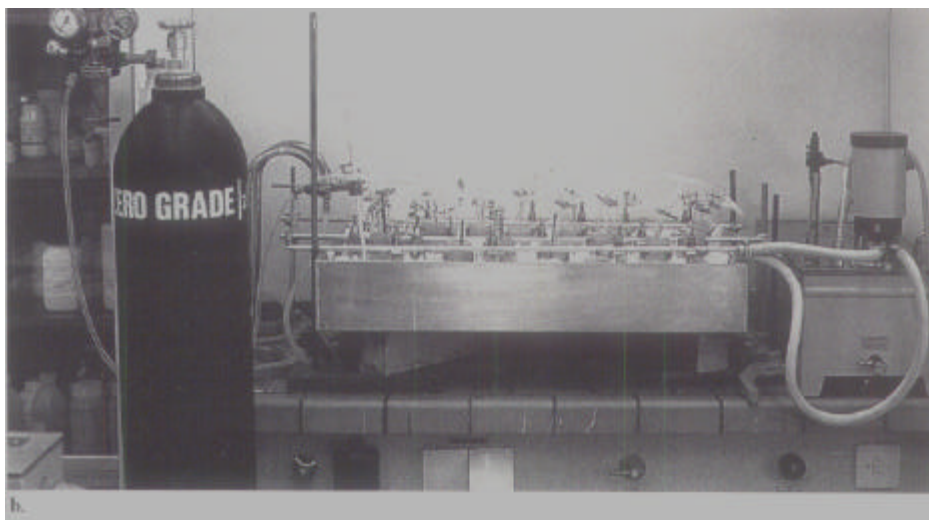
Sample strands were always cut and manipulated by means of micro-tools and tweezers. They were mounted onto the AES stage with a minute amount of DAG suspended in pure isopropyl alcohol.

Accelerated test method

All accelerated screening test⁸ has been devised based on the work of Anthony & Brown¹. Essentially two 200mm-long samples are taken from each batch of wire or cable submitted. One length is totally stripped into its constituent materials and closely inspected for signs of contamination or corrosion. 20 mm of the insulation is stripped from one end of the second sample, which is inserted into a rubber stopper fitted to the neck of a conical flask containing de-ionised water. The exposed end of the sample is positioned 20 mm above the water surface and pure oxygen bubbled into the water, which is held at 58°C. The test jigs are shown in Figure 10.

Figure 10a. Conical-flask set-up for accelerated corrosion testing of RF-shielded cable to ESA PSS-01 -720 (draft)

Figures 10b & c. Fourteen samples under test, with flasks held at 58°C in a water trough (evaporation minimised by particles of floating polystyrene)



The test environment ensures that the silver-plated conductors of the sample are subjected to a 100% relative humidity, saturated in oxygen, at 58°C. The specified test duration is 240h (10d), but some duplicate samples were also tested for periods of between 90 and 108 h (approximately 4.5 d). At the end of the test period the samples were removed from the flasks and stripped of their various insulating layers. The silver-plated strands were inspected within 3h of their removal from the test jig. The extent of corrosion (per 200mm sample) was based on the following visual inspection criteria:

Code	Extent of corrosion
0	None
1	One Point, on one or two adjacent strands
2	Slight, on two to eight adjacent strands in one location along sample length
3	Moderate, two to eight adjacent strands in a few locations along sample length
4	Moderate, two to ten adjacent strands in several locations along sample length
5	Severe Corrosion, affecting more than 50% of the total strands from any conductor in any one location

Codes 0 to 4 would not be expected to affect the electrical service properties of the wire/cable.

These codes are based on subjective visual inspections. The extent of corrosion was later quantified by means of metallographic preparations.

Analysis of water from accelerated test

The initial EDAX and AES analyses of the corroded braids detected the presence of varying amounts of chlorine and fluorine on the surface and subsurface of those silver-plated strands. Soluble chloride and fluoride ions might be expected to affect the rate of reaction at any electrochemical corrosion couple. The conditions of the accelerated corrosion test ensure that water, condensed onto the exposed silver strands, is drawn by capillary attraction into the strand interstices/insulation voids along the sample length. This water will dissolve soluble ions from the silver surface, which will migrate down the sample interior and drip back into the conical flask. At the end of the 240 h test period, the flask waters were sent for analysis at the Central Laboratory of the Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek (TNO).

The fluoride content was determined by an autoanalyser with a fluoride electrode in the buffered sample solution (accuracy > 5%). The chloride content was determined using Instrumental Neutron Activation Analysis (INAA). To improve the detection limit, 3ml of the sample solutions were evaporated at 60°C. The remains were neutron-irradiated for 30min with a neutron flux of 10^{13} neutrons/cm²/s. A Ge(Li) detector recorded the gamma spectrum, from which the trace elements and their concentrations could be determined. The conditions for these analyses provided for an accuracy of 5 -10%.

Metallography

The method of metallographic preparation followed that described on page 311. Generally, only single strands were longitudinally sectioned after they had been cut from the tested wires/cables. Occasionally the entire wire or cable was mounted and complete transverse sections made across sites of corrosion.

Wire- and cable-material variables

- a. Conductor strands, copper finished with:
 - 2 mm silver, 1 mm silver
 - 1 mm nickel with flash of silver
 - tin
 - nickel

b. Insulation material and application methods:

- FEP melt extruded directly onto wires and cables
- PTFE ram extruded directly onto wires and cables
- Kapton-wrapped tape, sonic with FEP coating sintered to form bond
- Tefzel-ETFE, melt extruded.

Results of laboratory investigations

Detailed test reports have been completed for each cable/wire sample submitted for evaluation, including source, purchase specification, type of product and construction. In some cases the strand suppliers were not known to ESA. Proprietary information and the individual wire/cable manufacturers' names appearing on individual test reports (retained by ESA) are not for general release. An example of a test report is shown in Figure 11.



CABLE MANUFACTURER : AAAAAA Test no. 6

DESIGNATION : 125 Ohm 8P cable DATE OF MANUFACTURING : November 1983
Special production to spec. 11111

CONSTRUCTION : OUTER BRAID
OUTER JACKET Natural FEP, Kapton binder 2 micron Ag
INNER CONDUCTOR INSULATION Natural PTFE INNER WIRE STRAND 2 micron Ag

VISUAL INSPECTION OF AS-RECEIVED CONDUCTORS (FOLLOWING STRIPPING):
OUTER BRAID good INNER WIRE STRAND good

SURFACE ANALYSIS OF AS-RECEIVED CONDUCTORS BY AUGER (FOLLOWING STRIPPING):

(atomic %)	S	Cl	C	Ag	O	F	Cu
OUTER BRAID	1.01	0.00	39.90	53.56	4.99	0.19	0.00
INNER WIRE STRAND	1.04	7.45	39.04	34.82	6.07	1.38	10.19

VISUAL INSPECTION OF CONDUCTORS AFTER 4 1/2 DAY CORROSION TEST (INSULATED AREA):
OUTER BRAID (3) INNER WIRE STRAND (0)

VISUAL INSPECTION OF CONDUCTORS AFTER 10 DAY CORROSION TEST (INSULATION AREA):
OUTER BRAID (3) INNER WIRE STRAND (2)

SURFACE ANALYSIS OF 10 DAY CORROSION TESTED CABLE BY AUGER (FOLLOWING STRIPPING):

(atomic %)	S	Cl	C	Ag	O	F	Cu
OUTER BRAID CORROSION SITE SHINY AREA	1.74	0.99	32.69	39.76	9.20	0.00	15.63
INNER WIRE CORROSION SITE SHINY AREA	1.46	6.66	19.39	58.49	9.13	0.19	6.76

HALIDES IN WATER FROM CABLES (ppm) :
Cl 5.0 F 0.02 Br 0.04

MICROSECTION RESULTS :
Both braid and inner conductors have 2 microns silver coverage,
braid corrosion extends into copper core, subsurface in worst strand.

OTHER RESULTS :



(x600)

(x600)

Figure 11. Typical information contained in a test report

Table 1. Results of surface analyses and accelerated corrosion testing

Test Sample number	Nominal silver thickness (μm) – outer braid (when present) – wire conductor	Grading from accelerated corrosion test (PSS-01-720 draft)	Analysis of surface elements by Auger method (atomic %) (as-received)				
			Cl	F	Cu	C	Ag
1	2	2	2.0	0.4	0.0	47	48
	2	3	5.0	4.0	6.0	47	35
2	2	2	1.4	1.0	1.2	75	18
	2	3	1.5	1.8	4.9	40	47
3	Nickel +	1	2.0	1.3	1.1	73	19
	2	2	6.7	0.1	9.1	23	52
4	Nickel +	1	0.9	1.0	0.0	76	20
	2	2	8.5	0.0	9.6	28	47
5	2	2	3.3	1.1	0.0	41	50
	2	1	8.0	0.7	9.3	27	49
6	2	3	0.0	0.2	0.0	40	54
	2	2	7.5	1.4	10	39	35
7	Nickel +	2	4.2	4.8	1.4	43	40
	2	2	6.0	0.0	7.4	35	42
8	Nickel +	2	0.6	0.9	3.7	34	58
	2	2	4.5	4.7	7.8	53	28
9	1	4	3.2	0.7	0.8	33	60
	2	3	5.4	0.4	14	23	47
10	Tin	0	0.0	0.2	15	4.7	30
							tin
11	1	1	1.1	0.0	8.1	70	17
12	1	2	1.0	0.0	4.1	50	43
13	2	2*	5.2	0.0	7.8	28	52
15	2	3–4	8.2	0.4	0.6	39	49
	2	2–3	5.1	0.4	4.8	21	57
16	2	3–4	4.4	0.0	0.8	35	57
	2	2	2.8	4.7	6.1	65	19
17	2	3	3.9	0.9	13	22	28
	2	0	4.9	0.6	14	27	43
18	1	0	–	–	–	–	–
	1	0	–	–	–	–	–
22		not tested	0.4	0.2	2.9	30	55
			1.2	0.1	2.0	49	36
24	2	0	6.0	0.0	3.4	58	28
26	2	3–4	5.3	1.2	4.8	10	72
28	2	0	–	–	–	–	–
30	2	2	–	–	–	–	–
32	2	0	5.7	1.1	5.2	37	44
34	2	5	4.0	1.3	5.0	20	64
36	2	1–2	–	–	–	–	–
38	?	3	–	–	–	–	–
39	?	4	1.9	0.4	9.5	86	1.7
		3	6.2	1.0	4.6	27	58
40	2	1	1.7	0.7	6.4	21	52
41	1	4	7.3	2.9	4.8	28	51
42	2	2	5.3	0.6	10	41	39
43	2	3	0.0	0.8	1.0	30	64
44	?	0	5.2	0.3	1.0	37	51
45	?	1–2	1.2	1.0	14	21	47
46	?	0	1.2	0.7	0.0	26	67
47	2	1	0.6	1.4	1.8	40	52
48	?	3	0.0	1.0	2.4	90	4.4
		0	1.5	2.2	4.2	21	66
49	2	1	1.4	0.3	1.4	59	30
	2	0	6.1	0.6	11	17	51
50	2	1	5.7	0.9	15	15	50
	2	1	6.0	0.7	8.3	28	42
51	2	2–3	5.0	1.0	8.3	27	48
		0	5.0	1.9	9.3	13	55

Notes: Samples 52 - 75 have not been surface analysed. Nickel + is nominally 2 mm nickel with 0.2 mm flash of silver. Sample 13 * supported silver tarnish, but no corrosion.

Visual inspection (as-received)

Each of the submitted wires and cables was stripped of insulation and the majority were noted to possess clean, bright silver-plated conductor strands. A wire, manufactured in 1977, supported very slightly tarnished spots. The surface of one recently supplied cable screen had a straw-coloured appearance and was thought to have been treated with a corrosion inhibitor.

Surface analyses

A series of 51 wire/cable specimens have been subjected to surface analysis. The results of the as-received conductors for the elements chlorine, fluorine, copper, carbon and silver are presented in Table 1. As will be noted from Figure 11, sulphur and oxygen were also recorded on the individual test reports, but are not included in Table 1 as they are not considered to play an active part in the red-plague corrosion mechanism. The surface analyses made after the corrosion testing are also not included as those results indicated that both chlorine and fluorine had been mobile during the test and after drying-out of the test samples each had been redistributed. The results of AES differed considerably from corrosion site to corrosion site. Large atomic percentages of copper and oxygen were identified as can be expected from the often thick layers of red cuprous oxide found adherent to such areas.

The results of the surface analyses are summarised in Tables 1 - 6.

Table 2. Auger surface analysis of contamination levels on unprocessed silver-plated strands (atomic %)

Sample details*	Cl	F	Cu	C	Ag	O	S
Manufacturer A	3.3	0.11	0.4	51	31	5.2	2.0
Manufacturer B	1.8	0.00	0.2	65	27	5.3	0.9
Manufacturer C**	0.0	0.00	2.4	59	35	3.1	0.3
Average	1.7	0.04	1.0	58	31	4.5	1.1

* Samples were taken from outside (exposed to factory storage environment) and internal turns of bobbins. The surface-analysis results are averages for each manufacturer.

** Manufacturers-A and -B produced 2 mm-thick silver plating on strands; Manufacturer-C produced 1 mm-thick silver-plating on strands.

The high levels of carbon observed on all samples in Table 2 are assumed to have been picked-up during strand fabrication from the lubricating organic oils utilised in drawing-down, annealing, and quenching operations on the plated copper strands. Measurable chlorine levels were found on the strand surfaces from Manufacturers A and B. Some traces of fluorine were also recorded. The source of these halides has not been determined, but such elements are known to be present at concentrations of ppm in the fluids employed during strand manufacture.

Table 3. Auger surface analysis of strands after processing into insulated wires and cables (atomic %, per element)

Strand manufacturer	Cl	F	Cu	C	Ag	O	S
A max.	8.2	4.8	14	76	72	31	8.9
min.	0.0	0.0	0.0	10	18	0.8	0.0
Average of all values	4.0	1.2	4.8	39	44	5.2	1.4
B max.	6.0	1.9	15	41	55	15	1.9
min.	5.0	0.0	1.0	15	39	3.1	0.5
Average of all values	5.4	0.8	8.5	28	48	8.0	0.9

Comparison of the results listed in Table 3 shows that, after application of insulation, there are no striking differences between the products of strand manufacturers A and B.

Table 4. Auger surface analysis of strands processed by different manufacturers (atomic %, per element)

Wire or cable manufacturer	Cl	F	Cu	C	Ag	O	S
W	4.4	1.2	5.8	38	43	6.0	1.4
X	3.1	0.8	5.1	31	53	4.9	2.1
Y	2.6	0.4	6.6	58	30	1.5	0.8
Z	1.1	0.4	3.8	33	48	4.9	8.9

It was thought that the high-temperature processing operations applied to the various types of insulation materials might cause them to partially decompose, releasing monomers and carbon-oxyfluoride compounds as they were being applied to stranded wires and braid. The average surface halide analyses are given in Table 5.

Only the kapton tape shows a significant difference, less fluoride being absorbed on the silver surfaces than from the other insulants. The kapton has a very thin FEP film which is sintered at a lower temperature than the melt extruded FEP insulations, and this may account for the lower fluorine levels.

Table 5. Halide concentrations (Auger analysis, atomic %) on silver conductors having various insulation materials

Insulation material and application method		Cl	F
FEP (melt extruded directly onto wires/cables)	max.	8.2	4.8
	min.	0.0	0.0
	average	2.8	1.1
PTFE (ram extruded and sintered or taped and sintered)	max.	8.5	4.7
	min.	1.5	0.0
	average	5.4	1.4
Kapton (wrapped tape with FEP coating that is sintered to form bond)	max.	5.3	0.6
	min.	1.0	0.0
	average	3.2	0.2
Tefzel-ETFE (melt extruded)	max.	7.3	2.9
	min.	0.0	0.3
	average	2.4	1.2

It was considered that the wire stranding and cable braiding operations might effect a change in contamination level. Superimposed on this would be the adsorption of halogens to the silver strand surfaces from the insulation applied. Table 6 compares the average surface contamination levels found on unprocessed strand material with those of processed braid and wire.

Table 6. Comparison of Auger surface analyses (atomic %) on new strands and strands processed into wire and cable

	Cl	F	Cu	C	Ag	O	S
New strand (average from Table 2)	1.7	0.04	1.0	58	31	4.5	1.1
Outer braid	2.8	0.9	3.4	48	38	5.0	1.4
Inner wire strands	4.3	1.1	6.6	40	47	5.3	2.2

It may be deduced from these various sets of results that the different manufacturing operations for processing individual silver-plated strands into finished wires or cables do modify the chemical structure of the strand surfaces. There is a marked increase in fluorine content, presumably absorbed during the high-temperature application of fluorocarbon insulation material to the strands.

Extrusion and sintering take place in a temperature region of 300-400°C. The increase in copper content can result from the mechanical damage of the outer silver coating during stranding and braiding, and by diffusion of copper into the thin silver layer during the high- temperature processes. The fall-off in carbon might be due to the removal of lubrication films as they are expelled by the high temperature processing. Little difference is seen between the average contamination levels of braid and wire strands.

Synthesis of accelerated corrosion test results

The results for the wires and cables tested to the Anthony & Brown procedure¹⁻⁸ have been presented in Table 1. They are also presented here in the form of bar charts to facilitate interpretation.

The influences Of Surface elements on the corrosion ratings of wires and cables are shown in Figures 12a-g. This graphical presentation highlights two unexpected findings:

- High amounts of C1⁺ are present with corrosion ratings of 0 and 4, whereas the intermediate ratings are connected to low amounts of C1⁺
- F⁻ apparently does not contribute to strong corrosion.

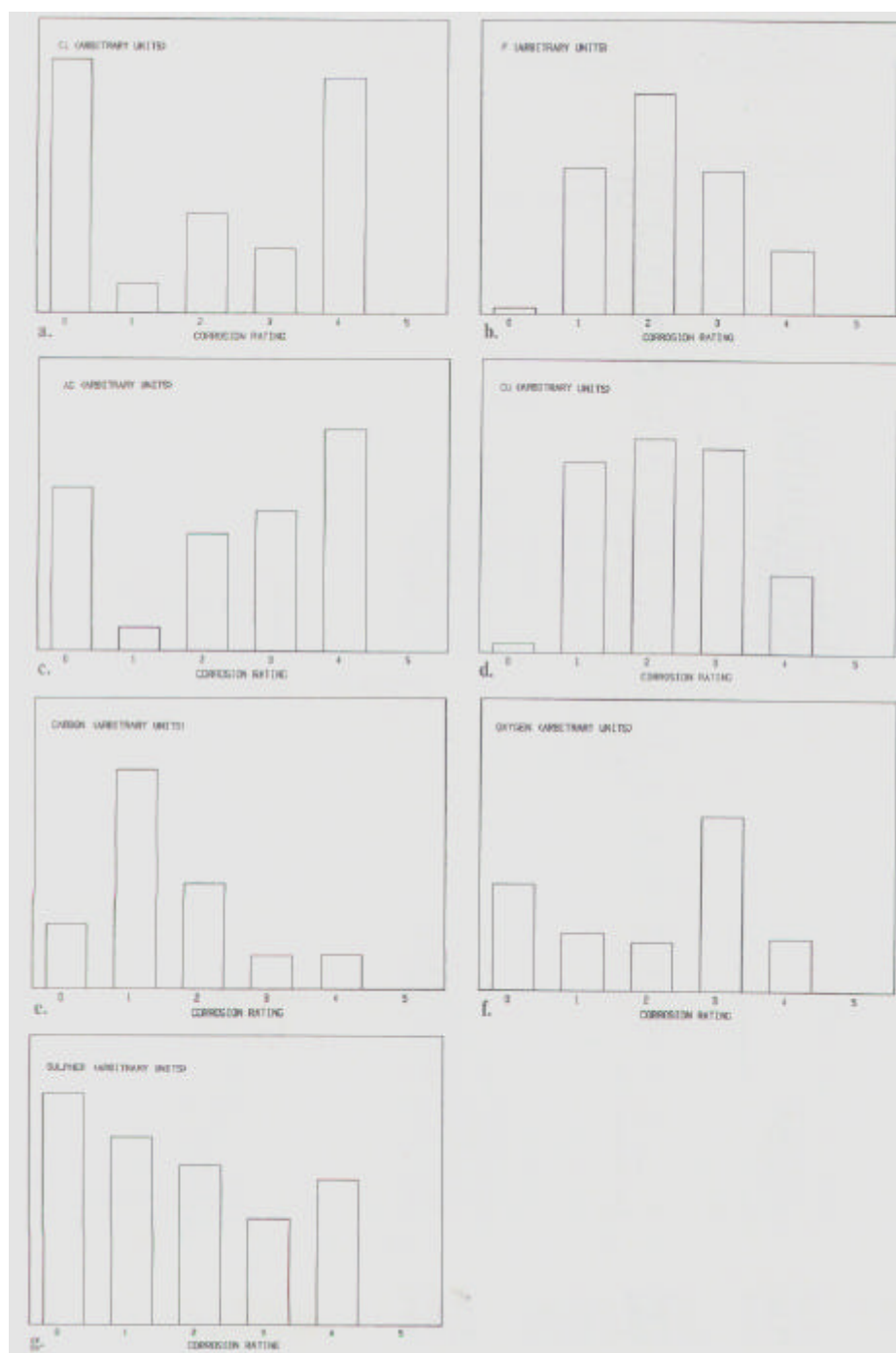


Figure 12a g. Influence of individual contaminants on the corrosion rating

A possible explanation is thought to be that chlorine and fluorine have different influences on the metals present.

The influence of the various types of insulation on the corrosion rating of wires and cables is illustrated in Figure 13. It appears that the high corrosion ratings (at least rating 4) are achievable in the test irrespective of the types of insulation used on the strands. FEP was mainly used as the loose-fitting outer jacket material on RF cables, and PTFE was mainly used as insulation material on inner conductors. PTFE had been sintered onto the strands and trapped only a minimal amount of air.

The influence of the strand manufacturer on corrosion rating is illustrated in Figure 14. These results show no marked difference (average of A = 2.1, of B = 1.3).

The influence of the wire and cable manufacturer on the corrosion ratings are illustrated in Figure 15. These results show that the accelerated test will produce corrosion on wires and cables from all manufacturers.

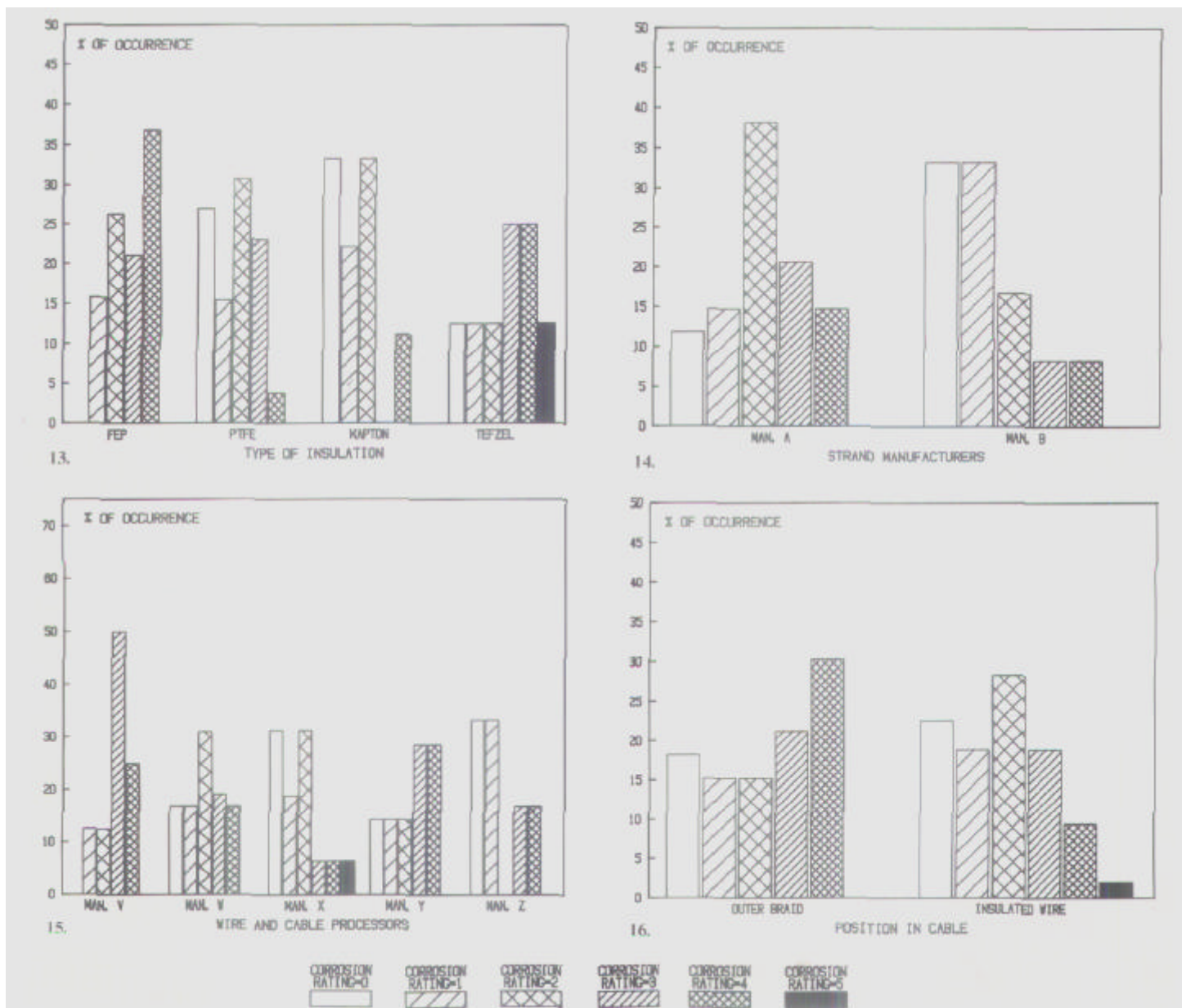
The influence of strand position - whether braid or stranded wire - is illustrated in Figure 16. It seems that the accelerated test is likely to produce slightly more corrosion on the braided strands than on the inner conductor. The amount of air trapped within the insulations depends on both the construction of the cable and the method by which the insulation is applied. The braids are surrounded by a far greater volume of air than the inner conductors, thus permitting the ingress of greater quantities of oxygen and moisture during the test exposure.

Figure 13. Influence of insulation material on corrosion rating of silver-plated strands

Figure 14. Strand manufacturer and corrosion rating for silver-plated strands

Figure 15. Wire and cable processor and corrosion rating for silver-plated strands

Figure 16. Positions of strand in cable and corrosion rating (for silver-plated strands). 'Insulated wire' includes inner conductor of cables and hook-up wires



Additional observations from accelerated testing are that:

- Samples exposed to the test environment for 10d have only a slightly higher corrosion rating than the 4.5d samples (from visual inspection only).
- Wire strands finished with either pure tin or pure nickel exhibit no form of corrosion from this test environment.
- Wire strands finished with 'nickel plus' (nickel with a 0.2 μm silver flash) show only slight corrosion in isolated spots, i.e. to a maximum of code 2. Corrosion only occurred under cracks in the nickel plating.
- Strands finished with 1 μm of silver tend to corrode more rapidly than those with a nominal 2 μm finish.
- When corrosion does occur in the strands of a wire or cable, it is usual that the end exposed within the flask supports a black corrosion product, while the centre part of the sample corrodes more extensively and is covered predominantly in red corrosion products.

Results of water analyses from accelerated tests

The halide contents of the water contained within the conical flasks during the 10d tests were noted to increase. The analytical results have been compared against the corrosion ratings for the wires or cables in Figures 17ab.

These figures show that contaminated water from the wire ends is returned to the flask in the form of drips. This confirms that the halides determined by AES existed in an ionic form rather than as monomers or polymers. There is a certain resemblance between Figures 17a,b and 12a,b.

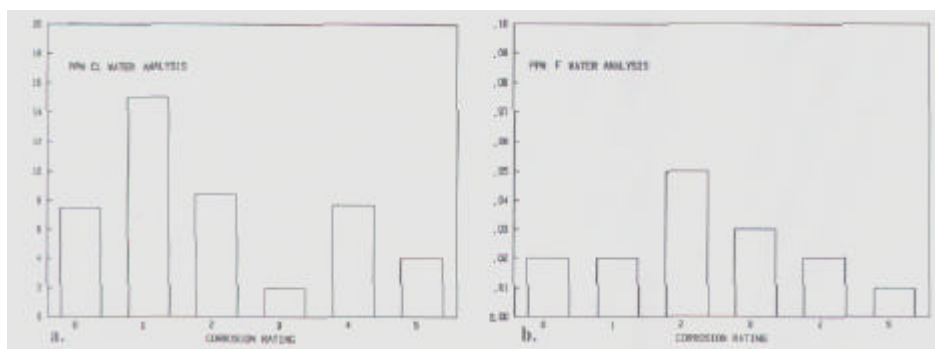


Figure 17a-b. Comparison of halide additions to water from test samples with their corrosion ratings

Metallographic findings and case studies

The results and discussions have so far concentrated on the subjective visual appearance of red-plague corrosion products adhering to the accelerated corrosion-test samples. It will be noted that single isolated defects in the silver-plated layer of copper strands can initiate galvanic corrosion. In the presence of water, the corrosion products may be dispersed over a wide surface area and, on drying-out, precipitate in the form of red and black crystals (Cu_2O and CuO). This process renders inspection and quantitative evaluation of the extent of corrosion extremely difficult.

A very important and complimentary aspect of the accelerated corrosion test programme has been the metallographic work. It was frequently found that micro-sections made transversely through wire strands that supported red plague failed to locate any corrosion of the copper core - only crystals of copper oxides were seen adhering to the outer silver surface. It therefore became standard laboratory practice to cut short lengths of red-covered strands from different corrosion sites on any one braid or stranded conductor. These lengths were distributed on the bottom of a mould then mounted and longitudinally sectioned. Often only one or two strands from the few dozen in the mount were noted to have actually corroded, and these sections were then photo- micrographed. Display of corrosion points selected in this manner can give an unduly pessimistic impression of the real extent of corrosion that exists in the total cross-section of conductor strands.

Four 'worst cases' are shown in Figures 18 - 21 to illustrate the metallographic findings.

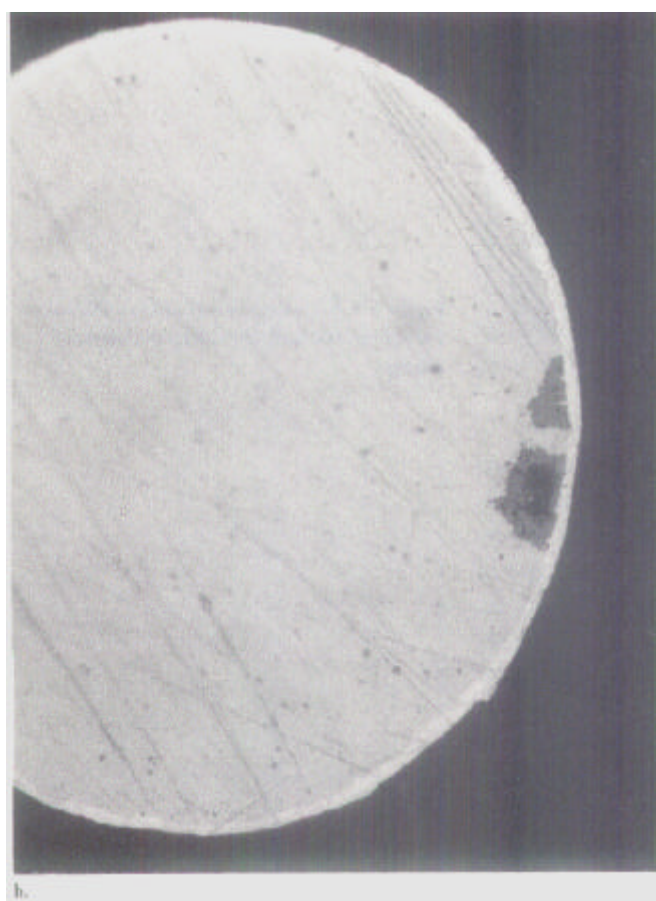
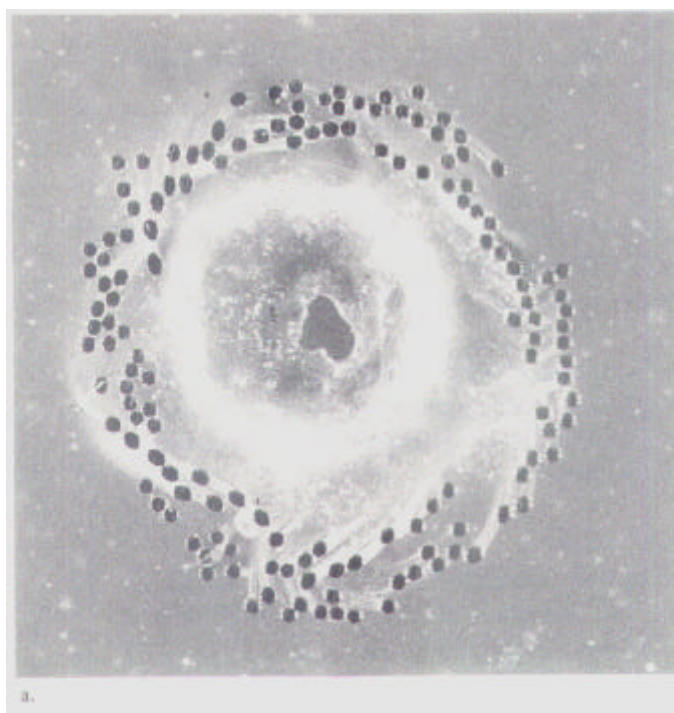


Figure 18. Transverse and longitudinal sections through red-plague corrosion site on sample no. 16. The braid consists of 144 strands, of which only two-support copper corrosion. All strands are of 2 mm silver-plated copper. The insulation materials are black FEP for the outer jacket and natural PTFE on the inner conductors. The longitudinal sections show that galvanic corrosion has initiated at local breaks in the silver plate (after 10d of accelerated corrosion testing).

- a. Outer braid sectioned across site of worst corrosion. Note braid has 144 strands, two of which show signs of internal corrosion
- b. Transverse section through worst corrosion site (x 800)
- c. Longitudinal section through worst corrosion site (x 600)

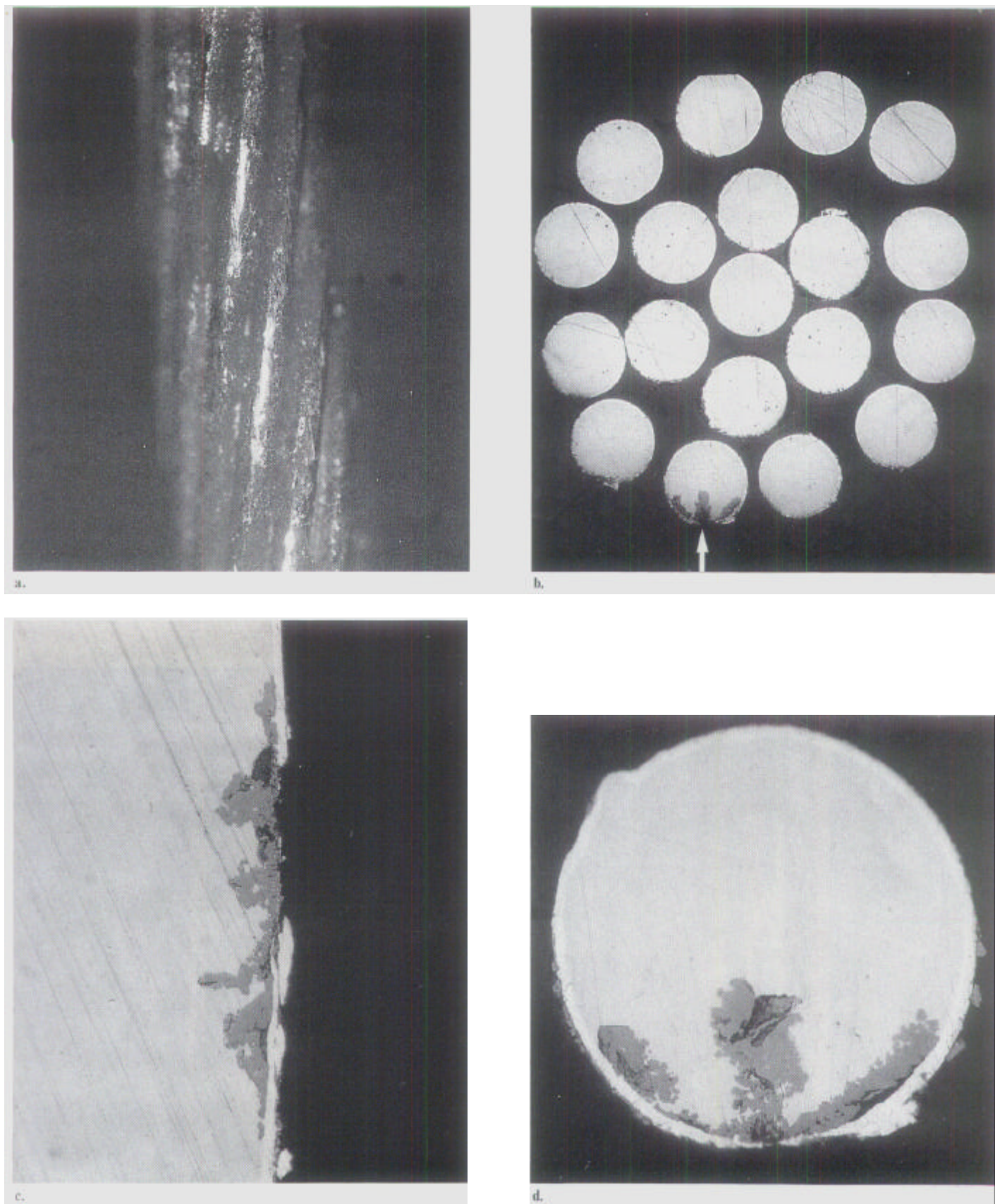


Figure 19. Transverse and longitudinal sections through red-plague corrosion site on sample no. 34. All strands are of 2 μm silver-plated copper. The insulation material is Tefzel-ETFE. In any transverse plane only one strand is noted to be corroded, initiation progressing from local defects in the Auer plating (after 10 d of accelerated corrosion testing).

- a. Extensive red corrosion on adjacent strands (x 60);
- b. Transverse section in most corroded area (x120);
- c. Longitudinal section through severely corroded area (x 600);
- d. Transverse section in most corroded area (x 600)

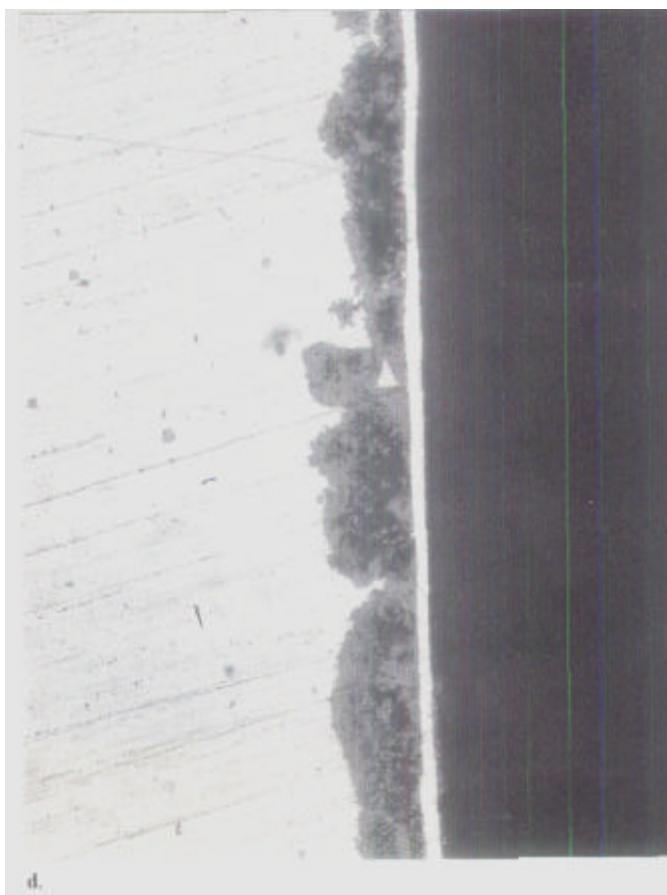
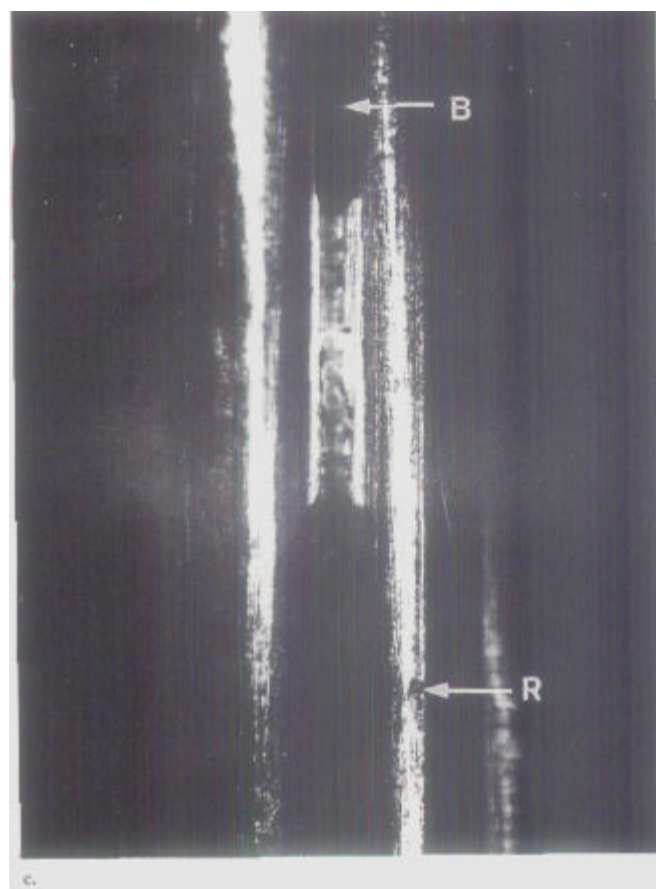
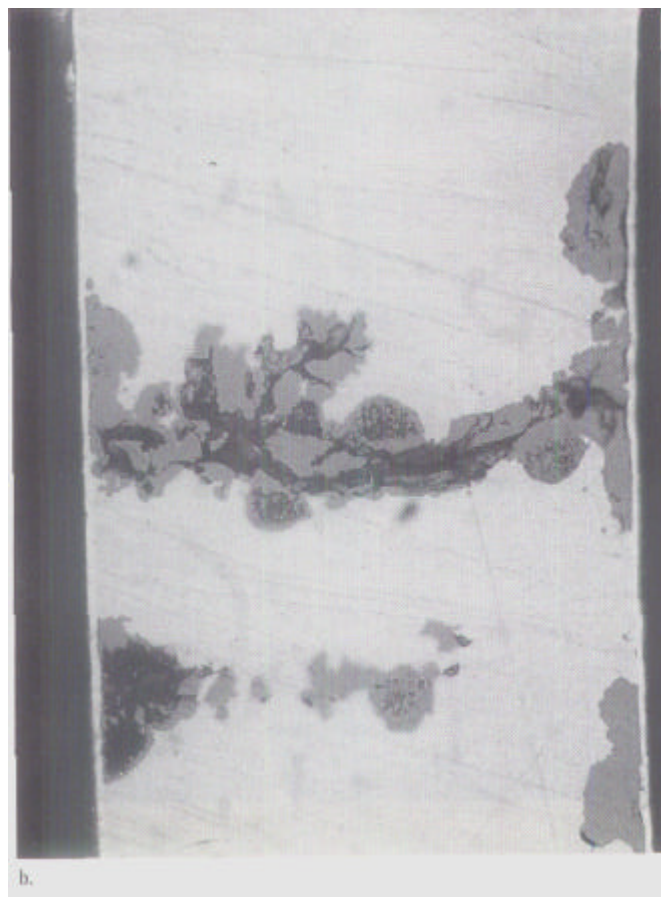
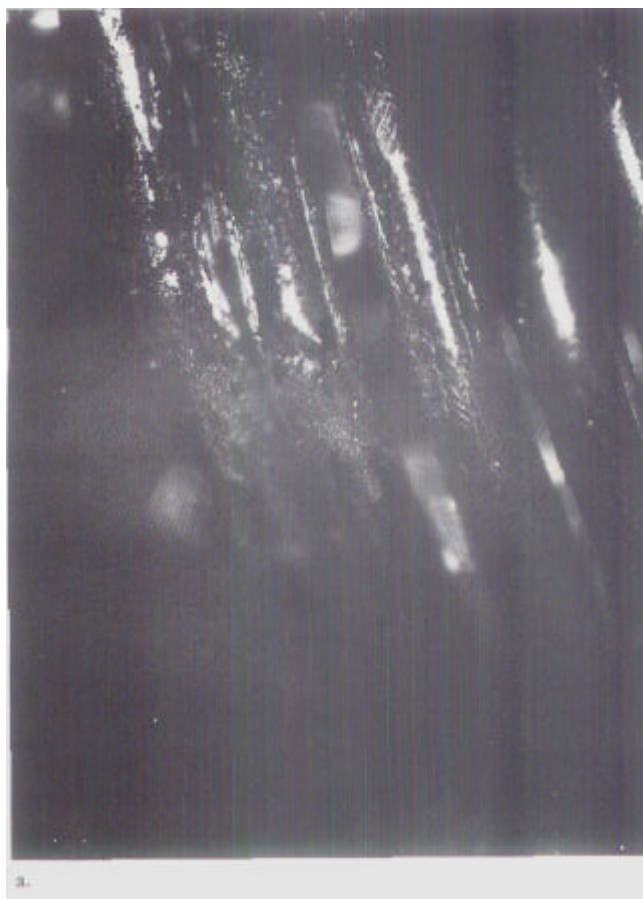


Figure 20. Longitudinal sections showing the most severely corroded strands (some oxidised throughout their section) from sample no. 9. Slight subsurface exists oil on one strand of the inner conductor, after 10d of accelerated corrosion testing. All strands are of 1 mm silver-plated

copper. The insulation materials are natural FEP for the outer jacket and natural PTFE on the inner conductors.

- a. Extensive red corrosion on adjacent strands (x 100);
- b. Corrosion and fracturing occurred through many strands (x 600);
- c. Inner conductor shows some red (R) and black (B) spots (x 100);
- d. internal corrosion (x 600)

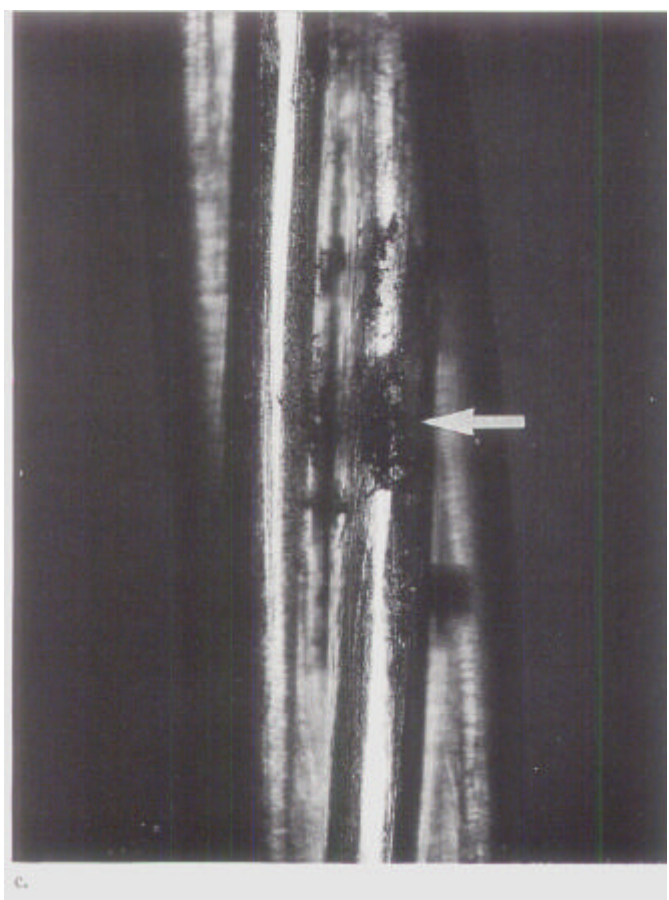
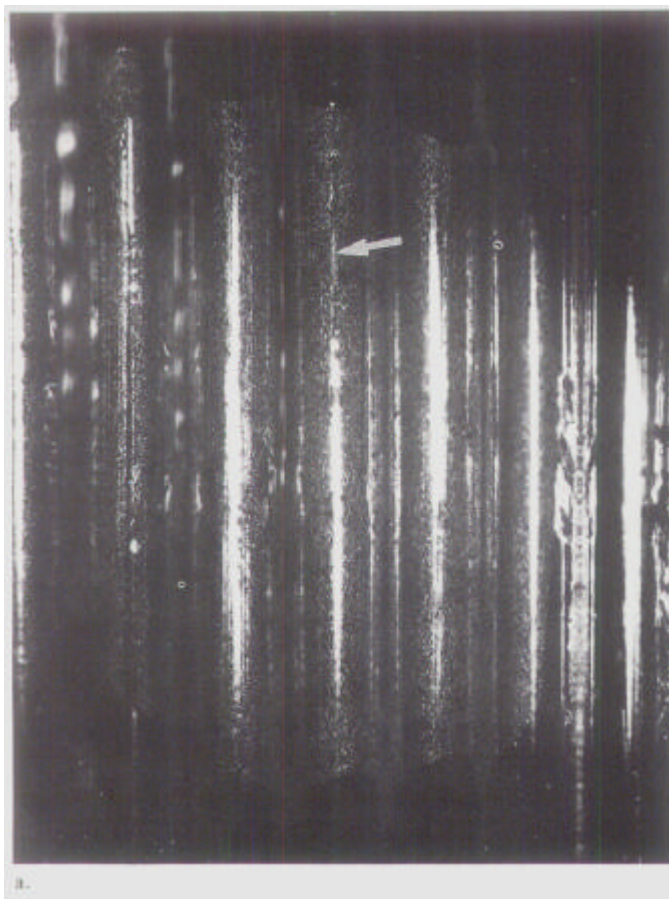


Figure 21. Longitudinal sections through the most severely corroded strand selected from sample no. 8, with Nickel-Plus braiding and 2 μm silver-plated stranded inner conductors after 10 d of accelerated corrosion testing. The insulation materials are natural FFP with kapton hinder for

the outer jacket and natural PTFE on the inner conductors. Subsurface cavities are formed at occasional breaks in the nickel plating, enabling localised corrosion couples to be set up. Corrosion of the inner conductor is extremely limited.

- a. Stained area with red spots (arrowed) (x 75);
- b. Break in nickel (arrowed) with thin oxide coverage (x 1600);
- c. Red-black spot (x 80);
- d. Oxide on surface (x 600)

The mechanisms of red-plague corrosion

The basic mechanisms that account for the red-plague corrosion of silver-plated copper stranded wires and cables were briefly reviewed in the beginning of this paper. The conditions for corrosion, as stated in the literature published in the 1960s, were for the simultaneous presence of moisture, imperfections in the silver-plating that expose the copper core and, if the corrosion reaction is to continue unchecked, an unlimited supply of oxygen. We will now discuss the individual mechanisms in greater detail, taking into account the findings from cables found to have corroded during storage as well as those from the corrosion-susceptibility programme.

Introduction of moisture

Apart from capillary wetting by immersion of non-sealed wires and cables into a water bath, moisture may also be deposited on the strands by condensation. For a known ambient humidity, the dew point can be calculated and plotted¹¹, as shown in Figure 22. It has already been noted that relatively large volumes of air are contained within the outer jacket of certain cables. This free channel, with a volume of approximately 4cm³ per metre of cable, readily provides for the ingress of water vapour throughout the unsealed length of these and similar cables. A very limited amount of water vapour may also permeate through the walls of the outer jacket insulation. Spacecraft cable is generally stored under well-controlled environmental conditions, but rapid changes in temperature, known to occur during transportation, can cause the water-vapour content of the air encapsulated within a cable's outer jacket to become saturated and condense onto the silver braid as water droplets. As shown in Figure 22, air with a relative humidity of 50% at ambient temperature will start to condense moisture onto surfaces whenever there is a 10°C fall in temperature.

The strands of the inner conductor wires within the cable in Figure 7a fit tightly into their surrounding insulation. Sharp temperature falls are then unlikely to cause moisture to condense onto the wire strands (either single or multiple wires located in cables) as the volume of encapsulated air is negligible.

Galvanic corrosion due to structural defects

The metallographic examinations of numerous stranded wires and cables revealed defects in the silver-plating caused by:

- an eccentric silver-plating coverage (e.g. poor plating distribution)
- very local thin spots in the silver due to a noncircular copper core (e.g. copper wire drawn through a rough die prior to silver plating and subsequent final drawing operations)
- mechanically damaged strands, invariable limited to the braid of cables (e.g. unsuitable processing equipment).

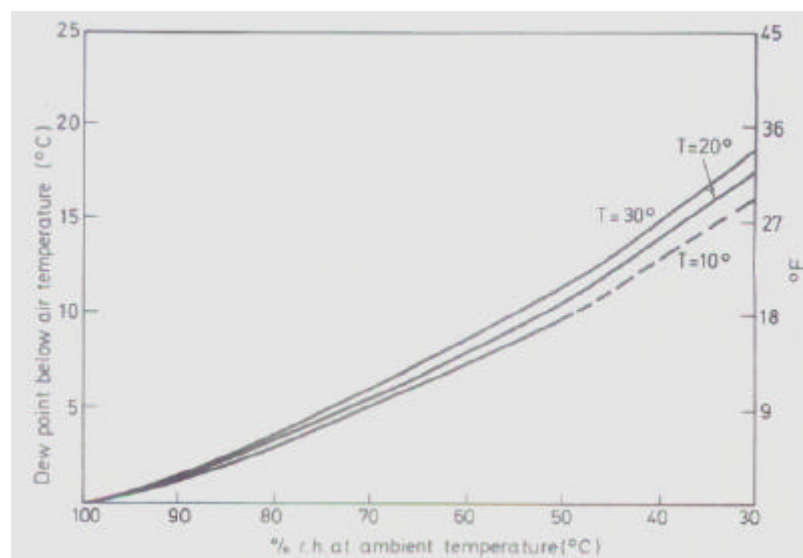
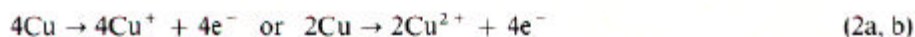


Figure 22. Dew-point depression below ambient temperature as a function of the relative humidity of the ambient atmosphere over a range of temperatures

The above imperfections may range from microporosity to deep scrapes in the silver-plated layer, but all will expose copper. Also, depending on the temperature, exceedingly thin coatings of silver can become rich in copper due to the solid-state diffusion process.

Once copper is exposed in the presence of moisture, initiation of galvanic corrosion is possible. Copper cathodically protects the silver and passes into solution. As with many other metallic couples, it is likely that there is a size relationship between the cathodic surface area (silver) and the anode (exposed copper). The occasional defect in a silver-plated strand might be expected to corrode more rapidly than if the silver surface contained frequent cracks or extensive porosity.

As both copper and silver are noble to hydrogen, the reduction of oxygen to form hydroxyl ions is the cathodic process for galvanic corrosion:



The OH^- ions formed at the cathode and the copper ions formed by the anodic dissolution will be brought together by migration and liquid diffusion, and will combine to form either



or



which are rapidly decomposed or oxidised to



or



or

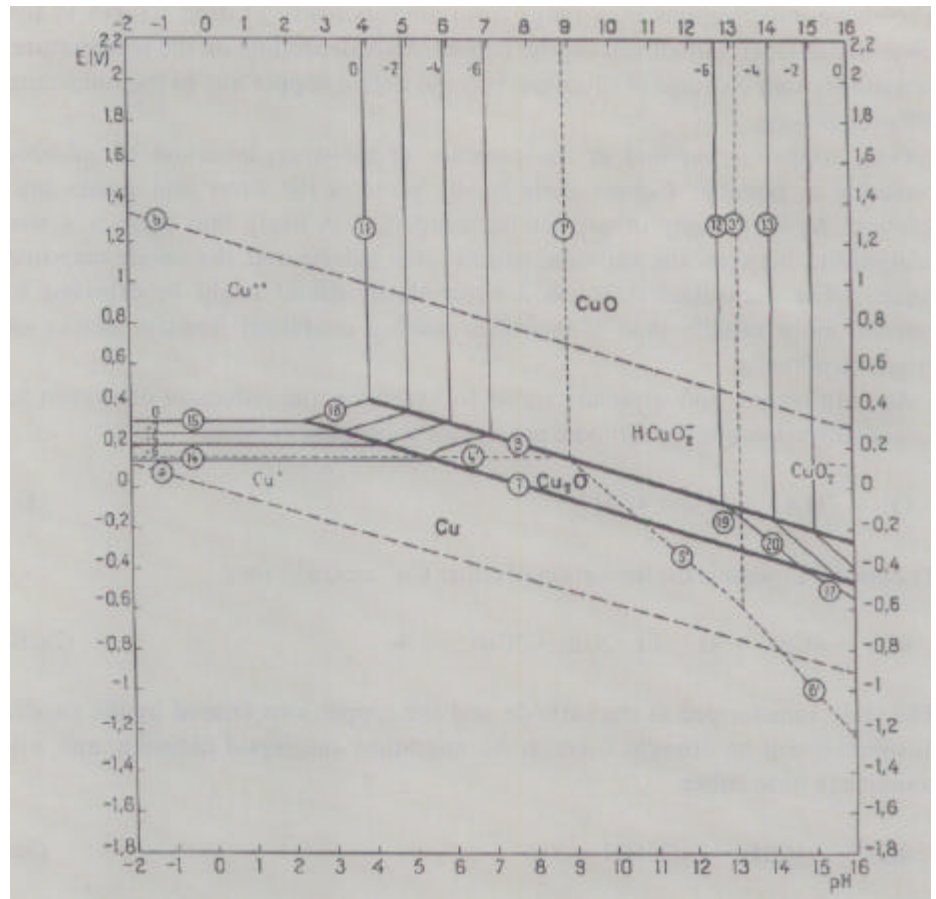


Note that water must be present, but is not consumed.

The intermediate reactions, such as those of Equations 3b and 4b, have been observed within the corroded stored cable, green-blue crystals of cupric hydroxide adhering to the strands, as seen for instance in Figure 2b. The decomposition products of red and black oxides also coexist on this cable.

At high partial oxygen pressures, the corrosion potential in the copper-water system is close to the open-circuit potential of the cathode and hence the potential is shifted to more positive values, and according to the Pourbaix diagram (Fig. 23) the black cupric oxide (CuO) is the stable phase. At low partial oxygen pressures, the corrosion potential is near the open-circuit potential of the anode. This value is more negative and according to the Pourbaix diagram the red cuprous oxide (Cu_2O) is more stable. These factors will account for the observations made during the accelerated Anthony & Brown corrosion test, that when corrosion does occur

Figure 23. Pourbaix diagram for copper-water system



in the strands of a wire or cable:

- the end exposed within the flask has a black (self-sealing?) oxide, and
- the centre part (exposed to a lower partial oxygen pressure) corrodes more extensively due to the formation of red cuprous oxide.

Influence of the ionic elements

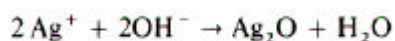
The corrosion of silver-plated copper strands is purely a galvanic process and the influence of the ionic elements that were detected on the processed strand surfaces has not so far been taken into account, nor has the specific electrical conductivity of the corrosive media been considered in the reactions in the last section. A greater corrosion activity can be expected to be associated with high electrolyte conductivities. Ionic elements have a remarkable influence on the resistivity of moisture. Two important elements were found to be present on the corroded shielded cable strands as well as on the wire and cable strands subjected to the accelerated corrosion test; namely chlorides and fluorides.

The chloride reaction with silver platings will form AgCl , which is insoluble in water and can be expected to coat the strand surfaces with a protective film. Opposing this reaction is the effect of fluorine on silver. The silver fluorides, AgF , AgF_2 and Ag_2F are all highly soluble in water, thus activating the strand surface.

It is also interesting to postulate the effect of these elements in the presence of isolated spots of exposed copper. Copper chloride (CuCl_2), is soluble in water and as such activates the small area of exposed copper, whereas copper fluorides (CuF and CuF_2), were insoluble and will tend to passivate such areas and inhibit further reaction. Naturally corroding copper cores will eventually be converted entirely into copper oxides surrounded by a shell of silver plating, as seen in the micro-sections of Figures 6 and 7. However, chlorine and fluorine do play a role in this oxidation reaction, as both were analysed to be present on the fracture surfaces of such oxide-degraded strands (Fig.4). As explained previously, both chloride and fluoride can activate and passivate, depending on the presence of defects in the silver plating. The influence of individual contaminants of the corrosion susceptibility of strands was shown in the results of the accelerated test.

programme (Fig. 12). When the graphs for chlorides and fluorides are considered, it is tempting to assume that the chlorides have protected the silver-plated copper strands against corrosion, but once a defect in the plating is present they increase the apparent amount of corrosion. The fluoride graph shows the reverse effect of corrosion behaviour.

These complex, interrelated, local reactions may be further complicated if the corrosion mechanism known as 'differential aeration' is considered to apply to such insulated wire strands. Differential aeration may create a macro-couple due to variations in the environment encapsulated by the outer insulation, such as differences in oxygen content and differences in pH along the silver-plated surface. The principle effect is, in theory, to cause localised corrosive damage in positions of least aeration and lowest pH. The real effect of this mechanism in the degradation, or thinning, of intact silver-plated layers is due to the fact that any dissolved silver is likely to form a self-sealing passivating film of insoluble silver oxide according to the reaction.



This mechanism can be expected to be slow acting.

The 'bleeding effect' of corrosion sites

Reference has been made to the difficulty of assessing the real extent of galvanic corrosion on wires and cables by visual inspection alone. As corrosion progresses, copper hydroxides are formed between the anodic and cathodic sites, by the migration and diffusion of the OH^- and metal ions. The decomposition and oxidation of CuOH (Eqns. 4a, b) and the decomposition of $\text{Cu}(\text{OH})_2$ (Eqns. 4c) can occur well away from the corrosion site. As can be seen in the micro-sections of Figures 6 and 7, this may cause the precipitation of red and black crystals over a wide area of adjacent strands. This effect calls into question the usefulness of the subjective visual criteria detailed in the accelerated corrosion test method⁸.

Since the corrosion products do not cover the original corrosion pits, they will not markedly influence the kinetics of the red-plague corrosion reaction.

Several hundred reels (spools) of silver-plated wires and cables from both new stock and remaining lengths of reels traced to ESA spacecraft projects were stripped of their insulation layers and examined for evidence of red-plague corrosion. Three lengths of stored cable (one 50 Ω and two 125 Ω RF cables) were found to support isolated patches of red plague on their silver-plated braided shields. No corrosion was seen on the current-carrying inner conductors. From the estimated several hundred kilometres of silver-plated wire products integrated into ESA spacecraft since 1965, this was the first incidence of red-plague corrosion.

The three lengths of corroded cable shields were submitted to extensive metallurgical investigations. In the worst case 3% of the strands making up the braid cross-section had some degree of corrosion, and occasionally the entire copper core of a single strand became converted to copper oxide. Metallography revealed that corrosion had initiated at isolated defects in the nominally 2mm thick silver-plating, and the corrosion products were subsequently precipitated over large surface areas of those shields.

Evaluation of the susceptibility of various wires and cables to red-plague corrosion under the *accelerating conditions of a laboratory test*⁸ shows that:

- When corrosion did occur, there was an insignificant variation between the extent of red plague induced on strands originating from different strand manufacturers.
- Red plague was more severe on braided strands than on inner conductors.
- The extent of corrosion was only marginally affected by the type of insulation material.

Overall conclusions

- d. The plating type and thickness of the plating influences the corrosion susceptibility of the strands. Conductors finished with either pure nickel or pure tin exhibit no form of corrosion from the test environment. Strands finished with 1mm of silver tend to corrode more rapidly than those with a nominal 2mm finish. Strands with defect-free silver finishes of 2mm did not corrode. Strands with Nickel Plus finishes showed only slight corrosion in isolated spots where defects existed in the nickel plating.
- e. There was no significant chemical difference between the average surface composition of strands supplied by different strand manufacturers once they had been processed into wires and cables. EDAX and Auger analyses identified relatively high concentrations of chlorine on the majority of the silver-plated conductors. Although products from different wire or cable processes gave a slight variation in the surface halide concentrations, this could not be correlated with the occurrence or extent of corrosion.
- f. The various manufacturing operations for processing individual silver-plated strands into finished wires or cables modifies the chemical structure of the strand surfaces. A marked increase was found in the copper and fluoride concentrations after processing.
- g. Metallography of the worst-case samples revealed that in any transverse plane less than 3%, of the strands had actually corroded.

Visual inspection used to quantify the extent of corrosion is subjective, due to the widespread precipitation of corrosion products onto strands adjacent to the corrosion site. Metallographic inspection can be used as an additional evaluation, as it will provide more quantitative data.

The onset of red-plague corrosion is totally dependent on the existence of *exposed copper* (resulting from defects in the silver-plated layer on copper strands), *together with* the presence of *moisture*.

This report discusses how moisture can be introduced to the strand surfaces and a mechanism is proposed for the corrosion process. Complex, interrelated surface reactions involving the presence of ionisable halides and the effects of differential aeration may have a secondary role once the basic conditions for the corrosion mechanism exist.

The investigation has not positively identified the direct reason for the corrosion discovered on the three reels described. It is, however, concluded that the basic conditions for red-plague corrosion had existed, i.e. silver-plating imperfection and the presence of moisture.

The mechanical or electrical integrity of wires and cables will not be severely degraded even in the event of corrosion existing to the extent seen on the worst case samples described in this paper.

Recommendations

The general requirements of SLP/2110¹⁰, which cover aspects of design, handling and processing, are adequate and necessary. It is emphasised that a greater effort must be made to follow those requirements.

All stranding and braiding machines must be controlled by wire and cable manufacturers to ensure that they do not damage the continuity of the 2mm silver-plating. If this is an area of concern, it would be expedient to procure strands to a greater nominal silver thickness, (possibly 3 - 4mm).

Humidity control for reels (spools) can be achieved by packaging in a sealed transparent plastic bag (polyvinyl chloride is prohibited). Desiccant or dry-nitrogen filling should be used in the packaging. An easy means for indicating that the humidity content is below 50%, RH should be provided, capable of being read without opening the package.

The accelerated corrosion test⁸ can be used as a screening method for silver-plated wires, particularly for very critical applications.

The authors are especially indebted to Barry Lamb and Paul Claxton at the STL Surface Analysis Centre who provided the AES results. They would also like to acknowledge the help and advice of Hendrik Wessels at ESTEC and those participants from the conductor manufacturing industries.

Acknowledgements

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Manuscript received 10 July 1984