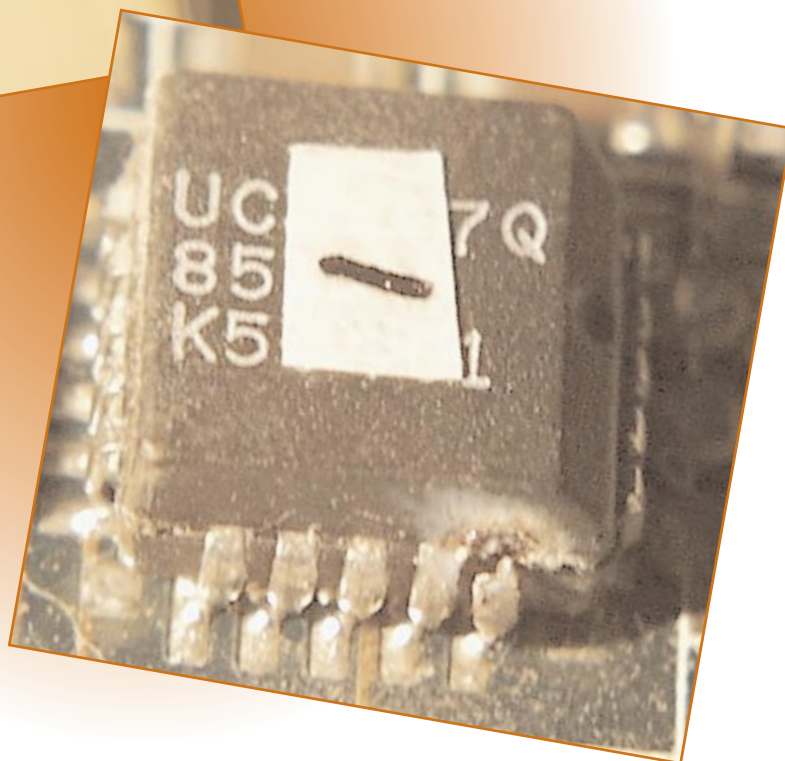




Corrosive Effects of Phosphine, Carbon Dioxide, Heat and Humidity on Electronic Equipment: Phase II

Canadian Leadership
in the Development of
Methyl Bromide Alternatives

Canada 



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Corrosive Effects of Phosphine, Carbon Dioxide, Heat and Humidity on Electronic Equipment: Phase II

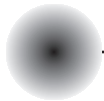
Canadian Leadership in the Development of Methyl Bromide Alternatives

November 1999

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This publication is also available on the world wide web at
<http://www.agr.ca/policy/enviroment>

In collaboration with:
the Methyl Bromide Industry Government Working Group;
Environment Canada; U.S. Department of Agriculture;
Degesch America Inc.; Sunzon Inc.; and the
Canadian National Millers Association.



Acknowledgement

This study was sponsored by the Government of Canada, the United States Department of Agriculture, the Canadian National Millers Association, Degesch America Inc., and Sunzon Inc. with support from the Canadian food processing industry, the Canadian Pest Control Association and David Mueller of Fumigation Service and Supply, Inc., Westfield, IN, U.S.A. This project has been conducted under the auspices of the Canada/U.S. Working Group on Methyl Bromide Alternatives.

Graphic Design and Printing:
Bonanza Printing & Copying Centre Inc., Ottawa, ON



Printed in Canada on Recycled Paper.

Table of Contents

ACKNOWLEDGEMENTS	i
FOREWORD	1
EXECUTIVE SUMMARY	2
FIGURE CAPTIONS	4
INTRODUCTION	7
EXPERIMENTAL	8
RESULTS	
a. Steady-state Exposures for 36 Hours	10
b. Cyclical Exposures for 8 Days	10
c. Forced Failures of Simple Electrical Components	10
d. Ship Fumigation	12
e. Galvanic Corrosion	13
DISCUSSION	
Wet/dry Regimes	13
Effect of Carbon Dioxide Concentration	14
Effect of Phosphine Concentration and Relative Humidity	14
Effect of Temperature	15
Effect of Exposure Time	15
Forced Failures and Cyclical Exposures	15
CONCLUSIONS	16
REFERENCES	17
FIGURES	18
APPENDIX A	32
APPENDIX B	37
APPENDIX C	39

Foreword

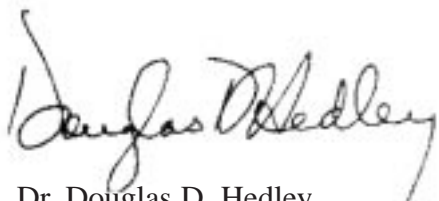
The *Montreal Protocol on Substances that Deplete the Ozone Layer* is a global agreement intended to protect the ozone layer by reducing the production of ozone depleting substances. Developed countries that are signatory to the *Montreal Protocol* - this includes Canada and the United States - must completely phase-out the production and consumption of methyl bromide by the year 2005.

Controls on methyl bromide as an ozone depleting substance have resulted in a critical need for the development of alternatives for its use as a soil, commodity, and structural fumigant. Through government research programs and commercial development of alternative technologies and products, we are making progress but more work is needed to ensure good control of pests and plant diseases in agriculture and food processing.

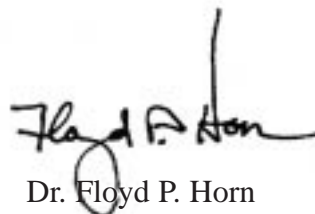
To maximize research collaboration and the development of alternatives, Agriculture and Agri-Food Canada (AAFC) and the United States Department of Agriculture (USDA) created an informal working group on methyl bromide alternatives. Agreement was reached to assist research scientist and industry to work together on common problems and projects and to share research results. Since a significant amount of methyl bromide is used in space fumigations for milling and food processing operations in Canada, and to a lesser extent in the United States, it was proposed that Canada lead this area within the working group. This report represents the third report of jointly funded collaboration between AAFC and USDA research scientists and private industry to develop methyl bromide alternatives.

This report represents the second and final investigation by this working group into the corrosiveness of phosphine. The first report (Phase I) answered many practical questions, however, it raised many more. The second report (Phase II) attempts to address the remaining questions in an effort to provide practical information to potential users of phosphine in field situations and to help ensure effective pest control.

This laboratory experiment also illustrates a key component of success in agri-food development. Research partnerships with industry and other government agencies are a cornerstone of AAFC's and USDA's programs. In this regard, the phosphine corrosion work could not have been conducted without the expertise of Dr. Robert Brigham. Furthermore, we are pleased with the continued advice provided by the industry and, in particular, the insights of David Mueller (Fumigation Service and Supply Inc.) and his provision of electronic equipment exposed to phosphine in the field. We would like to express our thanks for the collaborative effort.



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EXECUTIVE SUMMARY

A preliminary series of steady-state exposure experiments of metals in phosphine (Phase 1) was completed in 1998 which included the following parameters:

- 4 materials (copper, brass, silver and solder)
- 3 temperatures (20, 30 and 40°C)
- 3 phosphine concentrations (35, 135 and 220 ppm PH₃)
- 4 levels of relative humidity (15, 25, 50 and 75%)
- 2 CO₂ levels (3.5 and 5%)
- 3 exposure times (12, 24 and 36 hours).

The preliminary results were presented orally at the 1997 Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions and the final report was published by Agriculture and Agri-Food Canada in 1998.

Based on the results and recommendations of the earlier work, a second series of experiments (Phase II) was undertaken. This study focused on the following four tasks:

Task 1 Expand the database for copper and nickel at intermediate relative humidities (RH) between 25 and 50% to define more closely the transition from wet to dry morphologies. Phase 1 results had clearly shown that copper exposed to phosphine at low relative humidity (25% and lower) developed shiny black wet surface films while at high relative humidity (50% and higher), dry crystalline deposits were formed. While both counter-intuitive and contradictory of anecdotal evidence, these wet/dry regimes have been confirmed in the present study and the transition from wet to dry has been found to occur in the range 35 to 45% RH with 400 ppm PH₃. No wet regime was observed at 85 ppm PH₃.

Task 2 Expand the database for copper and nickel to 400 and 600 ppm PH₃ and 0% CO₂ to more closely reflect current technology. The weight gain (due to the deposition of oxides of phosphorus, either phosphoric acid in the wet regime or copper phosphate in the dry regime) and weight loss (due to the corrosion of copper) data have been obtained in this study for 36-hour exposures at relative humidities ranging from 25 to 75%. These results have been found to complement the data in Phase 1 where PH₃ concentrations did not exceed 220 ppm.

Task 3 Cyclical/repeat exposures were performed to determine the cumulative effect in terms of weight change. Exposures at 220 ppm PH₃ were carried out on copper samples for four periods of 46 hours at both 25 and 75% RH followed by 8 days of aging at 25 and 75% RH. In all cases, weight changes were additive with each additional cycle. Samples originally exposed at 75% RH (dry regime) showed little weight change when aged at either high or low RH. On the other hand, samples originally exposed at 25% RH (wet regime) showed large weight changes during exposure and these weight changes were significantly increased with aging, particularly aging at 75% RH.

Task 4 Forced failures of electrical components were attempted to verify possible failure mechanisms. Possible failure mechanisms identified in Phase 1 included:

-
- high contact resistance due to the build-up of non-conducting surface films;
 - electrical shorting due to the formation of conducting liquid phases; and
 - disruption of circuits due to the corrosion of metals.

Telephone jacks, floppy disk connectors and a relay were used for this investigation and they all proved to be more robust in high concentrations of phosphine than expected. However, persistent exposures demonstrated that all of the proposed failure mechanisms could be achieved.

In addition, copper samples were included in a ship fumigation demonstration project carried out in Toronto on June 5-8, 1999. The results of this field trial using PH_3 were entirely consistent with the laboratory data in terms of both reaction rates and morphology. In the same fumigation, a working computer was exposed until it failed. Investigation showed that failure resulted from the thinning of a lead to an integrated circuit chip due to corrosion and the subsequent over-heating in service.

FIGURE CAPTIONS

- Figure 1. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper (85 ppm PH_3 / 30°C / 0% CO_2)
- Figure 2. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper (85 ppm PH_3 / 30°C / 5% CO_2)
- Figure 3. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper (400 ppm PH_3 / 30°C / 0% CO_2)
- Figure 4. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper (400 ppm PH_3 / 30°C / 5% CO_2)
- Figure 5. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper (600 ppm PH_3 / 30°C / 0% CO_2)
- Figure 6. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper (400 ppm PH_3 / 20°C / 0% CO_2)
- Figure 7. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper (600 ppm PH_3 / 20°C / 0% CO_2)
- Figure 8. Effect of exposure time and aging on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper in four cyclical exposures followed by aging for 8 days (75% R.H.)
- Figure 9. Effect of exposure time and aging on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper in four cyclical exposures followed by aging for 8 days (25% R.H.)
- Figure 10. Picture of female telephone jack showing the bridging of corrosion products between adjacent wire electrodes
- Figure 11. Picture of complete floppy drive connector with factory insert and the broken lead wire
- Figure 12. Picture of a piece of floppy drive connector with a copper bridge completing the circuit used in Expt #43
- Figure 13. SEM picture (secondary electrons) of the copper bridge in Fig. 12 showing the foot print of the brass connector in the surface film
- Figure 14. SEM picture (backscattered electrons) of the copper bridge in Fig. 13 showing the thinned area (where current flowed) as a bright area
- Figure 15. SEM picture (secondary electrons) of the brass contact in Fig. 12 (Expt. #43) showing the accumulated surface film
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- Figure 16. SEM picture (secondary electrons) of the brass contact in Fig. 12 (Expt. #43) after chemical cleaning showing the extensive localized corrosion
- Figure 17. SEM picture (secondary electrons) of the corroded wire from Expt. #55 after chemical cleaning
- Figure 18. Picture of the relay used in exposure experiments
- Figure 19. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper exposed in the ship fumigation in Toronto on June 5 to 8, 1999
- Figure 20. Picture of the hard drive controller card from David Mueller's computer which failed during the Toronto ship fumigation
- Figure 21. Picture of the chip (designated "1" in Fig. 20) showing the location of the hot spot in a lead near the body of the chip
- Figure 22. SEM picture (secondary electrons) of the failed lead in Fig. 21
- Figure 23. EDAX spectrum of the corrosion products in the vicinity of the failure in Fig. 22
- Figure 24. Summary of weight gains (due to the deposition of oxides of phosphorus) and weight losses (due to corrosion) of copper exposed for 36 hours at 30°C to 400 ppm PH₃ at various relative humidities comparing the effect of 0% and 5% CO₂
- Figure 25. Summary of weight gains (due to the deposition of oxides of phosphorus) and weight losses (due to corrosion) of copper exposed for 36 hours to 30°C and 0% CO₂ to various relative humidities and phosphine concentrations
- Figure 26. Summary of weight gains (due to the deposition of oxides of phosphorus) and weight losses (due to corrosion) of copper exposed for 36 hours to 30°C and 5% CO₂ to various relative humidities and phosphine concentrations
- Figure 27. Summary of weight gains (due to the deposition of oxides of phosphorus) and weight losses (due to corrosion) of copper exposed for 36 hours to 20°C and 0% CO₂ to various relative humidities and phosphine concentrations
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CORROSIVE EFFECTS OF PHOSPHINE, CARBON DIOXIDE, HEAT AND HUMIDITY ON ELECTRONIC EQUIPMENT: PHASE II

Introduction

A preliminary series of steady-state exposure experiments of metals in phosphine (Phase 1) was completed in 1998 involving the following parameters:

- 4 materials (copper, brass, silver and solder)
- 3 temperatures (20, 30 and 40°C)
- 3 phosphine concentrations (35, 135 and 220 ppm PH₃)
- 4 levels of relative humidity (15, 25, 50 and 75%)
- 2 CO₂ levels (3.5 and 5%)
- 3 exposure times (12, 24 and 36 hours).

The results were presented orally at the 1997 Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions and the final report was published by Agriculture and Agri-Food Canada(1).

Based on the results and recommendations of this study, a second phase (sponsored by the Government of Canada, the USDA, the Canadian National Millers Association, Degesch America Inc., and Sunzon Inc.) focused on the following tasks:

Task 1 Expand the database for copper and nickel at intermediate relative humidities (RH) between 25 and 50% to define more closely the transition from wet to dry morphologies. Phase 1 results clearly showed that copper exposed to phosphine at low relative humidity (25% and lower) developed shiny black wet surface films while at high relative humidity (50% and higher), dry crystalline deposits were formed.

Task2 Expand the database for copper and nickel to 400 and 600 ppm PH₃ and 0% CO₂ to more closely reflect current technology.

Task 3 Cyclical/repeat exposures to determine the cumulative effects of repeated fumigations in terms of weight change. Exposures at 220ppm PH₃ were carried out on copper samples for four periods of 46 hours at both 25 and 75% RH followed by 8 days of aging at 25 and 75% RH.

Task 4 Forced failures of electrical components to verify possible failure mechanisms identified in Phase 1 including:

- high contact resistance due to the build-up of non-conducting surface films;
 - electrical shorting due to the formation of conducting liquid phases; and
 - disruption of circuits due to the corrosion of metals.
-

In addition to the work outlined above, copper samples were included in an experimental ship fumigation that involved various concentrations of phosphine and was carried out in Toronto on June 5-8, 1999. A working computer was also exposed during this trial until it failed.

Experimental

The experimental approach in this study was identical to that in the earlier Phase 1 work in which the experimental apparatus was designed to facilitate the manipulation of all the variables independently. To accomplish this, an air stream (1 litre/min) was saturated with water at low temperature in one Haake Model K constant temperature bath (to give 100% RH) and then the temperature of that stream was increased in a second Haake bath to the test temperature (20, 30 or 40°C) to give a lower pre-determined RH. In addition, CO₂ (from a cylinder of pure compressed gas) and PH₃ (from a N₂ - 1%PH₃ gas mixture) were bled into the second bath for pre-heating and mixing. This dilution lowered the RH in the carrier stream and that was adjusted by trial and error to the desired level as indicated by a VWR hygrometer. Gas flow rates were controlled by mass flow meters and the resulting PH₃ concentration was monitored periodically throughout the 36-hour experiments with a PortaSens PH₃ meter. CO₂, air and N₂ flow rates were measured at the beginning and end of each experiment with soap-bubble flow meters and the long-term stability was found to be within the $\pm 2\%$ accuracy claimed by the manufacturer of the mass flow meters.

For Tasks 1 and 2 which were performed to expand the existing data base, the earlier techniques were repeated. In this case, each run was started by placing 8 weighed metallic samples (quadruplicate samples of Cu and Ni) with dimensions of approximately 50 x 13 x 0.1mm (surface area of 0.13 dm²) in polyethylene cups with sides and top partially removed to allow free access and exit of the gas. The samples were mounted in the cups in a parallel orientation as had been adopted in the earlier work. Copper (99.9%) and nickel (99+%) with as-rolled surfaces were exposed. The samples were chemically cleaned in 50/50 HCl for 2 minutes before exposure. The cups containing the samples were placed in 3 chambers and the gas stream was routed to give exposures of 12, 24 and 36 hours. Steady state conditions of temperature and relative humidity as indicated by the digital hygrometer were achieved with a mixture of air, CO₂ and N₂. When the system had stabilized, the hygrometer was removed and a two-way valve was turned to replace the N₂ stream with the N₂ - 1% PH₃ mixture. Thereafter, bath temperatures and the PH₃ concentration were monitored regularly to ensure stability.

After each run, the samples were re-weighed in the as-removed condition, cleaned to bare metal by immersing in inhibited 50/50 HCl for 2 minutes and re-weighed.

In the case of the cyclical experiments, the technique was modified slightly. Nine copper samples were mounted parallel in each cup and the series of experiments was begun with samples exposed in chamber 1 (the inlet point) and chamber 2 (into which chamber 1 exhausted). After 46 hours of exposure to 220 ppm PH₃ at either 25 or 75% RH, the phosphine was switched off and the system flushed. The samples in chamber 1 were left in place but those in chamber 2 were removed and replaced with a cup containing 9 new samples. The desired flow rates and relative humidity were re-established and the phosphine flow was started again after a 2-hour interruption. After a further 46-hours, a new sample cup with 9 additional copper samples was inserted in chamber 3 during the 2-hour re-calibration period. After the fourth 46-hour exposure, all the samples were removed.

From each cup containing 9 samples, 3 samples were removed for weighing, cleaning in HCl and re-weighing. A further 3 samples were weighed and then transferred to a container for aging at room temperature for 8 days at nominally 25% RH and the remaining 3 samples were weighed and then transferred to a container for aging at room temperature for 8 days at nominally 75% RH. The closed containers in which the aging was carried out contained saturated solutions of potassium acetate (22.5% RH at 25°C) and sodium chloride (75.5% RH at 25°C)(2). After aging, the samples were weighed, cleaned and re-weighed in the standard way.

In an attempt to force simple electrical components to fail, telephone jacks, floppy disk connectors and a relay were used in laboratory exposures. Telephone jacks were chosen initially for exposure and the concept was to monitor the resistance of the connection continuously as a function of time generally following ASTM B 539, Test Method C(3). This “dry circuit testing” technique uses a potential of 0.020V and limits the current to 100mA. An EG&G Princeton Applied Research Model 363 potentiostat was used to supply the constant DC voltage and to monitor the resultant current. After initial tests in which telephone jacks could not be made to fail, they were used as connectors in subsequent exposures of floppy disk connectors and the relay. The exposure conditions for the testing performed are listed below.

Expt No.	Component	Temp °C	PH ₃ ppm	RH %	Time
37	Telephone jack - as received	30	400	75	48 hrs
38	Telephone jack - degreased	30	600	75	46.5 hrs
39	Telephone jack - degreased	30	600	25	46 hrs + repeated exp
40	Telephone jack - scraped to Cu	30	600	25	46.5 hrs
41	Floppy disk connector - as received	30	600	25	46.5 hrs + repeated exp
42	Floppy disk connector - Cu bridge	30	600	75	46.5 hrs + aging
43	Floppy disk connector - Cu bridge	40	600	25	46 hrs + aging
44	Floppy disk connector - brass	40	600	25	46 hrs + aging
45	Floppy disk connector - brass	40	600	75	46 hrs + aging
46	Relay	40	600	75	46.5 hrs + aging
47	Floppy disk connector - Cu & brass	40	400	75	46.5 hrs
48	Relay - close only with no PH ₃	40	400	75	20 hrs
49	Relay - close only with no PH ₃	40	600	75	19.5 hrs
50	Relay - close only with no PH ₃	30	400	75	23.5 hrs
51	Relay - close only with no PH ₃	30	220	75	55 hrs
52	Floppy disk connector-brass-hi amp	room	400	50	21.8 hrs
53	Floppy disk connector-brass-hi amp	room	400	50	25 hrs
54	Floppy disk connector-brass-hi amp	room	400	50	5.25 hrs
55	Floppy disk connector-brass-hi amp	room	400	50	5% CO ₂ , repeated exp

In Experiment #41, factory components were used and the current was passed between two adjacent electrical contacts. In subsequent tests the connector was cut into smaller parts of 2 or 3 pairs of opposed electrical contacts and the connecting bridges were fabricated from small copper blocks approximately 1mm thick or brass shim stock 0.1mm thick formed into a “U” and inserted between the opposed electrical contacts. In the cases where the conducting bridge was fabricated from copper or brass, the current was passed through the bridge from opposing contacts. In experiments where high currents were used to induce failure, a Hewlett Packard Model 6030A power supply was used.

Results

a. Steady-state Exposures for 36 Hours

During the steady-state exposures, phosphine is oxidized by water vapour and copper by the oxygen in air. These oxidation reactions result in surface deposits, either wet or dry, and a weight gain. These weight gains are listed in the tables in Appendix A for copper. The tables of data also indicate whether samples were wet or dry when removed. Nickel showed no weight gain or loss under any exposure condition and no P signature was found with energy dispersive analysis by x-rays (EDAX) on nickel surfaces exposed under aggressive conditions (600 ppm PH_3 , 25% RH and 30°C) for 36 hours.

The corrosion products on copper, whether wet (phosphoric acid) or dry (copper phosphate) were removed to bare metal by immersion in 50/50 HCl, a non-oxidizing acid. However, the black shiny deposit observed in some cases on wet samples was only sparingly soluble and required some scrubbing for removal. The resulting weight loss of the copper samples gives the corrosion rate of the metal. Weight losses after stripping to bare metal are also given in Appendix A.

The weight gain and weight loss data presented in Appendix A are plotted in Figures 1 to 7 as averages for the quadruplicate samples. Note that oversize samples were used for exposures at 85 ppm PH_3 .

b. Cyclical Exposures for 8 Days

Weight change data during repeated exposures of 46 hours (nominally 2 days) to 220 ppm PH_3 at 25 and 75%RH and further weight changes during 8 days of aging at 25 and 75%RH are presented in Appendix B. These data are plotted in Figures 8 and 9 as averages for the triplicate samples. In Fig. 8, data for 4 and 6 day exposures have not been plotted because they deviated from the trend line as a result of inadequate experimental control of the phosphine concentration. However, they have been listed in Appendix B. Because of the very large weight gains at 25%RH, the wet mode, the PH_3 concentration was depleted by the first samples in the gas stream (the 8 day samples in chamber 1) so that down-stream samples saw only reduced phosphine concentrations. Measured phosphine concentrations at the exhaust of chamber 3 were approximately 205 ppm after 2 days, 150 ppm after 4 days, 135 ppm after 6 days and 125 ppm after 8 days. These PH_3 concentrations were sufficiently low that samples exposed for 4 and 6 days in down-stream positions exhibited a dry morphology as noted in Appendix B.

c. Forced Failures of Simple Electrical Components

After the initial concept to study failure mechanisms by monitoring the resistance change in telephone jacks proved to be overly simplistic, the various attempts which were improvised to cause failures in electrical components are tabulated above. They involved:

Telephone Jacks

The metallic contacts in female telephone jacks are fabricated from copper wire coated with nickel and finally a thin flash of gold. Small defects in the Ni coating are inevitable and make possible the

corrosion of the underlying copper and the generation of corrosion products which can increase contact resistance. In Experiments 37, 38 and 40, the telephone jacks showed no changes in resistance in nominally 2 days at 400 and 600 ppm PH_3 . The telephone jack in Expt. 39 was exposed for 46 hours and then repeatedly through Expt. 55 for a total of 30 days. When dis-assembled, corrosion products had caused bridging between the electrode wires as shown in Fig.10 and a re-examination of the resistance records suggest that bridging first occurred after approximately 22 days. The extent of the short-circuit was measured with the “dry circuit” set-up consisting of a potentiostat giving a DC voltage of 0.020V and a current limiting resistor of 0.230S which restricted the current to 87.0mA. In the female telephone jack, the wires are arranged black, red, green and yellow and the steady-state currents were: black to red - 7.2 μA , black to green - 6.6 μA , black to yellow 0 μA and red to green 10.3 μA . Initial currents were higher but quickly decreased to these steady-state values. Telephone jacks were so robust that they were used throughout as “quick connectors”. In Expt.55 where the circuit was subjected to high currents which were increased in a step-wise fashion, the telephone jack failed after 17 minutes at 5.0A as a result of melting of the plastic components.

Floppy Disk Connectors

A 486 computer mother board which Paul Fields(4) had fumigated for 3 days at 1000 ppm PH_3 in the Toronto ship fumigation trial showed extensive build-up of corrosion products on some of the brass contacts which appeared to be very similar to floppy disk drive connectors - electrical components which are readily available. In Expt. 41, a floppy disk connector with factory insert was exposed for 46.5 hours at 600 ppm, then repeatedly through Expt. 43, then aged 2 days in air and then repeatedly re-exposed in Expt. 45 through 50. At that point, after 17 days, one of the lead wires broke at the soldered joint as shown in Fig. 11.

In Expt. 42, a small piece of a floppy disk connector with a copper bridge completing the circuit was exposed at 30°C to 600 ppm PH_3 and 75%RH for 46.5 hours. This exposure was expected to produce a dry morphology but both the copper bridge and the brass connectors were wet when the sample was removed. Because other exposed copper on the sample showed the dry morphology, it was obvious that local heating at the contact due to the monitoring current was sufficient to lower the relative humidity locally to values causing the wet morphology. Wet contacts did not show an increase in electrical resistance but when #42 with wet contacts was aged at 75% RH, the wet area appeared to dry with time and after 11 days the resistance went to infinity. The sample is shown in Fig.12. Experiment 43 was exposed at higher temperature (40°C) in the wet regime for 46 hours but showed no change in resistance until aged at 75%RH for 23 days. Some sign of impending failure could be obtained by gently squeezing the assembly during the aging process and noting a change in resistance due to the slight motion at the contact points. This type of failure resulting from the build-up of non-conducting surface films was characterized with the scanning electron microscope (SEM). Figure 13 shows the foot print of the brass connector in the copper phosphate corrosion products covering the copper bridge. When observed with backscattered electrons (BSE) in Fig. 14, the thin spots in the surface films at the point of electrical contact become obvious because the metallic copper reflects electrons more efficiently than the coating and appears bright. The brass connector with corrosion products is shown in Fig. 15 and when chemically cleaned, Fig. 16, extensive corrosion is observed.

In Expts. 44 and 45, thin pieces of brass bent into a “U” were used as the bridging material in the

cut-up floppy drive connectors because they were less rigid and more likely to fail. Wet (#44 at 25% RH) and dry (#45 at 75% RH) morphologies were compared in these experiments at high temperature and high phosphine concentration followed by aging at 75% RH. In the wet sample, the resistance rose gradually by approximately 25% throughout the aging period until it failed after 28 days. In the dry sample, the resistance started to increase after 25 hours of aging, doubled after 46 and failed at 58 hours.

Expts. #52 to #55 used pieces of floppy drive connectors with brass “U” bridges to evaluate resistance changes under high current conditions. In #52, a current of 2.0A was passed before and during phosphine exposure to keep the contact area hot and free of liquid phases. Open circuit occurred after 21.8 hours. In #53, liquid phases were encouraged by starting the phosphine first and warming the assembly gently with 5 warming cycles of 2.0A lasting one minute every 15 minutes at the beginning of a 4 hour exposure in phosphine. The current was the switched on continuously for 21 hours at 2.0A, 3.5 hours at 3.0A, 1 hour at 3.5A and 19.5 hours at 4.0A. No increase in electrical resistance occurred. In #54, 5.0A caused rapid failure but in the telephone jack connector. Experiment #55 ran for 11 days in the wet mode in 400 ppm PH_3 and 5% CO_2 with no increase in resistance. After removal, extensive corrosion was observed to have occurred in the wet mode on copper wire at one of the soldered joints. The extent of attack is shown in Fig. 17 after chemical cleaning.

Relay

Because stationary contacts proved to be more robust than expected, a series of exposure experiments were carried out on moving contacts using a relay of the type shown in Fig. 18. In Expt.# 46, the relay was exposed to 600 ppm PH_3 at 40°C and 75% RH for 46.5 hours with no effect on contact resistance. However, the contacts were wet when the dry mode had been expected but other exposed copper parts were dry. Local heating in PH_3 during the resistance measurements was believed to have lowered the relative humidity locally resulting in the wet regime. Aging a further 47.5 hours in laboratory air at approximately 25°C resulted in a tripling of the contact resistance. In subsequent experiments with the relay, the system was flushed before the solenoid was activated to ensure that the contacts would remain dry. At 40°C and 75% RH, contact resistance became infinite between 7.5 and 20 hours at 400 ppm PH_3 (#48) and between 7 and 19.5 hours at 600 ppm (#49). At 30°C and 75% RH, the relay failed due to high contact resistance in 23.5 hours at 400 ppm (#50) and in 55 hours at 220 ppm (#51)

d. Ship Fumigation

Triplicate copper samples were exposed in the Toronto ship fumigation trial in combination with its efficacy studies. The weight change data are given in Appendix C and the average values are plotted in Fig. 19. Visual examination of the samples 2 weeks after they were removed showed some evidence of shiny black areas on every sample exposed to phosphine but most of the areas were small and none exceeded 15 or 20% of the total surface area. This observation indicates that the exposure had occurred close to the wet/dry boundary but definitely on the “wet” side (less than approximately 45 or 50% RH). Paul Fields later confirmed that the relative humidity varied from 32 to 48% with temperatures in the range 20 to 30°C.

During the fumigation, David Mueller of Fumigation Service and Supply, Inc., exposed an old but working “Zenith Data Systems” computer to 500 ppm PH_3 and relative humidity in the range of

approximately 35 to 45% in the hold. It failed after approximately 25 hours with the error message “bad hard drive controller” displayed. The computer was taken apart in the laboratory and the hard drive unit exposed. When the power was switched on to reconfirm the error message, a hot spot was observed through a hole in the hard drive housing and the computer failed completely. The hot spot was traced to the hard drive controller card shown in Fig. 20 and particularly to the integrated circuit or chip labelled “1”. A close-up of the melted lead (which is made of copper coated with Pb-Sn solder) is shown in Fig. 21 and the SEM picture of the failure and the EDAX spectrum confirming P in the corrosion products are shown in Figs. 22 and 23, respectively. The chip labelled “2” in Fig. 20 was found to have a similar failure which is believed to account for the original error message and most of the remaining leads showed at least some copper phosphate corrosion products indicating that attack was a general phenomenon.

e. Galvanic Corrosion

Because corrosion of copper in phosphine in the wet regime had been noted in combination nickel and solder coatings, copper samples with area of 0.13dm² were exposed in triplicate to 86 and 43% H₃PO₄ with and without electrical coupling to equal areas of nickel sheet and solder-coated copper sheet. The average weight changes after 72 hours are given below.

Sample Area 0.13 dm ²	Copper	Copper coupled to solder	Copper coupled to nickel
86% H ₃ PO ₄	Nil	Nil	Nil
43% H ₃ PO ₄	-0.1 mg	Nil	+0.1 mg

Discussion

Wet/Dry Regimes

The behaviour of copper, ie. wet at low relative humidity and dry at high, is unexpected and counter-intuitive. However, the effect has been confirmed consistently in this study as well as in the ship fumigation field trial.

During the exposures, the phosphorus in phosphine can be oxidized from the -3 valence state to higher oxidation states at metal surfaces in the presence of water vapour according to the following reactions(5):

- P oxidized from -3 to +1 (catalysed by Cu, Ni, Pd, C)

$$\text{PH}_3 + 2\text{H}_2\text{O} = \text{H}_3\text{PO}_2 + 4\text{H}^+ + 4\text{e}^-$$
 (orthophosphorous acid)
- P oxidized from -3 to +3

$$\text{PH}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 6\text{H}^+ + 6\text{e}^-$$
 (phosphorous acid)
- P oxidized from -3 to +5

$$\text{PH}_3 + 4\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 8\text{H}^+ + 8\text{e}^-$$
 (phosphoric acid)

Copper is thermodynamically stable in non-oxidizing acid solutions such as orthophosphorous, phosphorous and phosphoric acid and, consequently, does not corrode in these solutions. This has been confirmed experimentally in the study of galvanic corrosion in 86 and 43% H₃PO₄ discussed above. However, copper does oxidize (corrode) in air at a rate controlled by the availability of

oxygen and any tendency to slow this process by means of protective passive films is prevented by the low pH solution. Any copper oxidized to Cu^{++} by oxygen in the air will dissolve in phosphoric acid (a liquid phase) where it can combine to produce copper phosphate (a solid phase). It appears that the choice of wet/dry morphology depends on subtle differences in the oxidizing power of the gas stream as a function of relative humidity. Higher RH results in more oxidizing conditions and the tendency to produce more Cu^{++} ions which are available to form dry copper phosphate.

In the earlier Phase 1 study, data were gathered at 15, 25, 50 and 75% RH and 20, 30 and 40°C. With 135 and 220 ppm PH_3 and 3.2 to 5% CO_2 , the transition between wet and dry morphologies occurred between 25 and 50% RH. No wet morphology was observed at 35 ppm PH_3 . In this study which had the objective of defining the transition more closely, no wet morphology occurred at 30°C with 85 ppm PH_3 but at 400 ppm, the transition as noted by visual observation occurred between 35 and 45% RH depending on the CO_2 concentration. Weight change data given in Fig. 24 suggest a wet/dry transition at slightly higher relative humidity.

At 20°C with 600 ppm PH_3 , the wet morphology persisted at 25, 50 and 75% RH.

As a general observation, wet surface deposits will occur on copper exposed to greater than approximately 100 ppm phosphine at ambient temperatures if the relative humidity is below approximately 50%.

Effect of Carbon Dioxide Concentration

The effect of different CO_2 concentrations (0% vs. 5.0%) can be compared directly in Fig. 24. At 400 ppm PH_3 , CO_2 has a small effect in promoting the onset of the wet regime at lower relative humidity (as indicated by a sudden increase in weight gain) and in increasing the total weight gain associated with wetness. CO_2 has no effect on weight loss values over the range of relative humidity from 25 to 75%.

As a general observation, CO_2 concentration has no effect on the behaviour of copper in phosphine.

Effect of Phosphine Concentration and Relative Humidity

Fig. 25 and 26 effectively summarize the effect of phosphine concentration and relative humidity on the weight gain (due to the deposition of surface films) and weight loss (due to corrosion) of copper after 36 hours at 30°C both with and without CO_2 . The data in Fig. 25 were generated in this study (Phase II) while those in Fig. 26 include both this study and the earlier work (Phase I) at 135 and 220 ppm PH_3 . Based on overall trends, gaps in the data have been interpolated as shown. As noted above, rapid increases in weight gain with decreasing RH are associated with the onset of the wet regime.

As a general observation, surface deposits, either wet or dry, increase with phosphine concentration with the magnitude of the weight gain being greater in the wet regime. On the other hand, the corrosion rate of copper depends only on the phosphine concentration.

Effect of Temperature

Decreasing the temperature from 30 to 20°C results in significantly less weight change in copper. The data in Fig. 27 can be compared with that in Fig. 25 to show that weight changes have been moderated by approximately a factor of 2 by lowering the temperature. These data confirm the trends that had been reported in the earlier Phase 1 work.

As a general observation, higher temperatures result in more surface films and more corrosion on copper.

Effect of Exposure Time

Reaction kinetics of copper in PH_3 as measured by weight change had been observed in Phase 1 work to be linear with time or to accelerate with time. An accelerating weight increase was attributed to the fact that nucleation was observed to occur at a number of points on the surface followed by growth of these deposits with time until they impinged leading to complete surface coverage and subsequent linear kinetics. Figures 1 to 7 indicate that the same behaviour has occurred in this study. Weight gain kinetics are seen to vary from linear to accelerating but the magnitude is highly dependent on relative humidity. On the other hand, weight loss kinetics tend to be linear and less dependent on relative humidity as would be expected since the reaction rate is controlled by oxygen availability.

As a general observation, surface films and corrosion rates on copper increase roughly linearly with time.

The weight changes in Appendices A, B and C and plotted in Figures 1 to 7 have been normalized in subsequent figures to weight change per unit area (milligrams per square decimeter) which can be converted into corrosion rates. For copper, a weight loss of 1 milligram per square decimeter per day (1 mdd) is equivalent to a penetration rate (on a planar interface) of 0.004 mm/year (0.00016 inches per year).

Forced Failures and Cyclical Exposures

In sophisticated electronic equipment, simple devices such as fixed or moving contacts were assumed to be the weak links leading to rapid failures but they have proved to be much more robust than expected even when exposed in a very aggressive way to phosphine. Of the three possible failure modes which had been identified, namely:

- high contact resistance due to the build-up of non-conducting surface deposits
- electrical shorting due to the formation of conducting liquid phases
- disruption of circuits due to the corrosion of metals,

the first, high contact resistance due to the accumulation of dry copper phosphate, had been assumed to predominate. However, experimentation proved that while this mechanism is possible, particularly on moving contacts, it is difficult to achieve in a circuit with even a small current flowing. Local heating at the contact tended to lower the relative humidity locally and induce the onset of the wet regime. Relay contacts failed due to the build-up of dry copper phosphate in less than 20 hours in 400 and 600 ppm PH_3 at 40°C and at 30°C in 23.5 hours in 400 ppm PH_3 and 55 hours in 220 ppm PH_3 . However, to achieve this result, the electrical resistance measurements could be

taken only after the system had been flushed to remove PH_3 . While this restricted condition was necessary in the laboratory to maintain dry conditions, dry conditions would be common in an actual fumigation because the power would be turned off and no local heating could occur.

When electric current was passed through a contact in the presence of PH_3 , the contacts invariably became wet and in that condition continued to pass current without an increase in resistance. Only after the wet contact was removed from the PH_3 environment, and aged in air, did failures occur. The aging process appears to involve the conversion of hydrogen phosphate (phosphoric acid), a liquid, to copper phosphate, a solid, as Cu^{++} ions become available through the oxidation of copper by the oxygen in air. This “drying” or, more correctly, chemical conversion, process eventually leads to sudden increases in resistance and open circuit failures but these typically occurred only after several days. The copper ions required for this chemical conversion from wet to dry come from the contact itself and considerable corrosion has been observed to take place as shown for example in Fig. 16.

Copper wires also corrode in PH_3 and after removal from PH_3 with a morphology characterized by deep localized attack as shown in Fig. 17. This localized thinning of copper conductors is believed to lead to hot spots which further exacerbate corrosion kinetics. In Expt. #41, a copper lead wire failed after approximately 2 weeks of repeated exposures to high PH_3 concentrations. Local hot spots also lead to the failure of David Mueller’s computer, first during shipboard fumigation trial where an error message was displayed and subsequently in the laboratory where the melting of a copper lead was observed.

The final proposed failure mechanism, shorting between conductors, has also been demonstrated. However, at least 3 weeks of cyclical exposures were required to get the result shown in Fig. 10.

The data generated in this study on cyclical exposures speaks directly to the mechanisms of forced failures. While repeated exposures in the dry regime produce weight changes which are additive, further aging at high or low relative humidity is quite benign as shown in Fig. 8. However, when repeated exposures are carried out in the wet regime, weight changes are still additive but much larger as shown in Fig. 9. It should be noted that the vertical axis in Fig. 9 is a factor of 10 larger than that in Fig. 8. While aging wet copper samples in air after exposure to PH_3 increases the weight gain only at high relative humidity, the amount of corrosion triples in 8 days at low RH and increases by a factor of 6 at high RH. The potential long-term danger to copper electrical components is clear if they have been exposed to PH_3 , either once or repeatedly, in the wet regime and this study has shown that it is difficult to avoid the wet regime if currents are flowing.

Conclusions

1. The data generated in this study in combination with the earlier work has expanded the database of weight gain and weight loss results to encompass PH_3 in the range 35 to 600 ppm, relative humidity in the range 15 to 75%, CO_2 in the range 0 to 5%, temperatures of 20, 30 and 40°C and exposure times up to one month. The trends are clear and, with the exception of the wet/dry regimes, serve to quantify already existing anecdotal knowledge.

2. This study has confirmed that copper develops shiny black wet surface deposits at low relative humidities and dry crystalline surface deposits at high relative humidities. A possible explanation is that wet/dry morphology depends on subtle differences in the oxidizing power of the gas stream as a function of relative humidity. Higher RH promotes the oxidation of copper to Cu^{++} ions and makes possible the formation copper phosphate (a solid phase) by combination with phosphoric acid (a liquid phase).

3. Simple electrical components were found to be much more robust than expected when exposed to phosphine but have been made to fail due to:

- high contact resistance due to the build-up of non-conducting surface deposits;
- electrical shorting due to the formation of conducting liquid phases; and
- disruption of circuits due to the corrosion of metals.

References

1. Corrosive Effects of Phosphine, Carbon Dioxide, Heat and Humidity on Electronic Equipment, Environment Bureau, AAFC, August 1998.
2. Paul W. Winston and D. H. Bates, Ecology, vol. 41, no.1, pg.232, 1960.
3. ASTM B 539, Standard Test Method for Measuring Contact Resistance of Electrical Connections (Static Contacts), Test Method C, Dry Circuit Testing.
4. Dr. Paul Fields, Agriculture and Agri-Foods Canada, Cereal Research Centre, private communication, 1999.
5. M. Pourbaix, Atlas of Electrochemical Equilibria In Aqueous Solutions, NACE/Cebelcor (1974), p. 509.

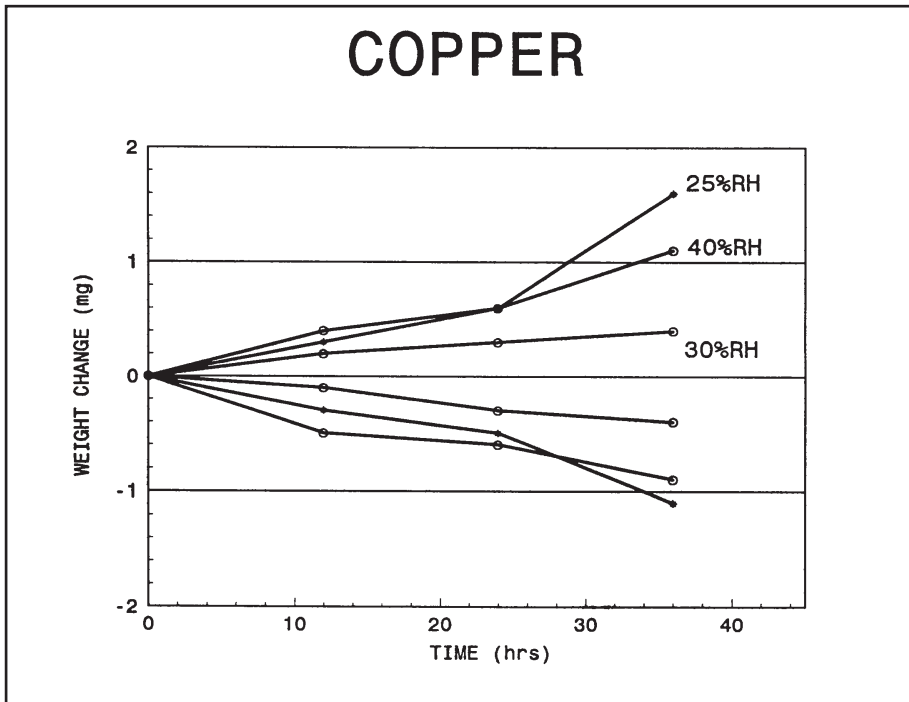


Figure 1. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

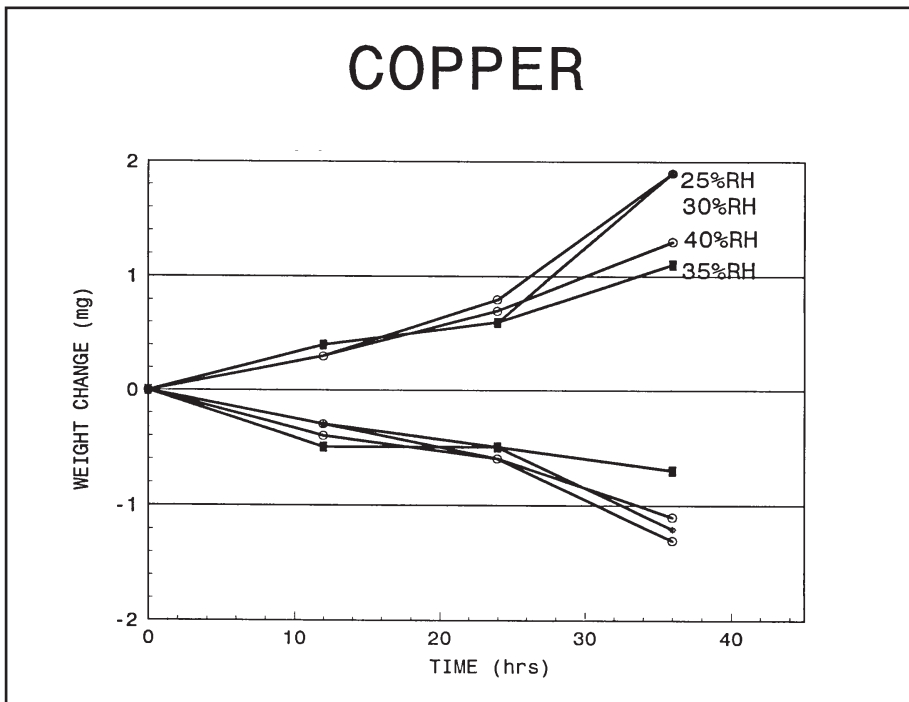


Figure 2. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

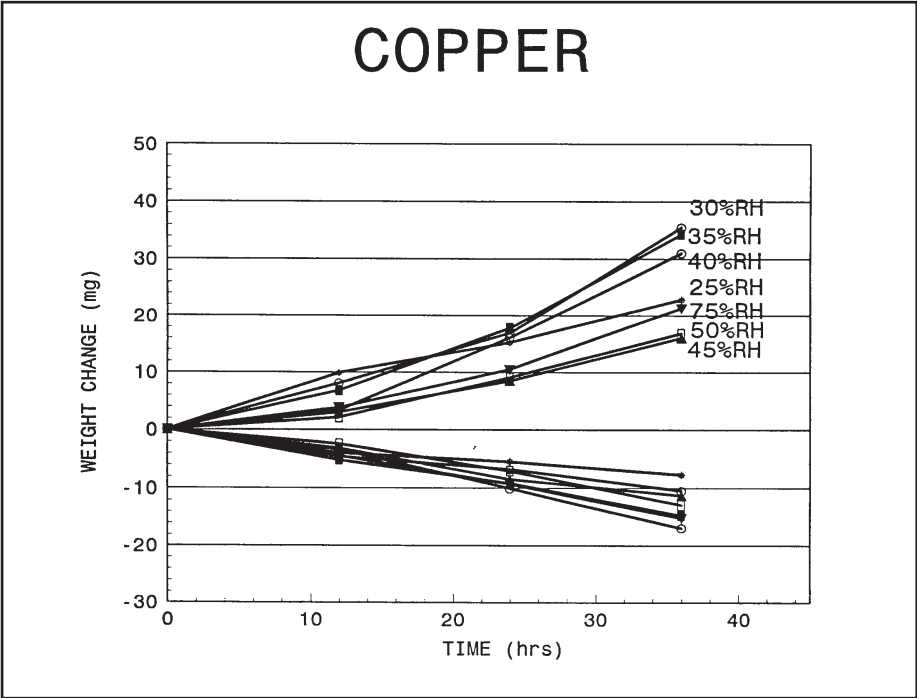


Figure 3. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

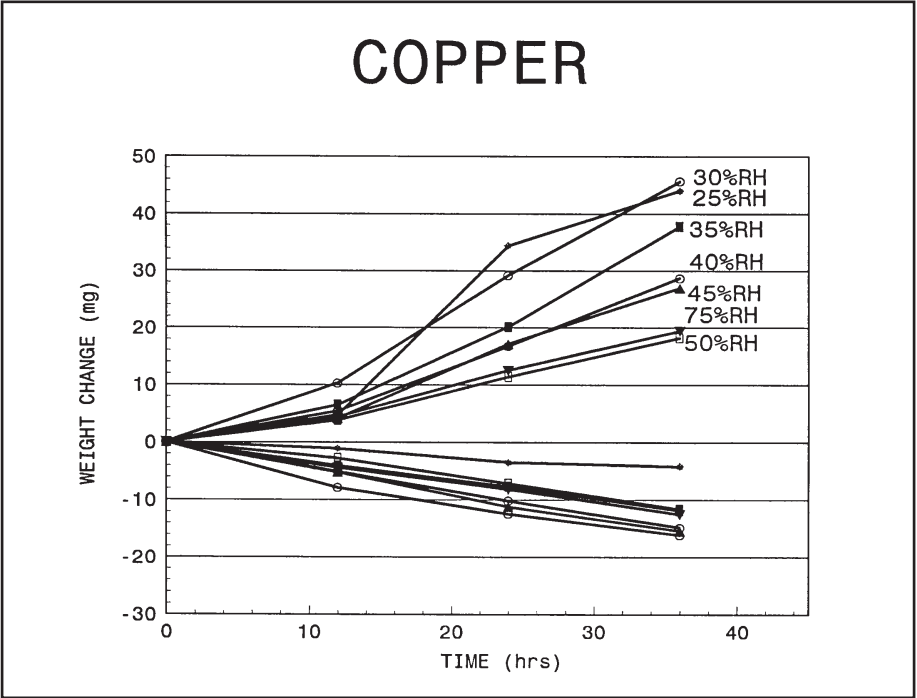


Figure 4. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

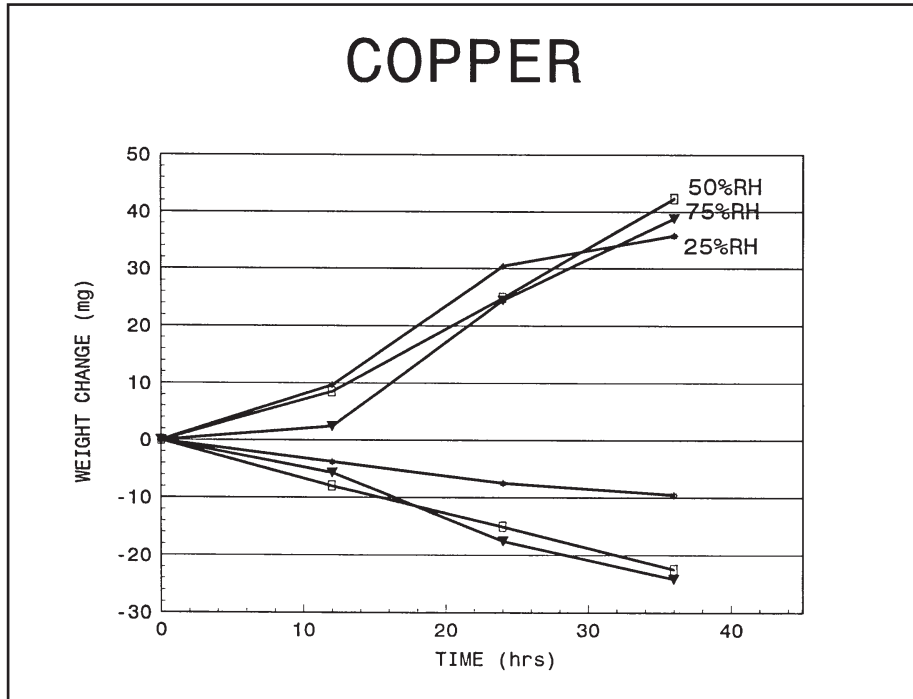


Figure 5. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

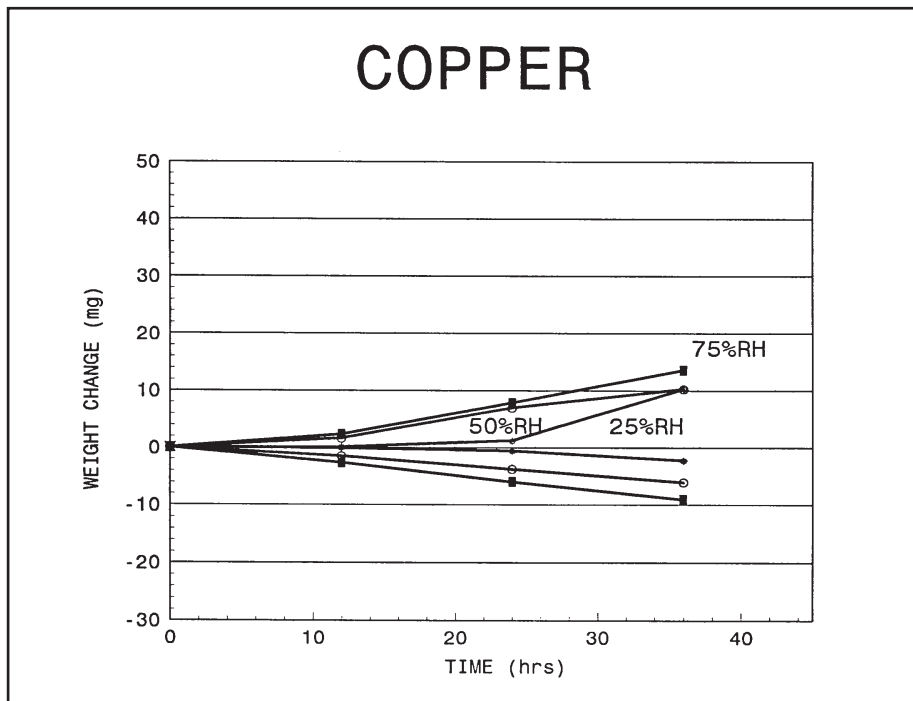


Figure 6. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

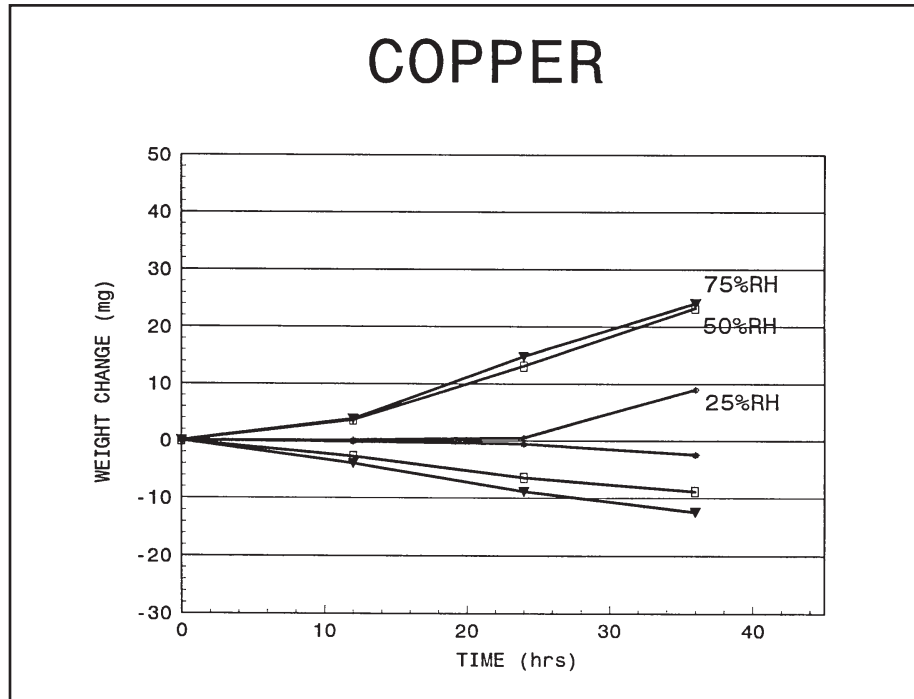


Figure 7. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

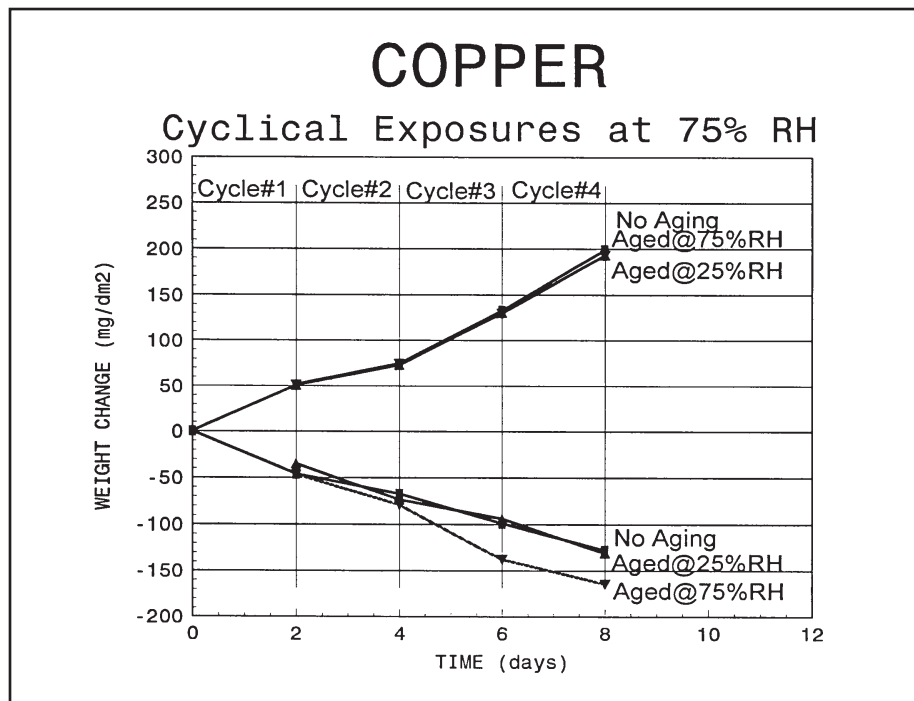


Figure 8. Effect of exposure time and aging on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper in four cyclical exposures followed by aging for 8 days

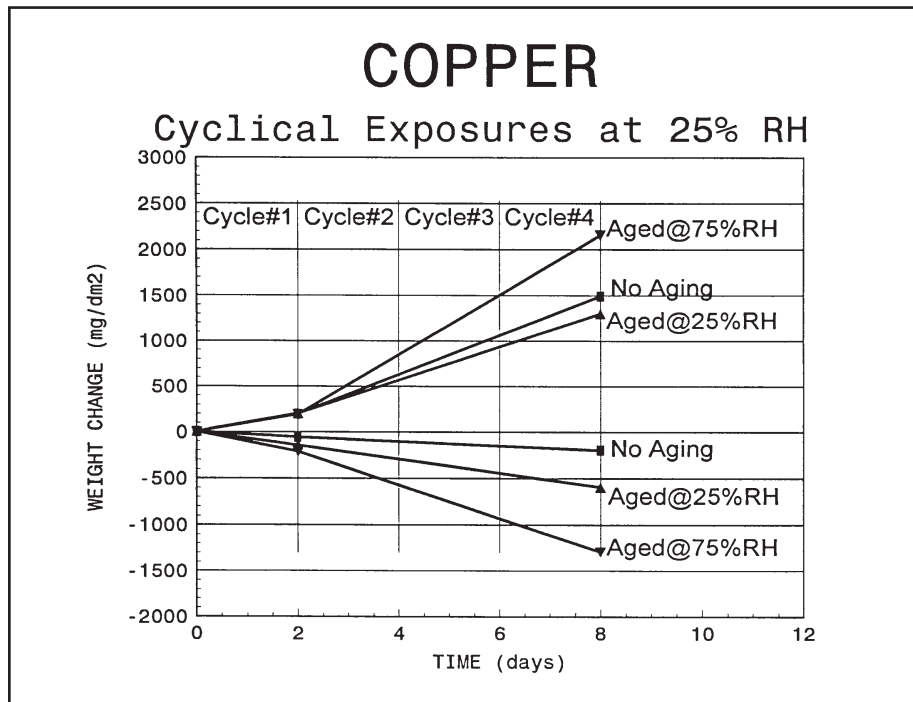


Figure 9. Effect of exposure time and aging on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper in four cyclical exposures followed by aging for 8 days

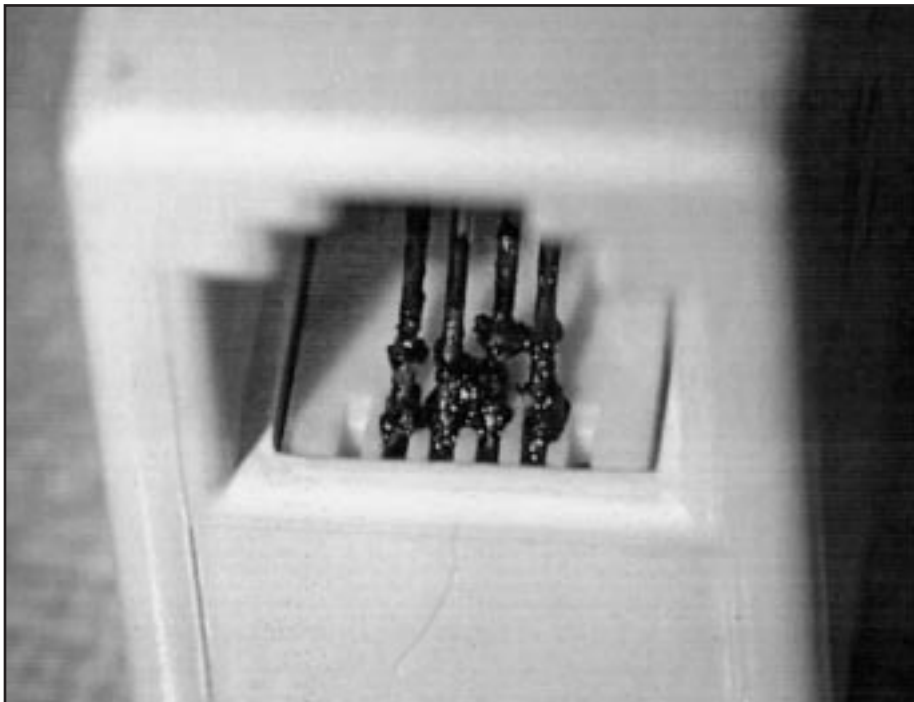


Figure 10. Picture of female telephone jack showing the bridging of corrosion products between adjacent wire electrodes

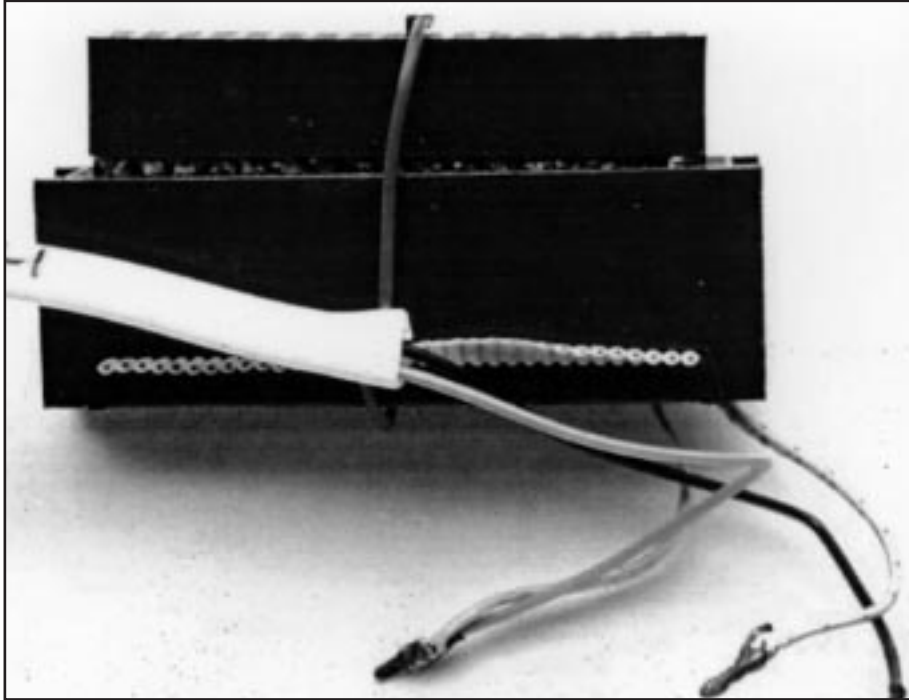


Figure 11. Picture of complete floppy drive connector with factory insert and the broken lead wire



Figure 12. Picture of a piece of floppy drive connector with a copper bridge completing the circuit used in Expt #43

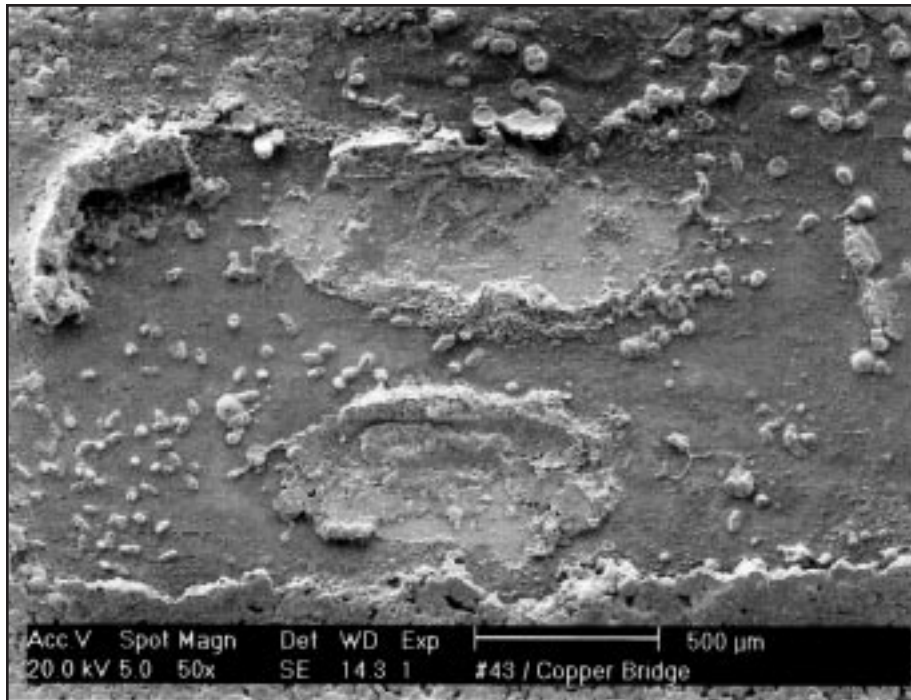


Figure 13. SEM picture (secondary electrons) of the copper bridge in Fig. 12 showing the foot print of the brass connector in the surface film

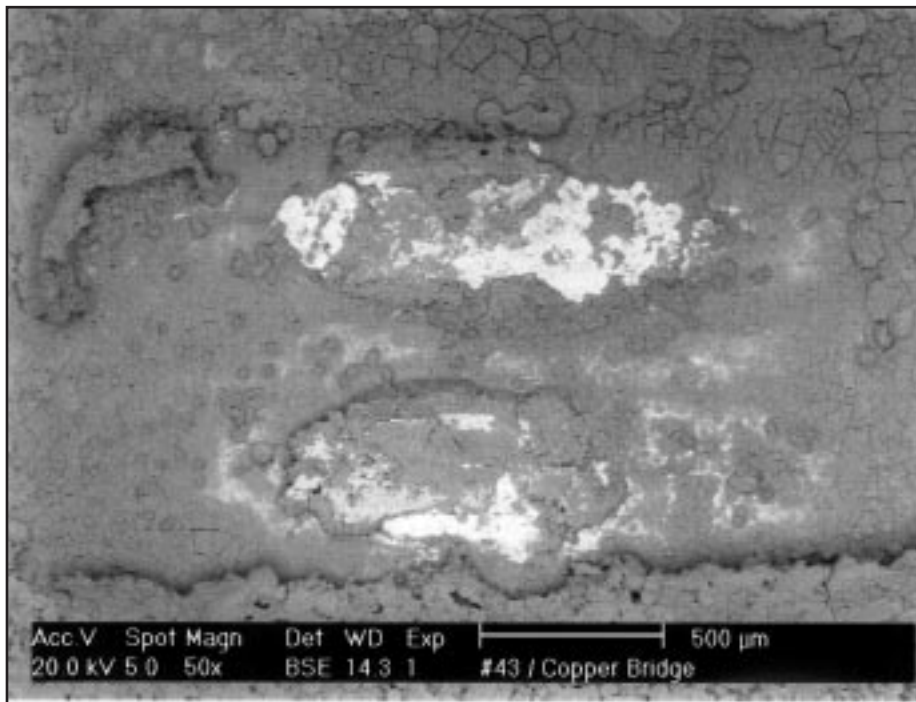


Figure 14. SEM picture (backscattered electrons) of the copper bridge in Fig. 13 showing the thinned area (where current flowed) as a bright area

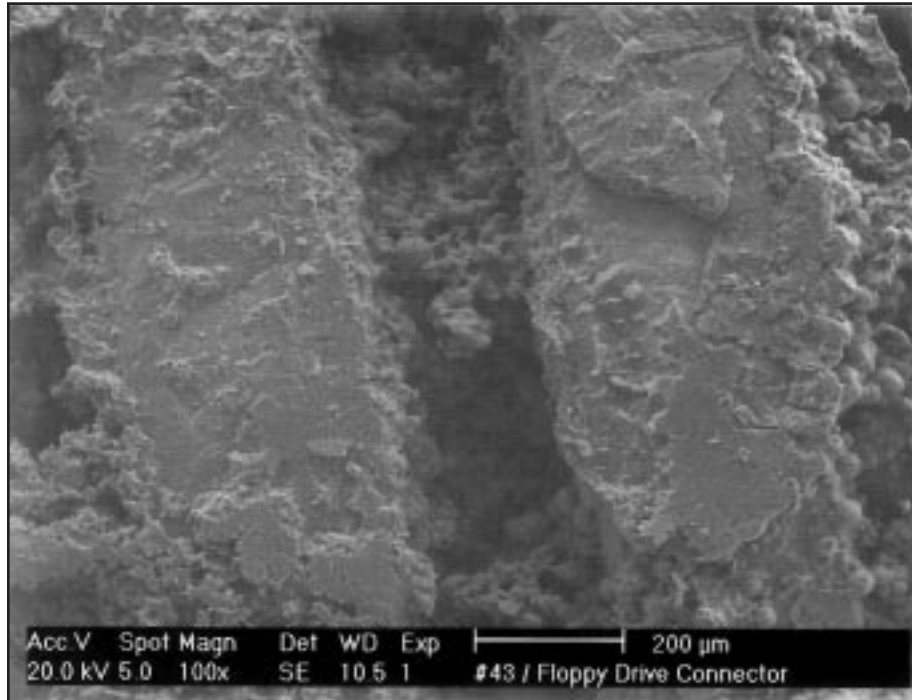


Figure 15. SEM picture (secondary electrons) of the brass contact in Fig. 12 (Expt. #43) showing the accumulated surface film

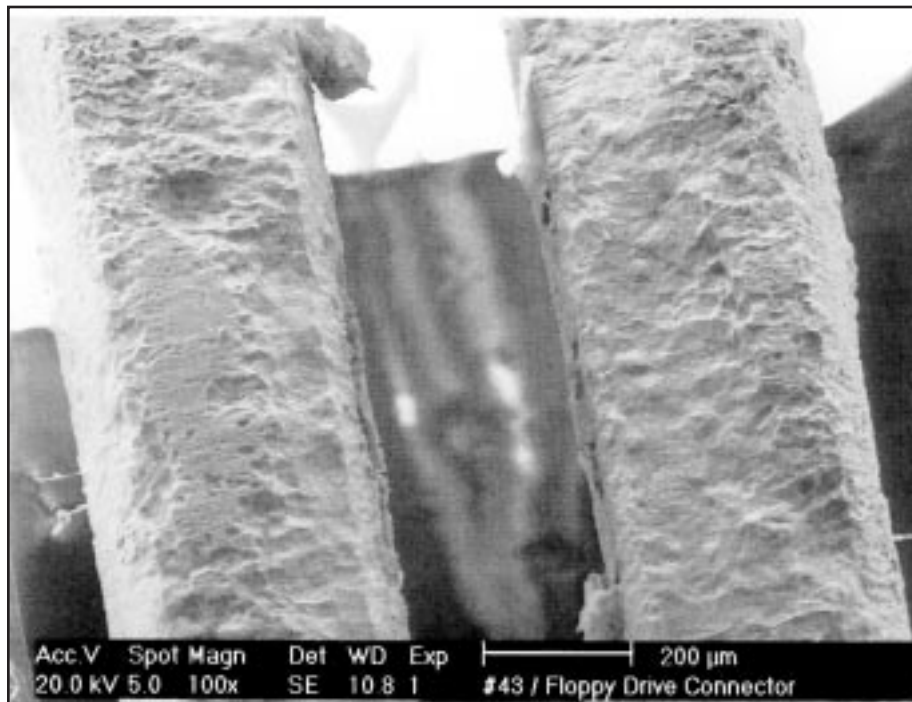


Figure 16. SEM picture (secondary electrons) of the brass contact in Fig. 12 (Expt. #43) after chemical cleaning showing the extensive localized corrosion

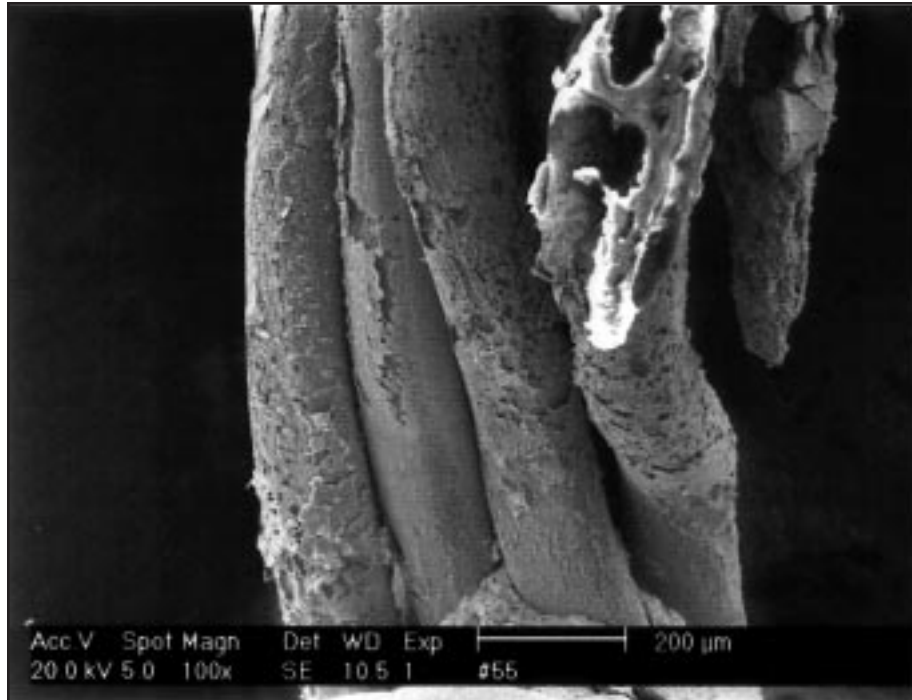


Figure 17. SEM picture (secondary electrons) of the corroded wire from Expt. #55 after chemical cleaning

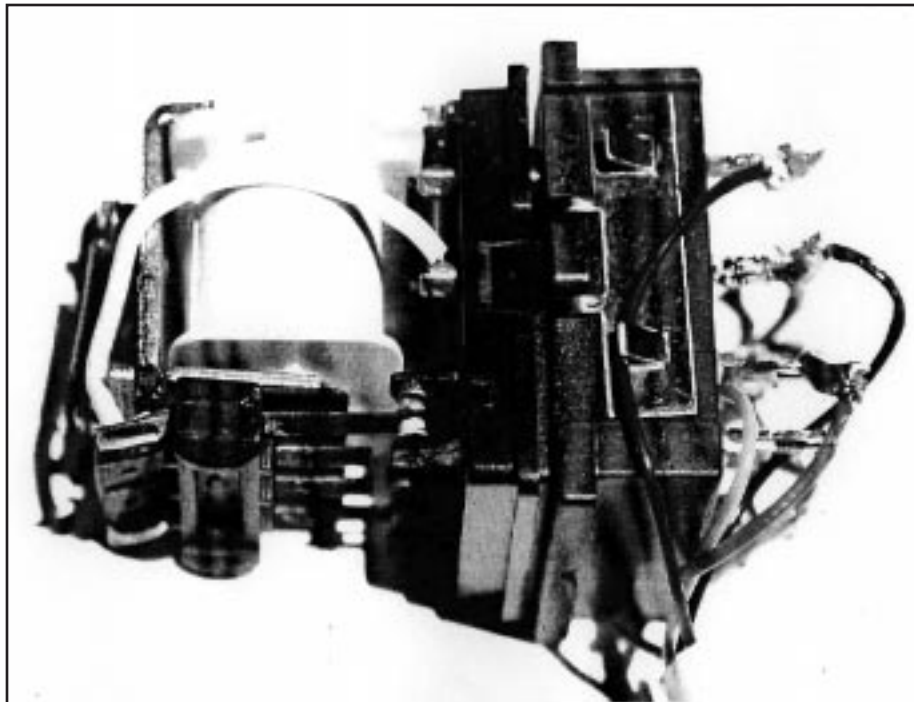


Figure 18. Picture of the relay used in exposure experiments

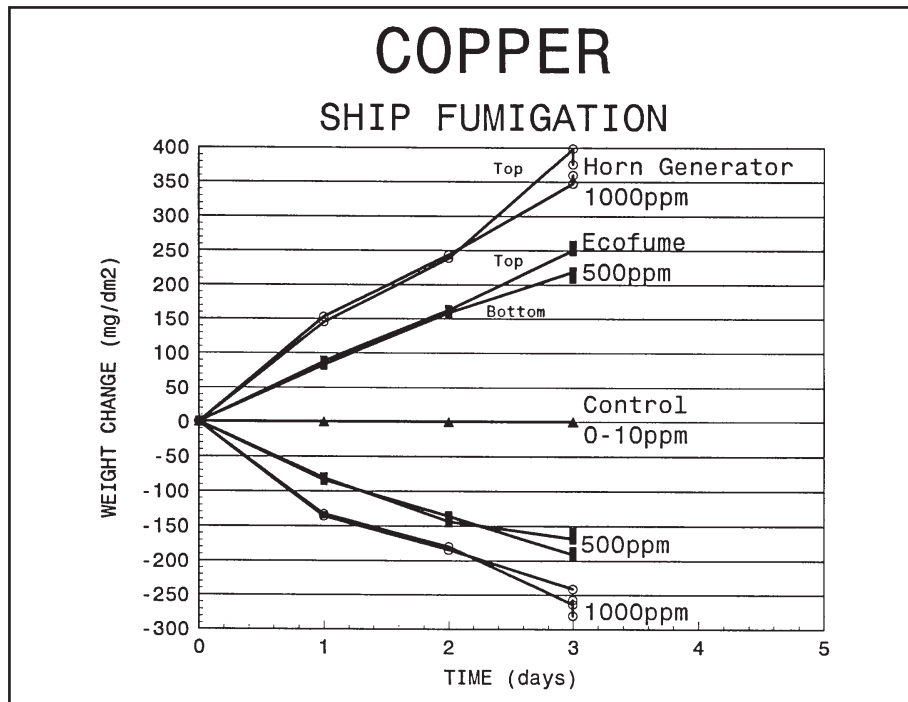


Figure 19. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper exposed in the ship fumigation in Toronto on June 5 to 8, 1999

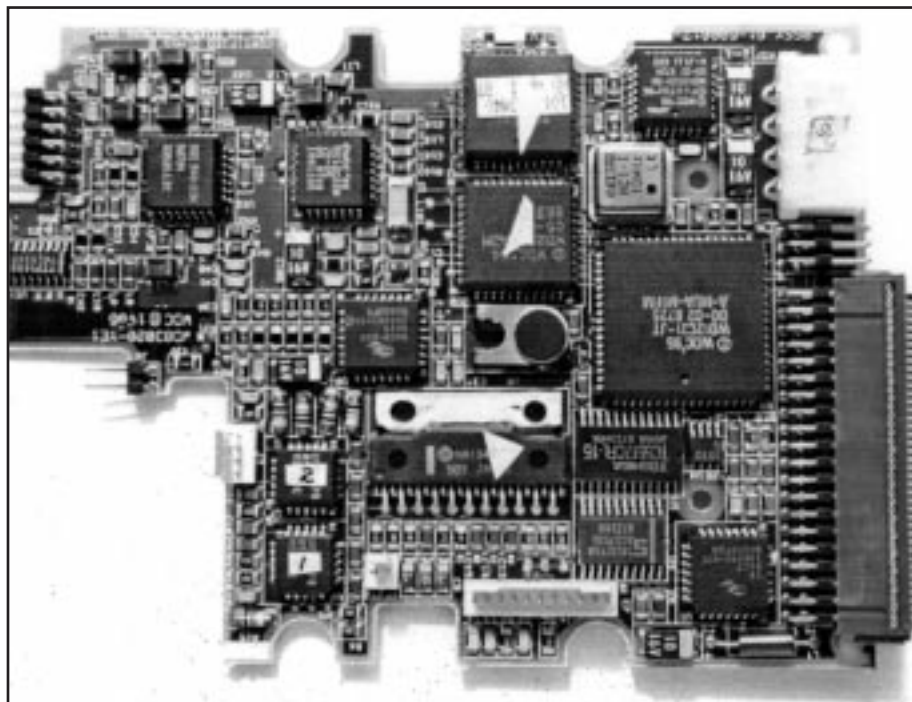


Figure 20. Picture of the hard drive controller card from David Mueller's computer which failed during the Toronto ship fumigation

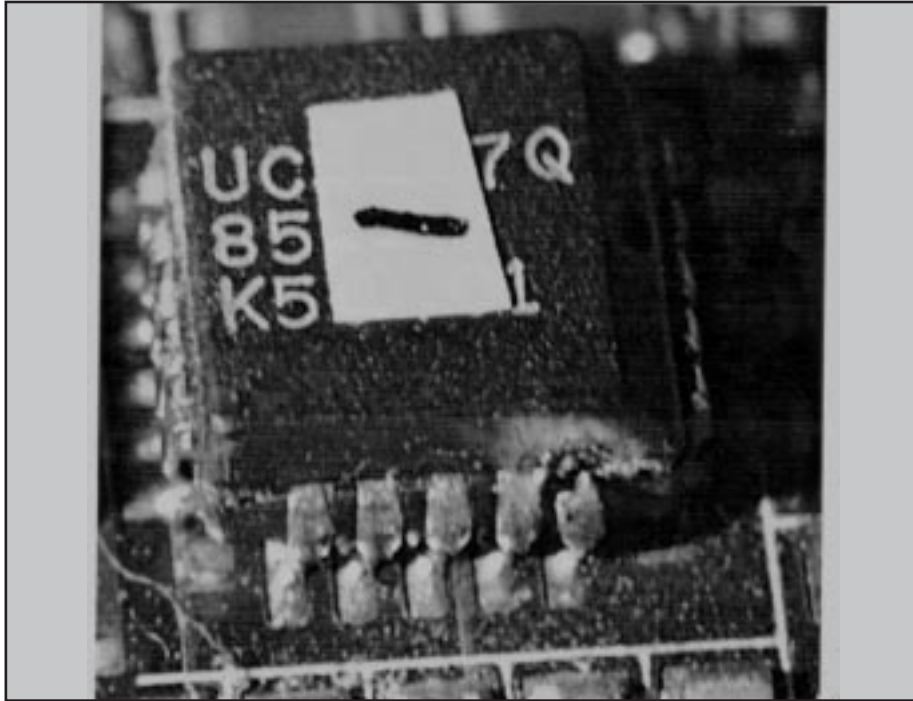


Figure 21. Picture of the chip (designated "1" in Fig. 20) showing the location of the hot spot in a lead near the body of the chip

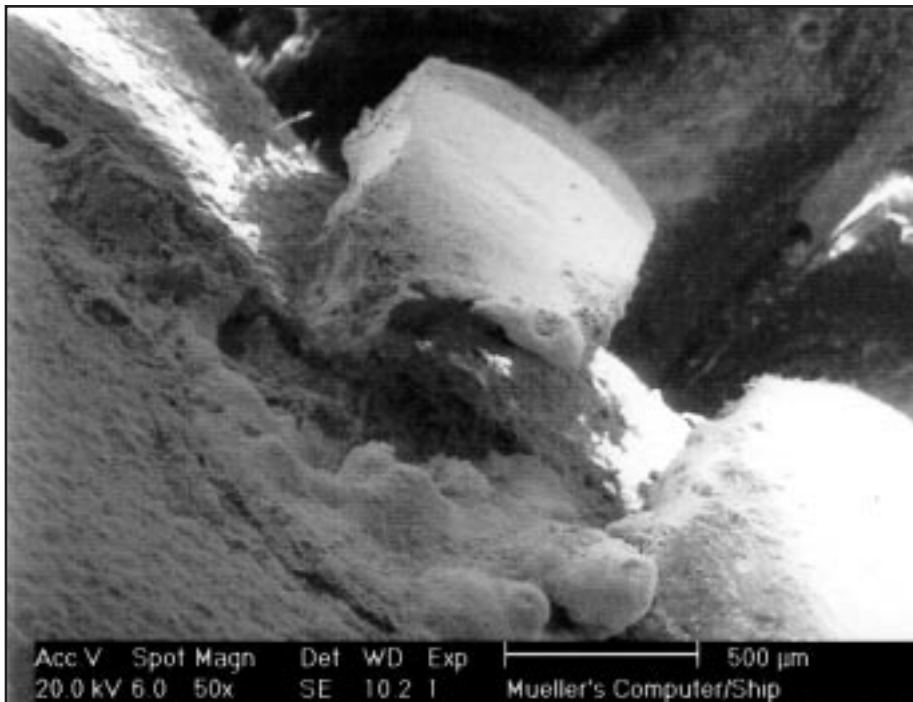


Figure 22. SEM picture (secondary electrons) of the failed lead in Fig. 21

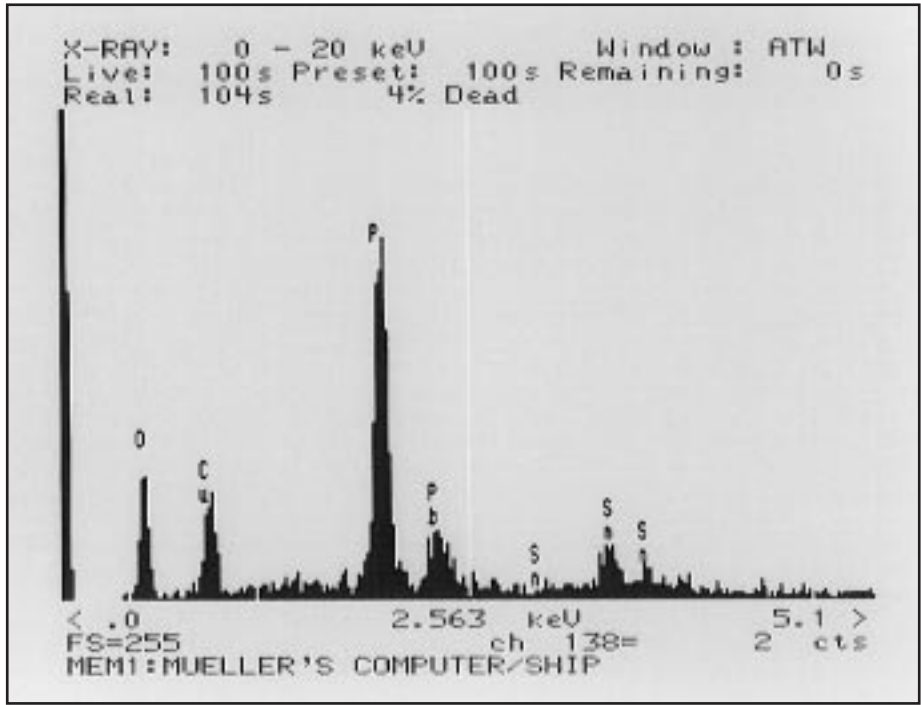


Figure 23. EDAX spectrum of the corrosion products in the vicinity of the failure in Fig. 22

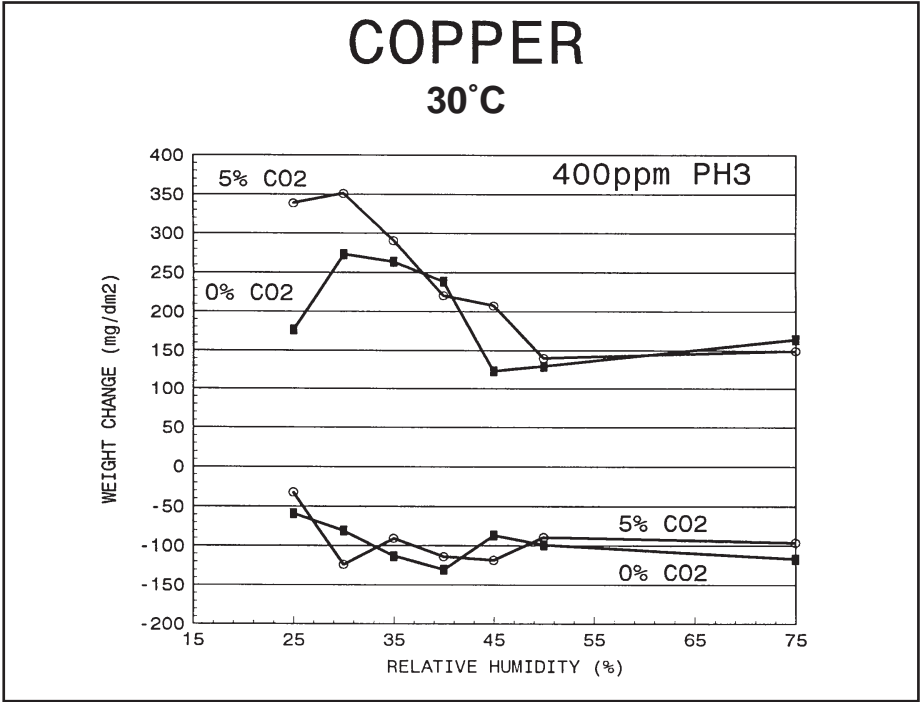


Figure 24. Summary of weight gains (due to the deposition of oxides of phosphorus) and weight losses (due to corrosion) of copper exposed for 36 hours to 400 ppm PH₃ at various relative humidities comparing the effect of 0% and 5% CO₂

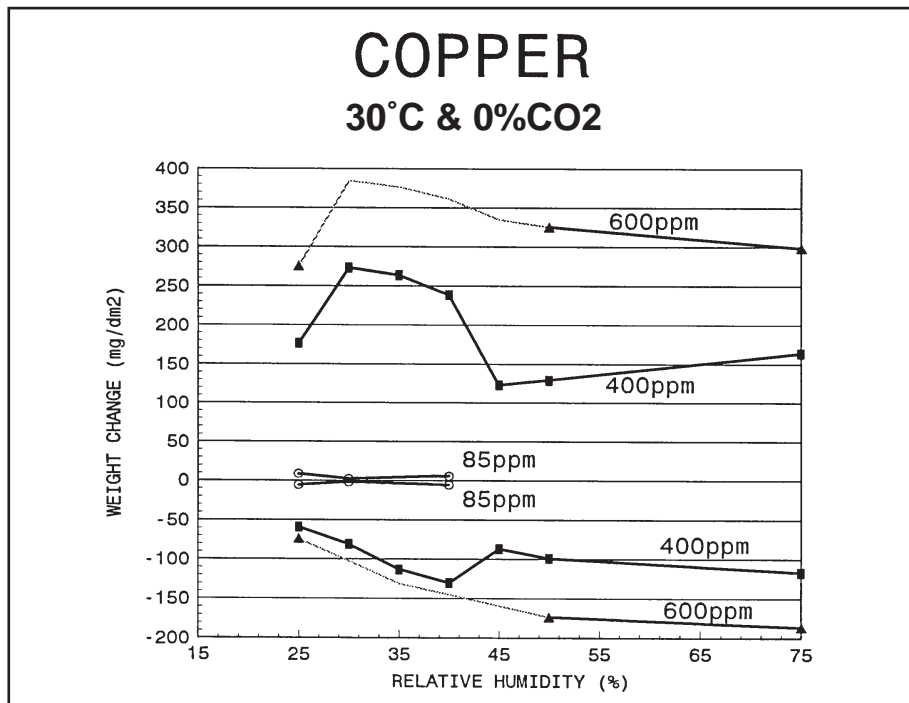


Figure 25. Summary of weight gains (due to the deposition of oxides of phosphorus) and weight losses (due to corrosion) of copper exposed for 36 hours to 30°C and 0% CO₂ to various relative humidities and phosphine concentrations

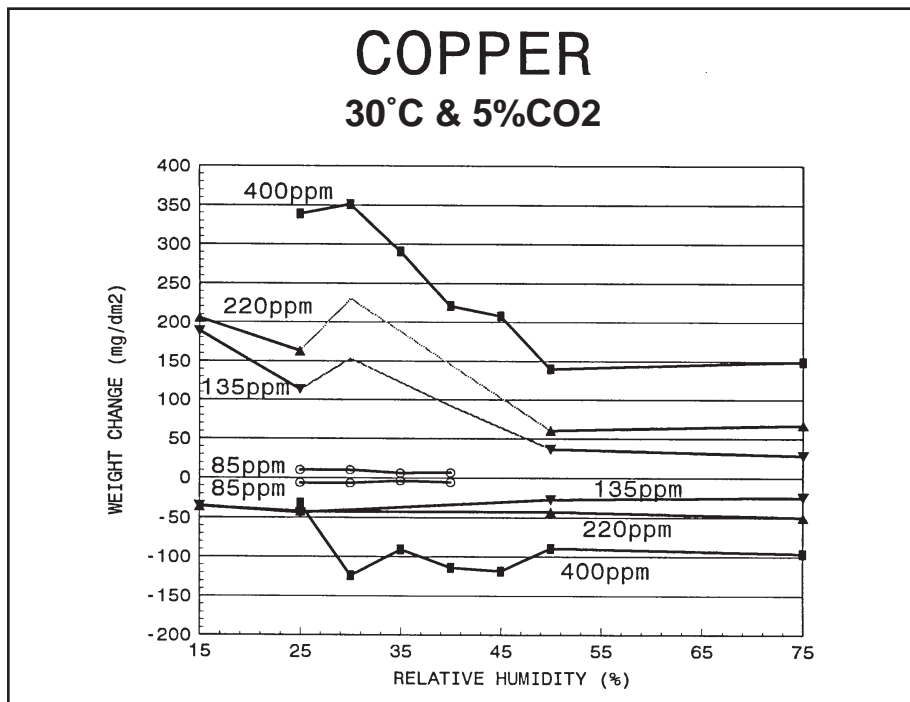


Figure 26. Summary of weight gains (due to the deposition of oxides of phosphorus) and weight losses (due to corrosion) of copper exposed for 36 hours to 30°C and 5% CO₂ to various relative humidities and phosphine concentrations

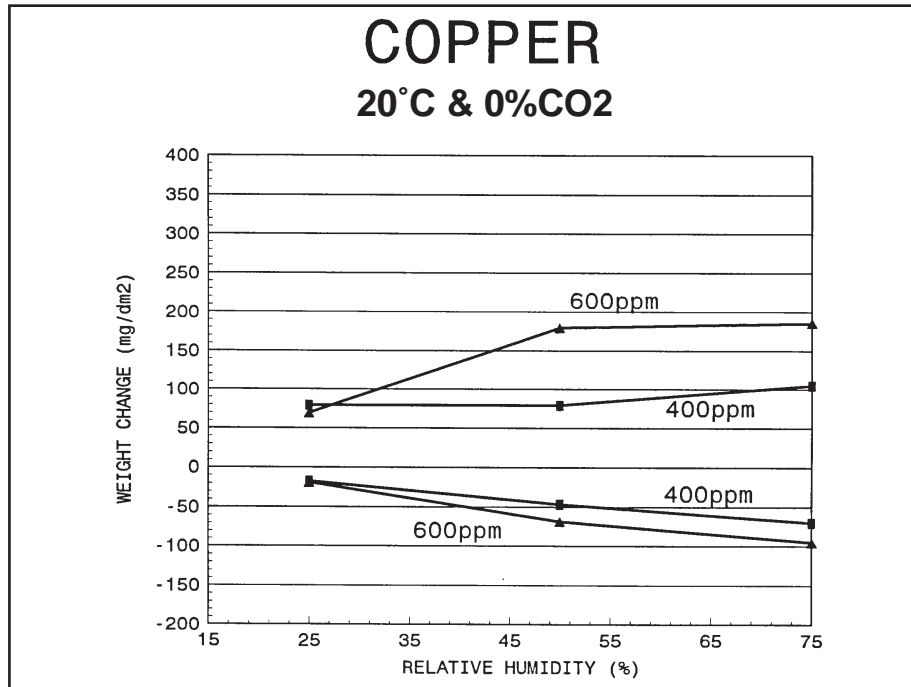


Figure 27. Summary of weight gains (due to the deposition of oxides of phosphorus) and weight losses (due to corrosion) of copper exposed for 36 hours to 20°C and 0% CO₂ to various relative humidities and phosphine concentrations

Appendix A

30°C/85 ppm PH₃ / 0%CO₂

Sample area 0.19 dm ²		Weight Gain (mg)				Weight Loss (mg)			
		25% RH	30% RH	35% RH	40% RH	25% RH	30% RH	35% RH	40% RH
Copper	12 hr	0.3	0.1	XX	0.4	0.5	0	XX	0.5
		0.3	0.2	XX	0.4	0.2	0.1	XX	0.6
		0.2	0.1	XX	0.5	0.3	0.1	XX	0.5
		0.3	0.3	XX	0.4	0.2	0.1	XX	0.5
	Avg.	0.3	0.2		0.4	0.3	0.1		0.5
	24 hr	0.5	0.3	XX	0.7	0.5	0.4	XX	0.6
		0.5	0.3	XX	0.6	0.5	0.2	XX	0.6
		0.5	0.4	XX	0.7	0.5	0.2	XX	0.8
		0.7	0.3	XX	0.6	0.6	0.2	XX	0.4
	Avg.	0.6	0.3		0.6	0.5	0.3		0.6
	36 hr	1.6	0.4	XX	1.1	1.2	0.4	XX	0.9
		1.7	0.3	XX	1.1	1.1	0.6	XX	0.9
		1.7	0.4	XX	0.9	1.2	0.4	XX	0.9
		1.6	0.5	XX	1.2	1.1	0.4	XX	1.0
	Avg.	1.6	0.4		1.1	1.1	0.4		0.9

30°C/85 ppm PH₃ / 5%CO₂

Sample area 0.19 dm ²		Weight Gain (mg)				Weight Loss (mg)			
		25% RH	30% RH	35% RH	40% RH	25% RH	30% RH	35% RH	40% RH
Copper	12 hr	0.3	0.3	0.5	0.3	0.2	0.2	0.5	0.5
		0.5	0.4	0.4	0.4	0.3	0.3	0.4	0.4
		0.4	0.2	0.4	0.4	0.5	0.4	0.5	0.4
		0.4	0.5	0.4	0.3	0.4	0.5	0.5	0.4
	Avg.	0.4	0.3	0.4	0.3	0.3	0.3	0.5	0.4
	24 hr	0.5	0.8	0.6	0.8	0.5	0.6	0.6	0.7
		0.7	0.9	0.6	0.6	0.6	0.7	0.5	0.6
		0.6	0.8	0.7	0.6	0.5	0.8	0.4	0.7
		0.7	0.9	0.6	0.7	0.5	0.5	0.5	0.5
	Avg.	0.6	0.8	0.6	0.7	0.5	0.6	0.5	0.6
	36 hr	1.8	2.0	1.2	1.4	1.3	1.2	0.7	1.0
		2.1	1.6	1.0	1.2	1.3	1.5	0.7	1.1
		2.0	7.5*	1.2	1.3	1.2	2.7	0.9	1.2
		1.9	2.1	1.2	1.4	1.1	1.3	0.7	1.3
	Avg.	1.9	1.9	1.1	1.3	1.2	1.3	0.7	1.1

* Sample was wet where it touched the holder. Data not used to calculate average.

30°C/400 ppm PH₃ / 0%CO₂

Sample area 0.13 dm ²		Weight Gain (mg)				Weight Loss (mg)			
		30% RH	35% RH	40%# RH	45% RH	30% RH	35% RH	40%# RH	45% RH
Copper	12 hr	8.7*	9.3*	3.6	2.9	4.8	5.8	4.2	3.4
		8.4*	7.0*	3.0	2.7	4.8	6.0	3.6	3.0
		7.9*	5.9*	2.9	3.0	4.3	5.2	2.7	2.8
		7.5*	5.0*	3.6	3.4	4.3	4.0	3.2	3.5
	Avg.	8.1*	6.8*	3.3	3.0	4.6	5.2	3.4	3.2
	24 hr	17.6*	19.8*	14.9	7.9	6.7	9.7	10.3	7.9
		19.3*	17.9*	15.8	8.4	7.4	11.0	10.0	8.4
		14.4*	14.8*	17.2	8.3	6.8	7.4	9.8	8.3
		16.5*	18.9*	16.6	9.3	6.2	8.9	10.4	9.3
	Avg.	16.9*	17.8*	16.1	8.5	6.8	9.2	10.1	8.5
	36 hr	38.5*	38.6*	32.7	15.4	10.2	15.6	17.6	11.7
		36.8*	38.7*	30.7	17.8	10.7	15.6	16.8	12.4
		38.1*	30.1*	29.0	16.8	11.0	13.8	16.3	11.6
		28.7*	29.7*	31.6	14.1	10.1	13.9	17.0	9.6
	Avg.	35.5*	34.3*	31.0	16.0	10.5	14.7	16.9	11.3

* Samples were wet # 450ppm PH₃30°C/400 ppm PH₃ / 5%CO₂

Sample area 0.13 dm ²		Weight Gain (mg)				Weight Loss (mg)			
		30% RH	35% RH	40% RH	45% RH	30% RH	35% RH	40% RH	45% RH
Copper	12 hr	11.5*	7.7*	5.4*	3.9**	8.4	4.4	4.9	6.0
		10.1*	6.9*	5.1*	3.8**	8.2	4.2	5.5	4.6
		8.2*	5.6*	5.5*	4.2**	7.0	3.7	4.8	5.7
		11.2*	5.8*	5.4*	4.3**	8.1	3.9	5.2	4.2
	Avg.	10.3*	6.5*	5.4*	4.1**	7.9	4.1	5.1	5.2
	24 hr	29.3*	18.9*	16.1*	18.9**	12.0	7.9	11.0	11.7
		28.3*	23.1*	18.8*	16.5**	12.7	7.2	10.3	11.0
		31.1*	16.5*	16.0*	17.4**	12.4	8.2	10.2	11.3
		28.0*	21.7*	16.0*	15.4**	12.3	7.4	9.4	10.9
	Avg.	29.2*	20.1*	16.7*	17.1**	12.4	7.7	10.2	11.2
	36 hr	48.1*	43.9*	30.4*	27.4**	15.3	11.0	15.6	16.3
		42.8*	34.6*	31.4*	28.5**	17.0	11.2	16.1	15.6
		44.6*	36.1*	26.4*	24.8**	16.2	11.6	13.9	14.7
		46.9*	36.4*	26.5*	27.3**	15.7	13.2	13.6	14.9
	Avg.	45.6*	37.8*	28.7*	27.0**	16.1	11.8	14.8	15.4

* Samples were wet ** Samples appeared damp

30°C/400 ppm PH₃ / 0%CO₂

Sample area 0.13 dm ²		Weight Gain (mg)			Weight Loss (mg)		
		25% RH	50% RH	75% RH	25% RH	50% RH	75% RH
Copper	12 hr	10.5*	2.2	3.9	4.0	2.4	5.0
		12.0*	2.1	3.0	4.3	3.1	3.9
		9.9*	2.1	4.0	4.2	2.3	4.6
		7.4*	1.9	4.1	3.4	2.1	4.6
	Avg.	9.9*	2.1	3.8	4.0	2.5	4.5
	24 hr	17.3*	8.2	9.9	5.9	6.1	9.4
		13.3*	10.2	11.3	5.2	7.6	9.7
		13.5*	9.2	10.2	5.4	7.0	8.8
		16.8*	8.8	10.7	5.5	7.5	9.3
	Avg.	15.2*	9.1	10.5	5.5	7.1	9.3
	36 hr	25.1*	16.0	23.3	8.0	12.6	16.3
		26.4*	17.3	21.0	7.1	12.8	14.6
		16.6*	16.2	18.6	7.8	12.1	14.3
		23.7*	17.8	22.4	8.1	13.1	15.6
	Avg.	22.9*	16.8	21.3	7.7	12.9	15.2

* Samples were wet

30°C/400 ppm PH₃ / 5%CO₂

Sample area 0.13 dm ²		Weight Gain (mg)			Weight Loss (mg)		
		25% RH	50% RH	75% RH	25% RH	50% RH	75% RH
Copper	12 hr	5.4*	3.1	4.7	1.2	2.7	4.6
		4.3*	3.5	4.2	0.8	2.5	5.3
		3.9*	4.2	4.3	0.9	2.8	3.8
		5.0*	4.4	4.3	1.3	3.1	3.8
	Avg.	4.7*	3.8	4.4	1.1	2.8	4.4
	24 hr	38.7*	12.2	13.3	3.5	7.4	9.0
		34.9*	11.4	11.7	3.3	7.3	7.7
		30.2*	10.0	12.2	3.5	6.8	8.1
		33.8*	12.0	12.9	3.6	7.1	8.1
	Avg.	34.4*	11.4	12.5	3.5	7.2	8.2
	36 hr	34.2*	18.2	18.4	4.3	11.4	11.9
		34.6*	19.0	22.1	4.0	11.8	13.9
		60.9*	15.4	19.0	4.2	10.7	12.3
		46.4*	20.2	18.2	4.1	12.3	12.0
	Avg.	44.0*	18.2	19.4	4.2	11.6	12.5

* Samples were wet

30°C/600 ppm PH₃ / 0%CO₂

Sample area 0.13 dm ²		Weight Gain (mg)			Weight Loss (mg)		
		25% RH	50% RH	75% RH	25% RH	50% RH	75% RH
Copper	12 hr	9.2*	9.0	2.8	4.1	7.9	6.0
		11.6*	8.5	2.1	4.0	8.3	4.0
		9.4*	7.4	2.4	3.7	7.6	5.4
		8.7*	9.2	2.3	3.5	8.0	7.5
	Avg.	9.7*	8.5	2.4	3.8	8.0	5.7
	24 hr	35.0*	24.4	23.7	7.4	14.8	17.9
		32.4*	25.0	24.4	7.9	14.8	16.4
		25.9*	24.9	24.6	7.3	15.8	18.1
		28.1*	25.4	25.4	7.4	15.0	18.0
		Avg.	30.4*	24.9	24.5	7.5	15.1
	36 hr	34.6*	43.2	40.4	9.4	21.9	23.7
		33.5*	42.5	38.2	8.5	27.6	24.6
		38.2*	42.4	37.6	9.3	18.3	23.3
		37.0*	40.9	39.1	11.0	22.1	25.0
		Avg.	35.8*	42.3	38.8	9.6	22.5

* Samples were wet

20°C/400 ppm PH₃ / 0%CO₂

Sample area 0.13 dm ²		Weight Gain (mg)			Weight Loss (mg)		
		25% RH	50% RH	75% RH	25% RH	50% RH	75% RH
Copper	12 hr	0.1	1.6	2.1	0.1	1.5	3.1
		0.1	1.7	2.4	0.1	2.0	3.1
		0.1	1.7	2.4	0.1	1.2	2.2
		0.1	1.5	2.4	0.1	1.2	2.5
	Avg.	0.1	1.6	2.3	0.1	1.5	2.7
	24 hr	0.8*	7.0	8.6	0.4	3.7	6.1
		1.3*	7.2	7.3	0.7	3.7	5.5
		1.5*	7.0	7.7	0.7	4.3	6.4
		1.3*	6.9	8.0	0.7	3.6	5.8
		Avg.	1.2*	7.0	7.9	0.6	3.8
	36 hr	10.3*	11.5	13.7	2.3	6.3	9.0
		10.0*	10.0	13.4	2.3	6.1	8.8
		8.6*	9.6	13.8	2.0	5.9	9.2
		12.2*	10.0	13.5	2.5	6.1	9.2
		Avg.	10.3*	10.3	13.6	2.3	6.1

* Samples were wet

20°C/600 ppm PH₃ / 0%CO₂

Sample area 0.13 dm ²		Weight Gain (mg)			Weight Loss (mg)		
		25% RH	50% RH	75% RH	25% RH	50% RH	75% RH
Copper	12 hr	0.1	3.5*	3.8	0.2	2.6	5.3
		0.1	3.8*	4.0	0.2	2.7	3.6
		0.1	3.6*	3.7	0.2	3.4	3.5
		0.1	3.4*	3.5	0.1	2.5	3.5
	Avg.	0.1	3.6*	3.8	0.2	2.8	4.0
	24 hr	0.5*	13.2*	15.0*	0.4	6.8	9.0
		0.5*	12.9*	14.3*	0.8	6.1	8.5
		0.4*	13.4*	15.1*	0.5	6.3	8.5
		0.7*	13.0*	14.6*	0.7	6.6	9.4
		Avg.	0.5*	13.1*	14.8*	0.6	6.5
	36 hr	11.9*	21.6*	22.7*	3.1	9.0	11.5
		8.6*	26.2*	23.4*	2.6	9.4	12.5
		6.7*	22.8*	24.2*	2.1	9.0	12.9
		8.8*	22.7*	26.0*	2.2	8.3	12.5
		Avg.	9.0*	23.3*	24.1*	2.5	8.9

* Samples were wet

Appendix B

Cyclical Exposures at 75% RH

Sample Area 0.13dm ²	Weight Gain (mg)	Aging Conditions		Wt. Change after Aging (mg)	Wt. Loss after Cleaning(mg)
		Days	%RH		
Cycle #1 (2 days)	6.9	0	NA	NA	5.8
	8.4	0	NA	NA	6.6
	6.7	0	NA	NA	5.7
					Avg. 6.0
	5.0	8	25%	0	4.0
	6.4	8	25%	0	4.8
	6.8	8	25%	0	4.9
				Avg. 0	Avg. 4.6
	6.3	8	75%	+0.1	6.2
	6.0	8	75%	+0.1	5.9
6.5	8	75%	+0.2	6.2	
	Avg. 6.6			Avg. +0.1	Avg. 6.1
Cycle #2 (4 days)	9.6	0	NA	NA	9.2
	8.4	0	NA	NA	7.8
	8.9	0	NA	NA	9.4
					Avg. 8.8
	9.8	8	25%	-0.2	9.3
	8.3	8	25%	-0.2	9.6
	11.1	8	25%	-0.2	9.9
				Avg. -0.2	Avg. 9.6
	10.4	8	75%	0	10.6
	10.4	8	75%	0	10.1
10.6	8	75%	0	10.1	
	Avg. 9.7			Avg. 0	Avg. 10.3
Cycle #3 (6 days)	20.9	0	NA	NA	14.9
	12.1	0	NA	NA	10.6
	15.7	0	NA	NA	13.1
					Avg. 12.9
	13.7	8	25%	-0.3	11.5
	13.8	8	25%	-0.3	10.8
	21.0	8	25%	-0.4	14.3
				Avg. -0.3	Avg. 12.2
	14.8	8	75%	-0.2	16.2
	27.8	8	75%	-0.7	22.7
16.1	8	75%	-0.3	14.8	
	Avg. 17.3			Avg. -0.4	Avg. 17.9
Cycle #4 (8 days)	31.0	0	NA	NA	19.3
	20.1	0	NA	NA	15.3
	21.1	0	NA	NA	15.3
					Avg. 16.6
	17.1	8	25%	-0.4	13.2
	23.7	8	25%	-0.7	16.6
	36.0	8	25%	-1.2	21.2
				Avg. -0.8	Avg. 17.0
	21.5	8	75%	-0.5	18.2
	31.0	8	75%	-0.9	22.3
31.8	8	75%	-1.0	23.7	
	Avg. 25.9			Avg. -0.8	Avg. 21.4

Cyclical Exposures at 25% RH

Sample Area 0.13dm ²	Weight Gain (mg)	Aging Conditions		Wt. Change after Aging (mg)	Wt. Loss after Cleaning(mg)
		Days	%RH		
Cycle #1 (2 days)	19.2*	0	NA	NA	8.3
	17.1*	0	NA	NA	7.1
	15.5*	0	NA	NA	6.7
					Avg. 7.4
	26.4*	8	25%	+0.5*	18.3
	28.2*	8	25%	0*	18.6
	27.2*	8	25%	+0.5*	18.8
				Avg. +0.3*	Avg. 18.6
	34.6*	8	75%	-0.9	28.6
	39.0*	8	75%	-1.8	31.9
	22.5*	8	75%	+0.4	21.4
Avg. 25.5*			Avg. -0.8	Avg. 27.3	
Cycle #2 (4 days)	17.5	0	NA	NA	11.0
	12.5	0	NA	NA	8.6
	11.2	0	NA	NA	7.6
					Avg. 9.1
	11.5	8	25%	-0.1	11.9
	16.7	8	25%	-0.2	11.7
	17.3	8	25%	-0.2	12.1
				Avg. -0.2	Avg. 11.9
	22.4	8	75%	+0.8	26.3
	28.4	8	75%	+0.5	26.1
	34.1	8	75%	-0.5	28.9
Avg. 19.1			Avg. +0.3	Avg. 27.1	
Cycle #3 (6 days)	38.2	0	NA	NA	17.5
	38.1	0	NA	NA	18.1
	41.1	0	NA	NA	19.2
					Avg. 18.3
	35.9	8	25%	-0.3	18.9
	36.7	8	25%	-0.5	20.2
	63.3	8	25%	-0.8	28.8
				Avg. -0.5	Avg. 22.6
	74.5	8	75%	+0.1	54.5
	88.2	8	75%	-0.2	63.0
	95.6	8	75%	-0.2	65.0
Avg. 56.8			Avg. -0.1	Avg. 60.8	
Cycle #4 (8 days)	86.5*	0	NA	NA	25.9
	93.5*	0	NA	NA	26.3
	116.3*	0	NA	NA	24.9
					Avg. 25.7
	92.5*	8	25%	-31.4*	49.0
	273.4*	8	25%	-54.2*	78.0
	279.1*	8	25%	+60.3*	104.7
				Avg. -25.3*	Avg. 77.2
	250.9*	8	75%	+148.5	184.2
	276.6*	8	75%	-45.4	149.6
	307.1*	8	75%	-16.3	169.0
Avg. 194.0*			Avg. +86.8	Avg. 167.6	

* Samples were wet

Appendix C

Weight Change in Copper Strips Exposed in Ship Fumigation June 5-8, 1999

Sample Area 0.075 dm ²		Weight Gain (mg)		Weight Loss (mg)	
Code	Exposure (days)	Triplicate Samples	Avg.	Triplicate Samples	Avg.
M1-1	1	0,0,0	0	0,0,0	0
M1-3	1	0,0,0	0	0,0,0	0
E1-1	1	4.9, 7.0, 8.0	6.6	5.4, 6.3, 7.1	6.3
E1-3	1	6.1, 5.0, 7.5	6.2	6.0, 5.7, 6.7	6.1
E2-1	2	16.0, 12.2, 8.4	12.2	12.5, 9.8, 8.3	10.2
E2-3	2	10.6, 10.1, 15.0	11.9	9.6, 9.9, 12.3	10.6
E3-1	3	26.0, 16.6, 13.9	18.8	18.6, 13.1, 11.3	14.3
E3-3	3	17.7, 12.7, 18.9	16.4	13.0, 11.0, 13.8	12.6
E4-1	3	21.2, 14.5, 20.3	18.7	15.4, 12.1, 14.4	14.0
E4-3	3	17.7, 14.9, 14.8	15.8	12.9, 11.7, 11.3	12.0
E5-1	3	20.4, 17.5, 20.1	19.3		
H1-1	1	10.8, 11.2, 10.6	10.9	9.7, 9.8, 10.5	10.0
H1-3	1	12.6, 11.0, 10.8	11.5	10.1, 10.2, 10.3	10.2
H2-1	2	17.6, 18.4, 17.6	17.9	13.4, 13.4, 13.6	13.5
H2-3	2	19.8, 17.7, 17.3	18.3	14.3, 13.9, 13.2	13.8
H3-1	3	28.0, 29.5, 27.0	28.2	18.4, 20.9, 18.7	19.3
H3-3	3	26.2, 26.6, 25.4	26.1	19.0, 17.5, 17.7	18.1
H4-1	3	32.0, 35.6, 28.8	32.1	21.3, 22.9, 18.7	21.0
H5-1	3	31.1, 28.9, 29.8	29.9	19.4, 20.0, 20.0	19.8
H5-3	3	26.7, 26.7, 27.6	27.0		
All Control		0,0,0	0	0,0,0	0

M = Methyl Bromide

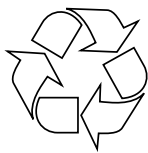
E = Ecofume (500ppm PH₃)

H = Horn Generator (1000ppm PH₃)

Control = 0 - 10ppm PH₃

-1 = top of rope

-3 = bottom of rope



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