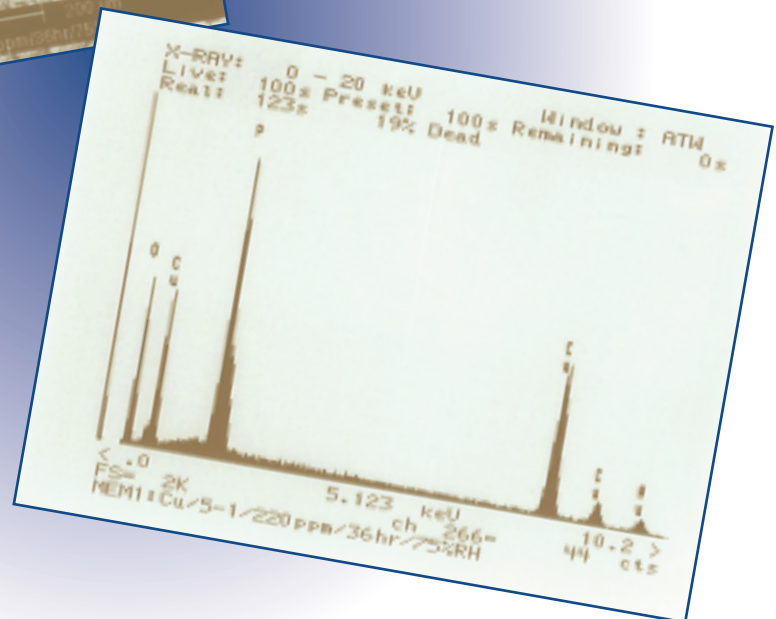
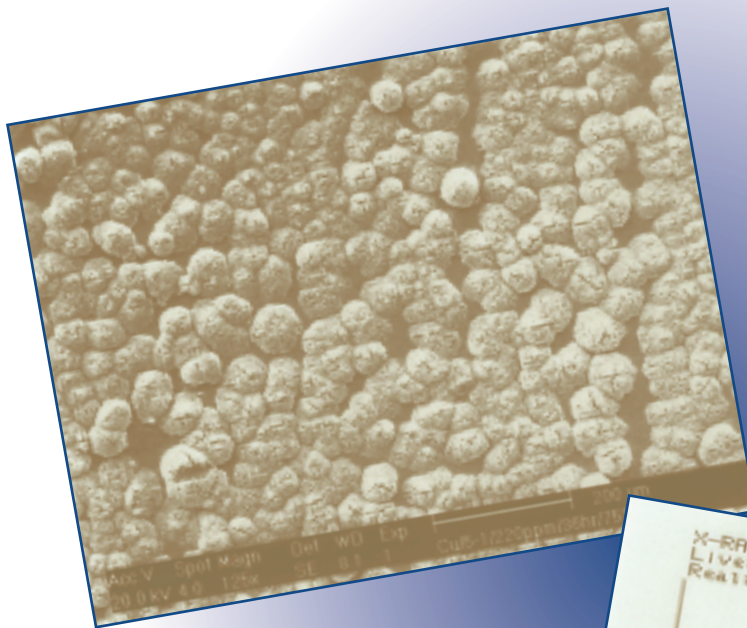




Corrosive Effects of Phosphine, Carbon Dioxide, Heat and Humidity on Electronic Equipment

Canadian Leadership
in the Development of
Methyl Bromide Alternatives



Government
of Canada

Gouvernement
du Canada



CANADIAN NATIONAL
MILLERS ASSOCIATION



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

Canadian Leadership in the Development of Methyl Bromide Alternatives

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and the Canadian National Millers Association

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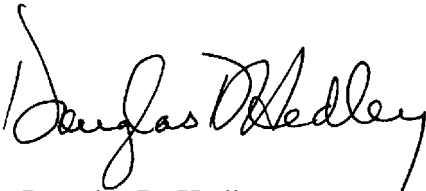
Foreword

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.

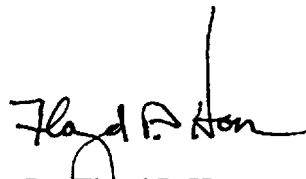
Controls on methyl bromide as an ozone depleting substance have resulted in a critical need for the development of alternatives for its use as a soil, commodity and structural fumigant. Through government research programs and commercial development of alternative technologies and products, we are making 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 scientists 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 second report of jointly funded collaboration between AAFC, USDA Agricultural Research Service scientists and private industry to develop methyl bromide alternatives.

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 of the Canada Centre for Mineral and Energy Technology (CANMET). Furthermore, we were pleased with the advice provided by the industry and, in particular, the insights of David Mueller (Fumigation Service & Supply Inc.) and his provision of corroded samples from field fumigations. The results of this laboratory experiment can easily be incorporated into field situations and will help to ensure effective pest control and reduce the risk of corrosion to electrical equipment by phosphine. We would like to express our thanks for the collaborative effort.



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EXECUTIVE SUMMARY

Four metals - silver (electrical contacts), copper (electrical conductors), brass (electrical components) and solder - were exposed to simulated fumigation parameters under carefully controlled steady-state laboratory conditions which included:

- three temperatures; 20, 30 and 40°C
- three concentrations of phosphine; nominally 35, 135 and 220 ppm
- four levels of relative humidity; 15, 25, 50 and 75%
- two levels of CO₂; nominally 3.5 to 5%
- three exposure times; 12, 24 and 36 hours

During the exposures, the phosphorus in phosphine was oxidized in the presence of water vapour to produce surface deposits of phosphorus oxides and the metals oxidized (corroded) in air at a rate controlled by the availability of oxygen to produce a weight gain. The corrosion products of metal oxidation (and the oxides of phosphorus) were removed to bare metal by immersion in 50/50 HCl and the resulting weight loss gave the corrosion rate of the metal.

The effects of surface roughness and carbon dioxide concentration were judged to be minimal so these kinetic data were lumped together in plotting the average effects of the other variables - relative humidity, temperature, phosphine concentration and exposure time.

The scanning electron microscope (SEM) with EDAX was used to observe the morphology and to determine the chemistry of surface deposits on the metallic coupons exposed in these experiments. The SEM was also used to reveal the morphology of corrosive attack of large copper strips which had been exposed at field fumigation sites. The typical morphology of corrosive attack of copper included areas with no attack, areas with general attack and areas with pits. Brass showed similar morphology to copper, but silver and solder were not attacked.

An unexpected result from this study concerned the identification of wet and dry regimes for copper exposed to phosphine as a function of relative humidity. Copper developed shiny black wet surface deposits only at low relative humidities (25% and lower); an observation which was both counter-intuitive and contradictory of anecdotal evidence. Dry crystalline surface deposits on copper were observed only at high relative humidities (50% and higher).

The table below summarizes the observations made in the course of this study on metal samples from a number of sources.

METAL	SOURCE	WEIGHT GAIN	CORROSION
Copper	This study Mueller samples	Extensive	Extensive
Nickel	Mueller calculator Mueller camera	Yes	?
Brass	This study	Yes	Yes
Silver	This study Mueller fumigation	Yes	No
Stainless Steel	Mueller camera	No P signature	None found
Solder	This study Mueller calculator Mueller fumigation	No	No

It should be noted that both surface deposits and corrosion morphology were identical whether produced in this study in the laboratory or in fumigations in the field.

Three possible failure mechanisms for electronic equipment exposed to phosphine have been identified:

- 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.

FIGURE CAPTIONS

- Figure 1a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH
- Figure 1b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH
- Figure 2a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH
- Figure 2b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH
- Figure 3a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH
- Figure 3b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH
- Figure 4. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH
- Figure 5. EDAX spectrum of the surface deposits in Figure 4.
- Figure 6a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH
- Figure 6b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH
- Figure 7a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH
- Figure 7b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH
- Figure 8a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH
- Figure 8b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH
- Figure 9. EDAX spectrum of the large black surface deposits in Figure 8a.
- Figure 10. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH
- Figure 11. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 75% RH
- Figure 12. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

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- Figure 13. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass
- Figure 14. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver
- Figure 15. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper
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- Figure 17. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver
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- Figure 21. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass
- Figure 22. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass
- Figure 23. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver
- Figure 24. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver
- Figure 25. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper
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- Figure 27. Scanning electron micrograph (BSE mode) showing the extent of surface coverage of copper sample in Figure 6a (SE mode)
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CORROSIVE EFFECTS OF PHOSPHINE, CARBON DIOXIDE, HEAT AND HUMIDITY ON ELECTRONIC EQUIPMENT

Introduction

The problem of metallic corrosion in phosphine has been addressed in early work in Canada(1) and more recent studies in Denmark(2) and the U.S.(3,4). However, the exposure conditions which promote attack and the corrosion mechanism are still not well understood. Consequently, this study was designed to quantify corrosion kinetics and morphology of metals commonly used in electronic equipment under carefully controlled laboratory conditions.

Four metals - silver (electrical contacts), copper (electrical conductors), brass (electrical components) and solder - were chosen for investigation. The materials were tested with both smooth surfaces and with abraded surfaces to increase the probability of water adsorption at a given relative humidity - a condition equivalent to having dust on the surface. It is believed that the corrosion behaviour of these four materials would indicate where corrosion problems with electrical components were likely to happen.

The grid of test parameters included:

- three temperatures; 20, 30 and 40°C
- three concentrations of phosphine; nominally 35, 135 and 220 ppm
- four levels of relative humidity; 15, 25, 50 and 75%
- two levels of CO₂; nominally 3.5 to 5%
- three exposure times; 12, 24 and 36 hours

Experimental

Conceptually, 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 - 0.5%PH₃ gas mixture purchased from Matheson) 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 ±2% accuracy claimed by the manufacturer of the mass flow meters.

Each run was started by placing 8 weighed metallic samples 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. Initial experiments were conducted with the samples mounted radially in the cups but in later runs with samples mounted parallel, the reproducibility seemed to improve. Copper (99.9%), brass (70/30 yellow brass shim stock), silver (99.9%) and solder (50/50 Pb-Sn) with as-rolled surfaces and surfaces abraded with 120 grit SiC 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 - 0.5% 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 50/50 HCl for 2 minutes and re-weighed.

Results

a. Kinetics

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 (catalyzed by Cu, Ni, Pd, C)

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

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

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

These reactions result in surface deposits of phosphorus oxides and a weight gain. These weight gains are listed in the tables in Appendix A for copper, brass and silver but not for solder which did not gain weight under any exposure condition.

The tables of data also indicate that some samples were wet and others dry when removed. These observations are summarized below:

Metal	Temperature	15 & 25% RH	50 & 75% RH
Copper	all	wet	dry
Brass	40°C	wet	dry
	20 & 30°C	dry	dry
Silver	all	dry	wet
Solder	all	dry	dry

The behaviour of copper, ie. wet at low relative humidity and dry at high, is unexpected and counter-intuitive. On the other hand, silver showed the more expected wet/dry behaviour but the extent of wetting was minimal as indicated by the weight change. Wet silver samples were merely cloudy to the naked eye and under the low-power stereo microscope, small “dew drops” covered the surface. Brass behaviour was intermediate between copper and silver with the low relative humidity wetting characteristic of copper observed only at 40°C. Solder showed no weight gain and no P signature with energy dispersive analysis by x-rays (EDAX) under any test condition.

Copper, brass and silver are thermodynamically stable in non-oxidizing acid solutions and, consequently, do not corrode in these solutions. However, they do oxidize (corrode) in air at a rate controlled by the availability of oxygen and any tendency to passivate is prevented by low pH solution. The corrosion products of metal oxidation (and the oxides of phosphorus deposited in the above reactions) can be removed to bare metal by immersion in 50/50 HCl, a non-oxidizing acid, and the resulting weight loss gives the corrosion rate of the metal. Weight losses after stripping to bare metal are also given in Appendix A.

b. Morphology

The scanning electron microscope (SEM) with EDAX was used to observe the morphology and to determine the chemistry of surface deposits on the metallic coupons exposed in these experiments. Because the surface deposits were electrically non-conducting, a thin evaporated gold coating was applied to minimize charging in the electron beam. The SEM was also used to reveal the morphology of corrosive attack on coupons after chemical cleaning with HCl. The same techniques were used to evaluate the morphology of large copper strips which had been exposed at fumigation sites by Fumigation Service and Supply, Inc.

Figures 1a, 2a and 3a show the typical morphology of surface deposits in the back-scattered electron (BSE) mode on copper (the dry regime) and Figures 1b, 2b and 3b show the progression of corrosive attack including areas with no attack, areas with general attack and areas with pits on the same samples after chemical cleaning to bare metal. The BSE mode clearly distinguishes between relatively bare metal where electrons are back-scattered efficiently and the area appears bright and coated areas which appear dark. Figure 4 reveals the morphology of Figure 3a more clearly in the secondary electron (SE) mode and it is clear that the surface after 36 hours is almost completely covered with small nodules. The EDAX spectrum in Figure 5 shows only P, O and Cu (H cannot be detected using EDAX).

The dry morphology shown in Figures 1, 2 and 3 can be contrasted with the morphology of the wet regime shown in Figures 6a, 7a and 8a (SE mode) for copper after 12, 24 and 36 hours at 40°C, 220 ppm PH₃ and 15% RH. The extent of corrosion on the same samples is shown in Figures 6b, 7b and 8b after chemical cleaning in the same way as samples in Figures 1b, 2b and 3b. At 40°C, the coating material is more resistant to the 50/50 HCl cleaning solution and a certain amount of residue remains in some pits (see Figure 8b). Although the surface coating formed on copper at 40°C is more resistant to dissolution, the EDAX spectrum in Figure 9 shows it to be chemically similar to the coating formed at 30°C (see Figure 5).

The wet and dry morphologies observed on brass were similar to those discussed above for copper but in the case of silver, the extent of surface coverage was minimal. Figure 10 shows the very limited extent of coverage on silver exposed for 12 hours at 40°C to 220 ppm PH₃ (dry regime for silver) and Figure 11 shows the increased, but still small, coverage at 75% RH (wet regime). No corrosion was found on chemically cleaned silver coupons.

In addition to laboratory coupons, the following observations have been made with respect to copper samples exposed in field fumigations(3,4)

- surface deposits on the copper are mainly colourless to slightly bluish crystals. A few random dark circular deposits seem to be associated with surface dust.
- these deposits are not electrical conductors and charge in the electron beam of the SEM.
- EDAX shows that the elements present are Cu, P and O.
- surface deposits nucleate at surface imperfections such as rolling marks and grow rapidly to increase surface coverage but in a non-linear way
- when the surface deposits were removed in 50/50 HCl, the copper substrate showed areas of no attack, areas of general attack and other areas with pitting.

Discussion

Because single coupons of each metal were exposed under each of the steady-state exposure conditions, the weight change data in Appendix A are characterized by considerable scatter and are not amenable to statistical analysis. However, a number of interesting trends are discussed below.

Effect of Surface Roughness

In Appendix A, any differences in weight change between smooth samples and samples abraded with 120 grit SiC paper seemed to be minimal and within the sample to sample scatter in the data. Consequently, the data for smooth and rough samples were averaged for trend analysis.

Effect of Carbon Dioxide Concentration

Differences in CO₂ concentrations (3.2% vs. 4.5% and 3.5% vs. 5.0%) had minimal effect on weight change data and results at high and low CO₂ were averaged for trend analysis. If CO₂ has an effect, it may be a small one in defining equilibrium conditions for wet/dry morphology - see for example the behaviour of brass in 220 ppm PH₃ at 40°C and 25% RH in 3.5 vs. 5% CO₂ (Appendix A).

Effect of Relative Humidity

Copper is clearly a special case where the effect of relative humidity on weight gain is entirely counter-intuitive. At 15 and 25% relative humidity, copper coupons were observed to be wet after exposure whereas at the higher humidity levels investigated - 50 and 75% RH - the copper samples were invariably dry and coated with crystalline material. In Figure 12, the average weight change

of smooth and rough copper coupons exposed to 3.5 and 5% CO₂ and 220 ppm PH₃ for 36 hours is plotted as a function of RH for the 3 exposure temperatures. The effect of wetness on weight gain is apparent at 40 and 30°C but not at 20°C. Wetness had only a minimal effect on weight loss (corrosion) as might be expected in the case where corrosion rate is controlled by oxygen availability.

For brass weight change results averaged in the same way and shown in Figure 13, it should be noted that wetness was observed only at lower relative humidities and only at 40°C. This was the case at lower PH₃ concentrations as well. As with the copper, weight loss (corrosion) was relatively unaffected by wetness and the corrosion rates of copper and brass were similar under most conditions as would be expected where oxygen availability controlled. Weight gains, however, were consistently lower on brass than on copper.

As shown in Figure 14, the data for silver (averaged in the same way as for copper and brass above) reflects the intuitive relationship of increasing weight change with increasing RH and, indeed, small droplets of moisture were observed at higher relative humidities. Based on the minute weight losses and morphological observations, it can be concluded that silver does not corrode in phosphine.

Effect of Temperature

An example of the effect of temperature on reaction kinetics is shown in Figure 15 for copper. In the wet regime (15 and 25% RH), increasing temperature has a significant effect on both weight gain and weight loss kinetics. In the dry regime (50 and 75% RH), only the highest temperature (40°C) leads to significant increases in reaction rates.

Unlike copper, brass (shown in Figure 16) is dry at low relative humidities (15 and 25%) and low temperatures (20 and 30°C) and shows no temperature dependence in this range. With the onset of the wet regime at 40°C, kinetics increase dramatically at 25% RH but are much more muted at 15%.

The weight gain kinetics of silver shown in Figure 17 are greatly accelerated with increasing temperature at all relative humidity levels but the absolute values are very small relative to copper and brass under the same conditions. Silver does not corrode in the temperature range 20 to 40°C.

Effect of Phosphine Concentration

In general, weight changes of copper, brass and silver vary in a linear way with increasing PH₃ concentrations. For example, Figures 18, 19 and 20 show the weight gains and weight losses on copper at 20, 30 and 40°C, respectively, with changes in PH₃ concentration from 35 to 220 ppm. At 35 ppm PH₃, the weight changes are essentially zero (<0.7mg in 36 hours) at all temperatures but change dramatically as PH₃ increases to 220 ppm. In the dry regime (50 and 75% RH), the weight increase appears to be linear while in the wet regime (15 and 25% RH) the increase is somewhat erratic but the trend is clearly upward and strongly temperature dependent. Weight losses

(corrosion) of copper also increase with PH_3 concentration but are insensitive to wet/dry variations except at the lowest temperature. The behaviour of brass parallels that of copper as shown in Figures 21 and 22 at 30 and 40°C, respectively, but with smaller overall weight changes.

Silver at 30°C (Figure 23) experiences minimal weight increases (<1mg in 36 hours) and is relatively insensitive to PH_3 concentration but at 40°C (Figure 24) the weight gain trends are similar to copper and brass. The corrosion rate of silver can be taken as zero at all PH_3 concentrations and temperatures.

Effect of Exposure Time

Reaction kinetics of metals in PH_3 as measured by weight change has been observed to be linear with time or to accelerate with time. Accelerating weight increase is consistent with nucleation at points on the surface, grow of these deposits with time leading to complete surface coverage and subsequent linear kinetics. This kind of behaviour is evident in Figures 1a, 2a and 3a for copper at 30°C. The related kinetics in Figure 25 show the weight change accelerating with time. However, at 40°C, Figure 26, the kinetics become linear after 12 hours; the time required for extensive surface coverage as shown in Figure 27, the BSE image which shows surface coverage more clearly than the SE image in Figure 6a.

On the other hand, as shown in Figure 28, brass kinetics are linear at 30°C (dry regime) because the degree of surface coverage remains low even after 36 hours. However, brass kinetics accelerate at 40°C as shown in Figure 29, particularly in the wet regime, where surface coverage approaches 100% after 36 hours.

The kinetics for silver are essentially linear with time and very slow relative to brass and copper consistent with the minimal surface coverage even after 36 hours of exposure. An example of silver at 40°C is shown in Figure 30. Silver does not corrode as indicated by both weight-loss results and SEM observations.

The weight changes plotted above can be converted into corrosion rates. For copper, a weight change of 1mg in 24 hours on a sample with an area of 0.13dm² produces a rate of 7.7mdd (milligrams per square decimeter per day) or a penetration rate (on a planar interface) of 0.03mm/year (0.0012 inches per year). Consequently, if the weight-loss data plotted in Figures 25 (30°C) and 26 (40°C) at each time are averaged, the following rates can be calculated for copper exposed to 220 ppm PH_3 :

EXPOSURE TIME (hrs)	RATE at 30°C (mdd)	RATE at 30°C (mm/yr)	RATE at 40°C (mdd)	RATE at 40°C (mm/yr)
12	18	0.7	52	2
24	27	1	62	2.4
36	29	1.1	65	2.5

As noted above, increasing rates are consistent with a mechanism involving nucleation at points on the surface followed by growth with time until complete surface coverage when rates become

constant. Constant rates are reached more quickly at 40°C than at 30°C because of the faster kinetics at higher temperature.

Comments on Morphology

Nucleation and growth of surface deposits has been observed in all cases but the size of deposits varies considerably depending on whether the steady-state conditions produce wet or dry behaviour. With copper, for example, nodules approximately 50 μ in diameter were observed in the dry regime (see Figure 4) but in the wet regime, large black blobs up to 1mm in diameter were formed after 36 hours(see Figure 8a). On a macroscopic scale, copper samples appeared black and shiny in the wet regime and only dulled in the dry regime.

Summary

Within the envelope of variables studied (20 to 40°C, 35 to 220 ppm PH₃, 15 to 75% RH), it is now clear that electronic equipment exposed to phosphine fumigations might fail by any of three mechanisms:

- 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 only failed electronic component examined in this laboratory was a switch supplied by Michelle Marcotte (6) in which the first possible mechanism - the build-up of non-conducting compounds rich in P and O - had occurred on the silver contacts. Reports of other failures in the field have been anecdotal and have suggested that high relative humidity was the primary factor which should be avoided - a conclusion not supported by this study.

The table below summarizes the observations made in this course of this study on metal samples from a number of sources.

METAL	SOURCE	WEIGHT GAIN	CORROSION
Copper	This study Mueller samples	Extensive	Extensive
Nickel	Mueller calculator Mueller camera	Yes	?
Brass	This study	Yes	Yes
Silver	This study Mueller fumigation	Yes	No
Stainless Steel	Mueller camera	No P signature	None found
Solder	This study Mueller calculator Mueller fumigation	No	No

It should be noted that both surface deposits and corrosion morphology were identical whether produced in this study in the laboratory or in fumigations in the field.

Conclusions

1. Within the grid of test parameters, the steady-state technique used in this study which facilitates the variation in all the parameters independently has clarified in a global sense the relative severity of metallic “corrosion” in phosphine by quantifying the extent of both surface deposit formation and metallic dissolution of the metals studied.
2. The most significant results from this study concern the identification of wet and dry regimes for copper as a function of relative humidity. Copper develops shiny black wet surface deposits only at low relative humidities (25% and lower); an observation which is both counter-intuitive and contradictory of anecdotal evidence. Dry crystalline surface deposits on copper are observed only at high relative humidities (50% and higher).
3. Different metals behave differently when exposed to phosphine in terms of wet/dry regimes and overall reaction rates. Copper, and to a lesser extent brass, develop massive wet surface coatings at low relative humidity whereas silver becomes slightly wet at high relative humidities. Copper, and to a lesser extent brass, form surface deposits and suffer pitting and general corrosion. Silver develops surface deposits but does not corrode. Solder is inert.
4. Three possible failure mechanisms for electronic equipment exposed to phosphine have been identified:
 - 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.

Recommendations

This study has made significant progress in clarifying in a global sense the relative severity of metallic “corrosion” in phosphine but the following additional work might be considered:

1. Additions to the existing data base.

Additional work is required to define more closely the relative humidity in the range 25 to 50% at which copper changes from the wet to dry regime. This work would be done at different phosphine levels, possibly 85 and 180 ppm and even one very high level >220 ppm, to expand the data base rather than duplicate existing information. It is clear that any additional work should include replicate samples of copper for subsequent statistical analysis and nickel, a common component of circuit boards on which oxides of phosphorus have been observed after field fumigations, should be included in the study. Data at 0% carbon dioxide may be of interest to some.
 2. Inducing failures in electronic equipment.

A number of possible failure mechanisms have been identified but, with the exception of one switch with silver terminals, no failed electronic components have been examined. The experimental parameters which are believed to be most aggressive have been identified and the experimental feasibility of carrying out long-term steady state exposures has been
-

demonstrated. Therefore, it is now possible to induce failures in small electronic components and carry out failure analyses to identify precisely the conditions to be avoided.

3. Evaluating of the effects of cyclical exposure parameters.

Work to date has been performed under steady-state conditions but it is possible to cycle independently the temperature, relative humidity, PH_3 concentration and CO_2 concentration to more closely duplicate the conditions of field fumigations. The effect of repeated exposures might also be of practical interest to the industry.

4. Understanding the chemistry of phosphine in contact with metals.

The chemistry involved in the wet/dry transition of copper exposed to phosphine is clearly not understood and is of great theoretical interest. Analytical equipment now exists which could clarify the reactions involved.

References

1. E. J. Bond, T. Dumas and S. Hobbs, Corrosion of Metals by the Fumigant Phosphine, J. Stored Prod. Res. Vol. 20, Pp. 57-63 (1984)
 2. Ebbe Rislund, Corrosion Aspects of Phosphine Fumigation, Danish Environmental Protection Agency Arbejdsrapport Tra Miljostyrelsen, Working Report No. 29 (1996)
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 5. M. Pourbaix, Atlas of Electrochemical Equilibria In Aqueous Solutions, NACE/Cebelcor (1974), p. 509.
 6. Michelle Marcotte, private communication
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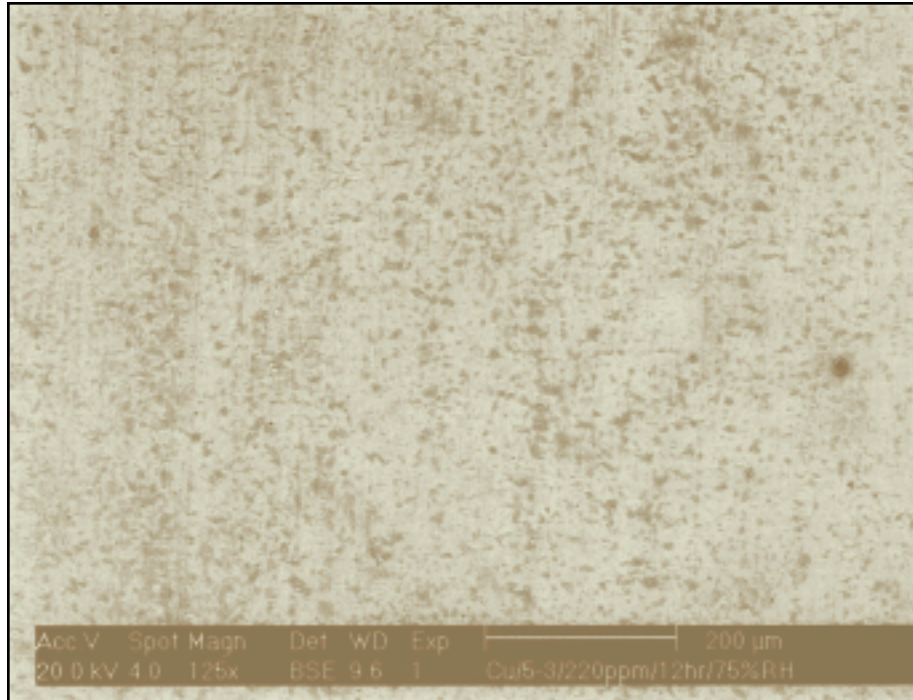


Figure 1a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH

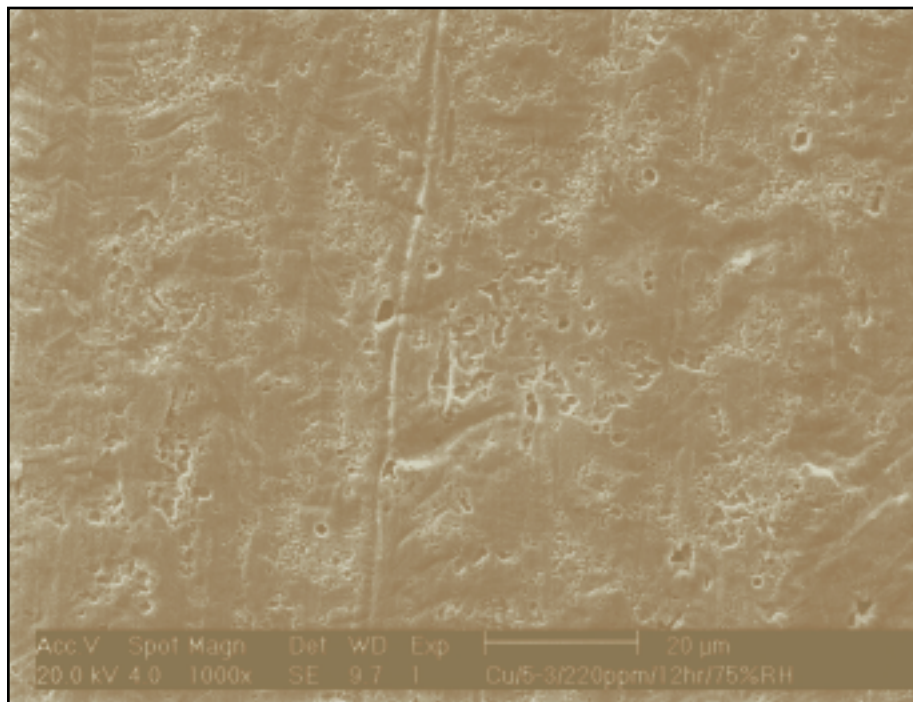


Figure 1b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH

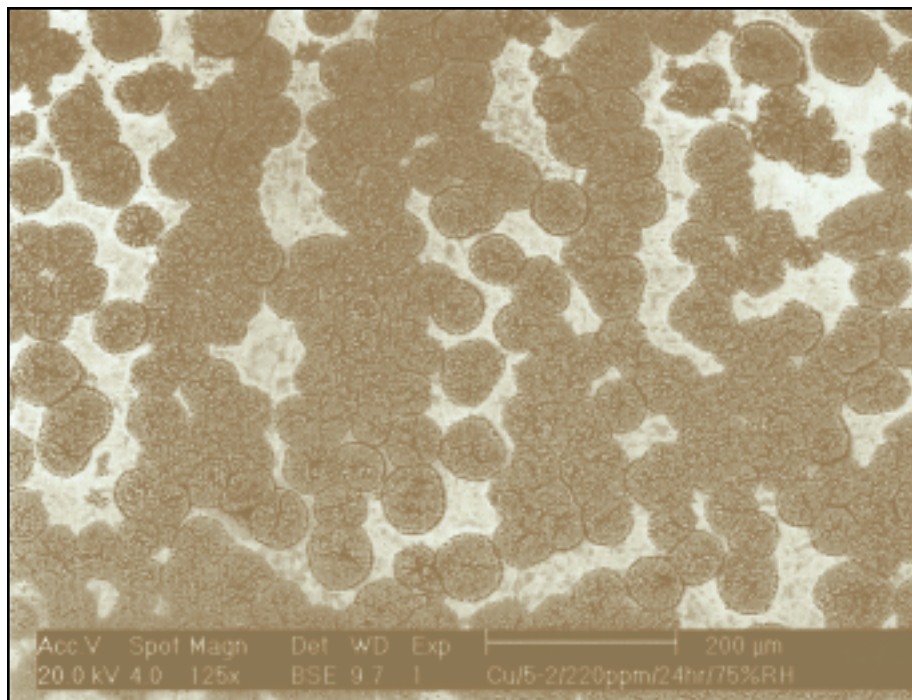


Figure 2a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH

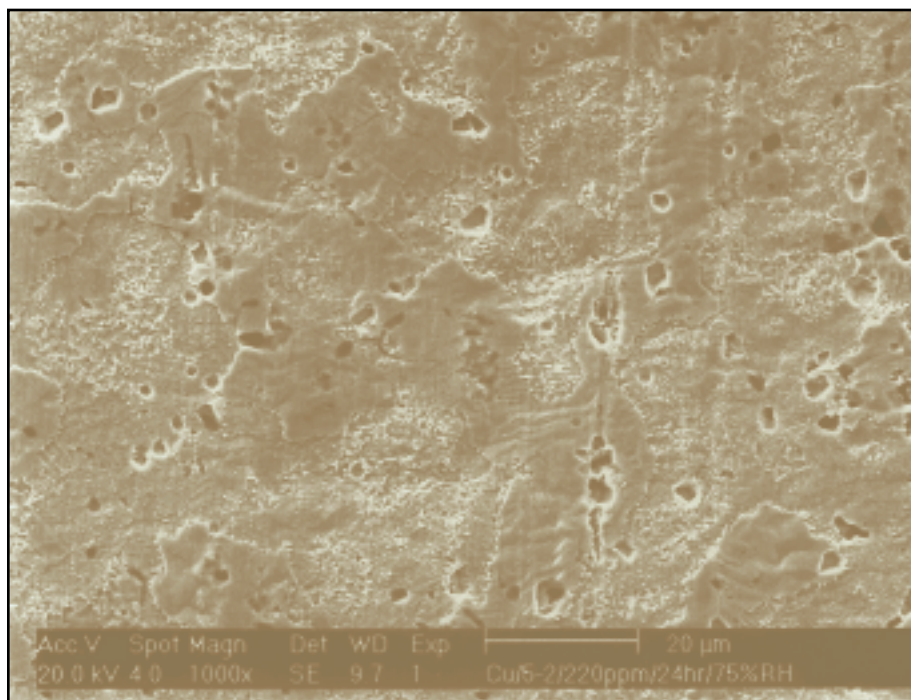


Figure 2b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH

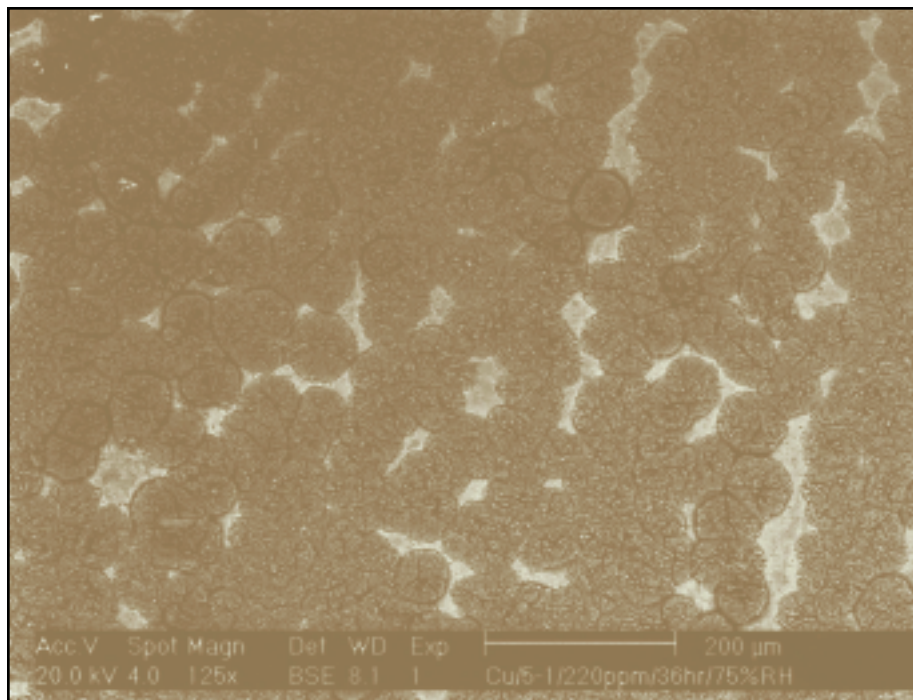


Figure 3a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

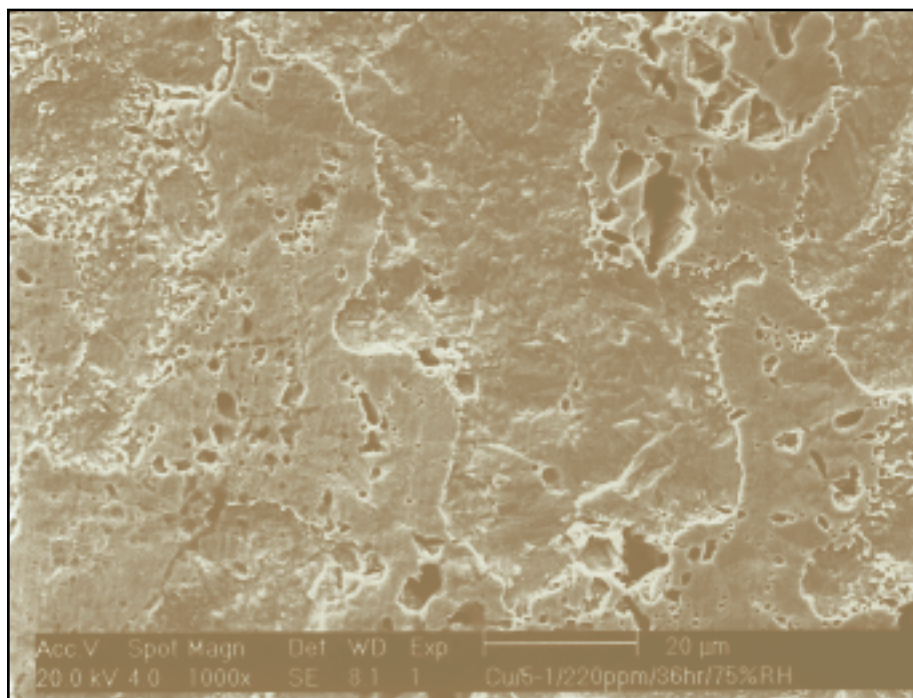


Figure 3b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH



Figure 4. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

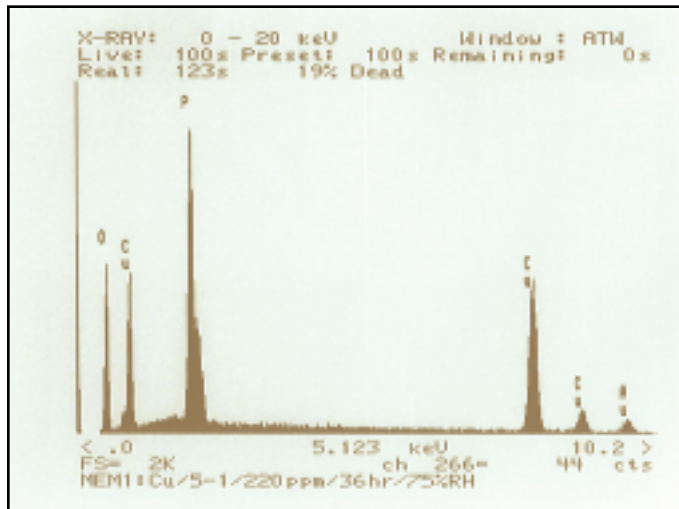


Figure 5. EDAX spectrum of the surface deposits in Figure 4.

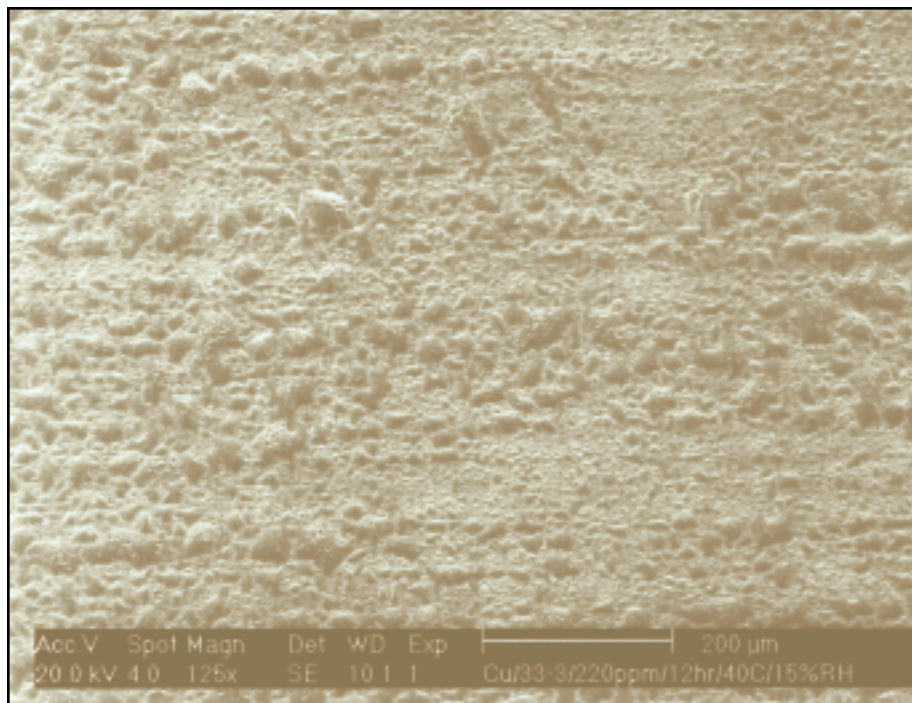


Figure 6a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

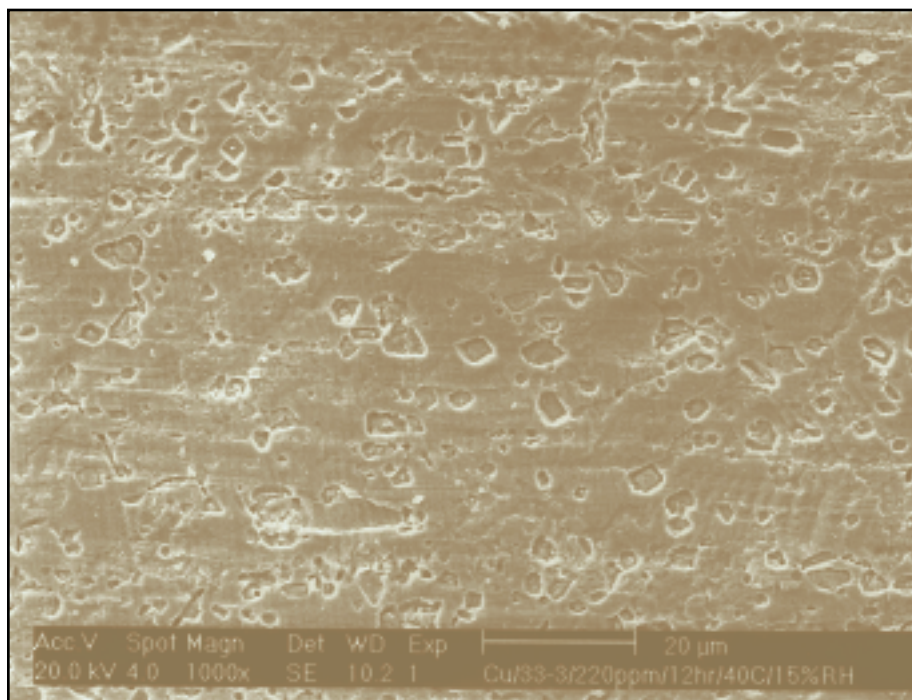


Figure 6b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

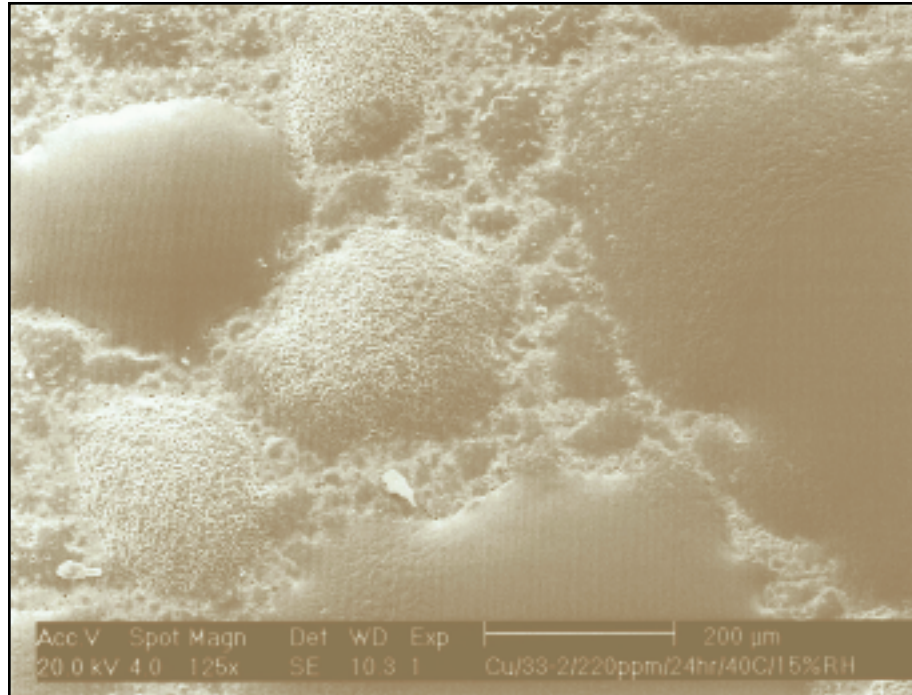


Figure 7a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH

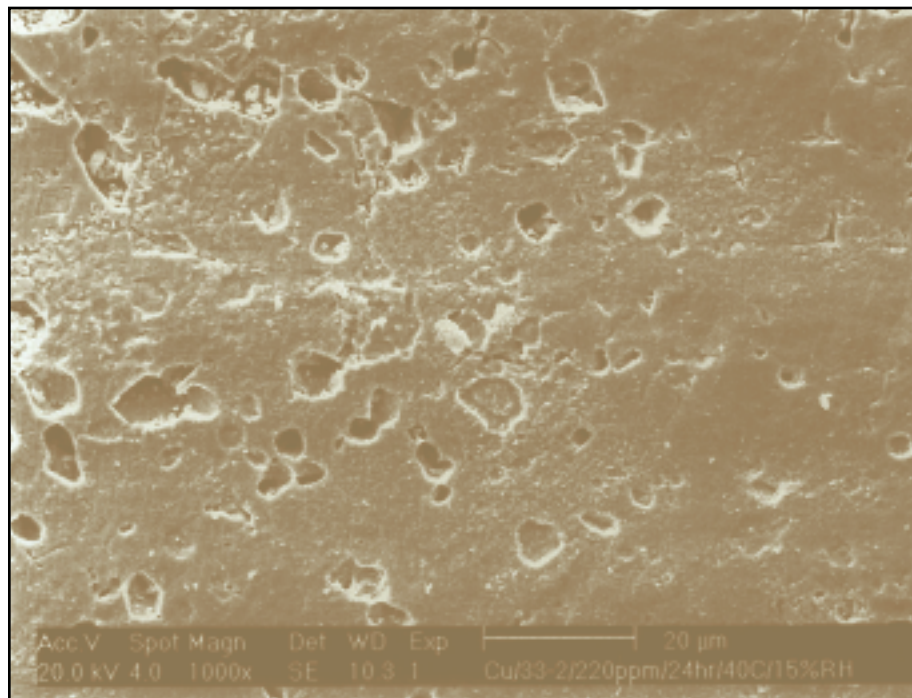


Figure 7b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH

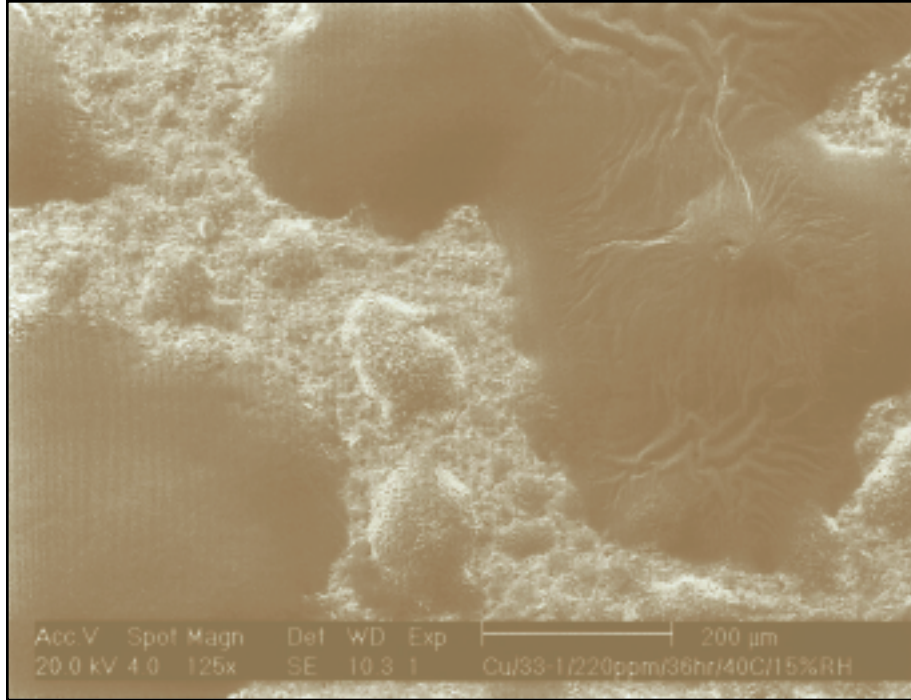


Figure 8a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH

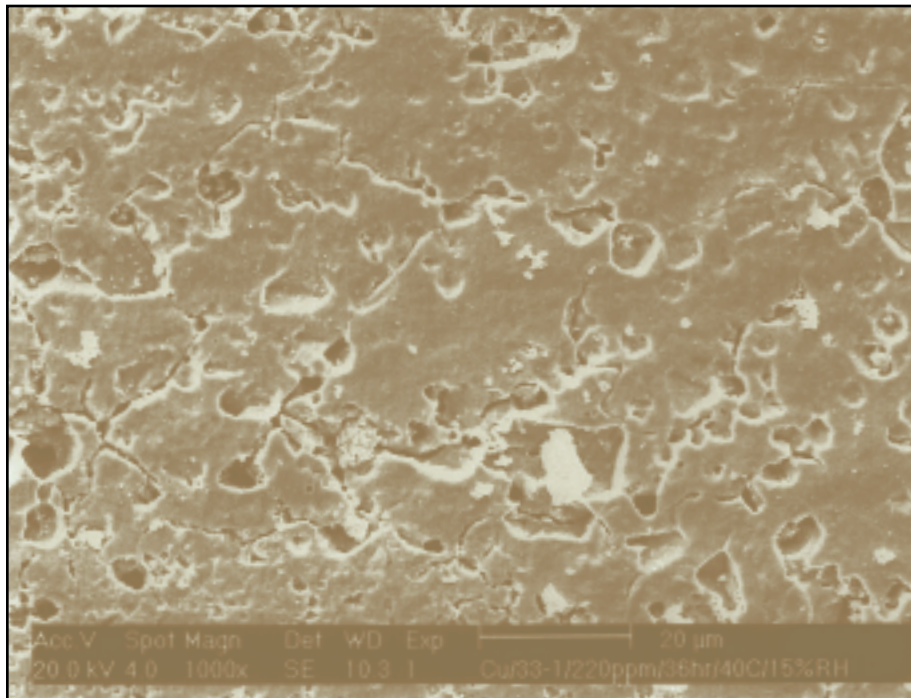


Figure 8b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH

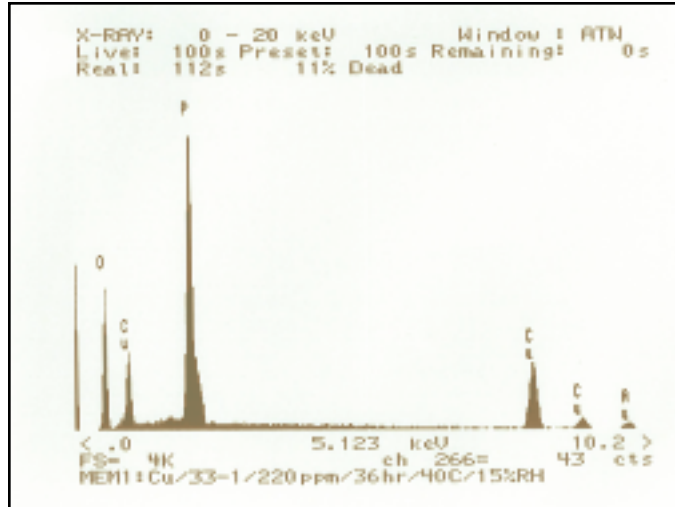


Figure 9. EDAX spectrum of the large black surface deposits in Figure 8a.

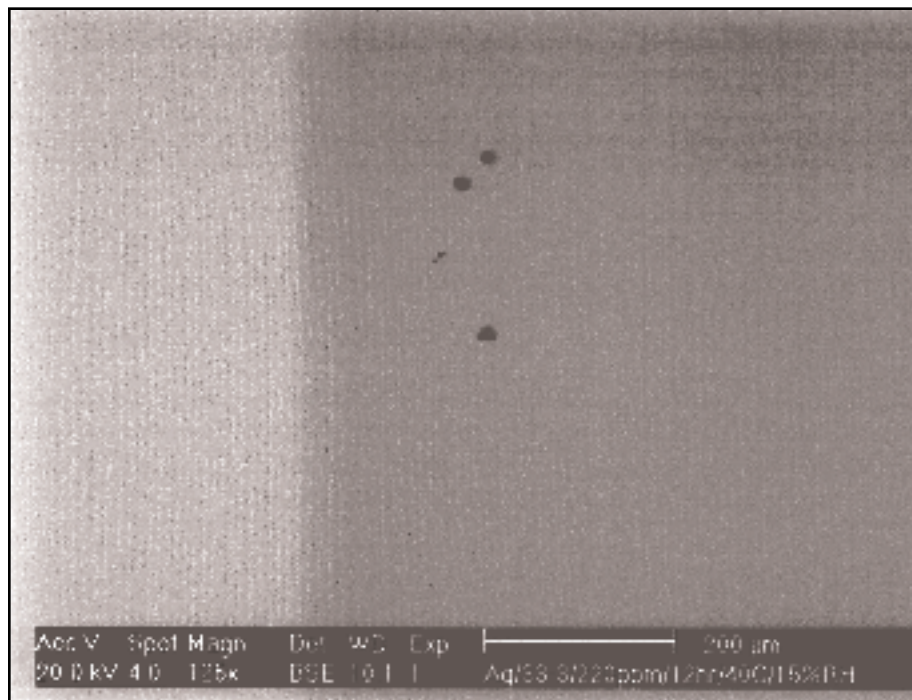


Figure 10. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

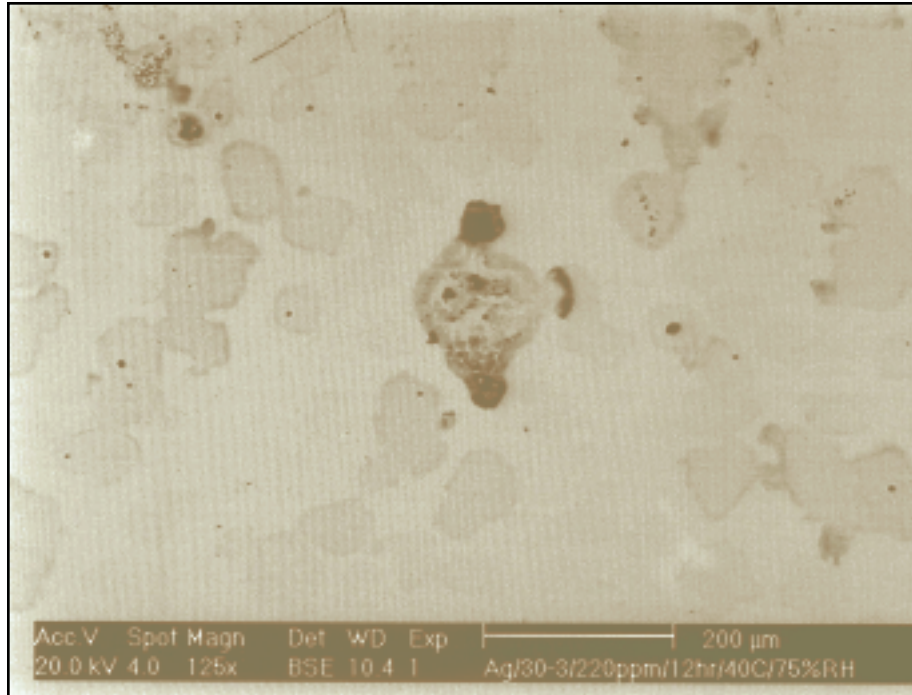


Figure 11. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 75% RH

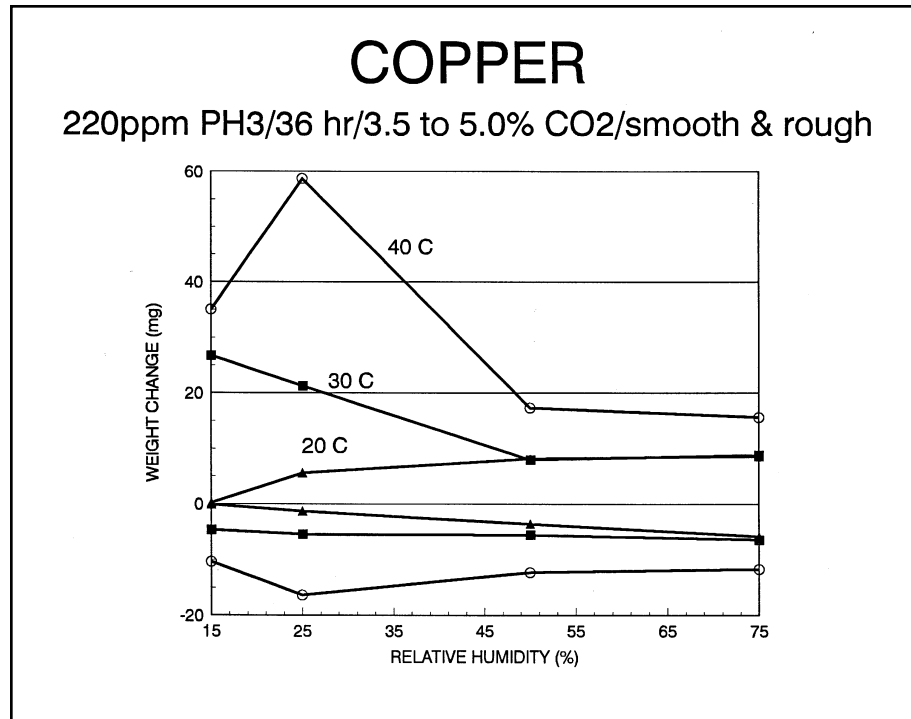


Figure 12. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

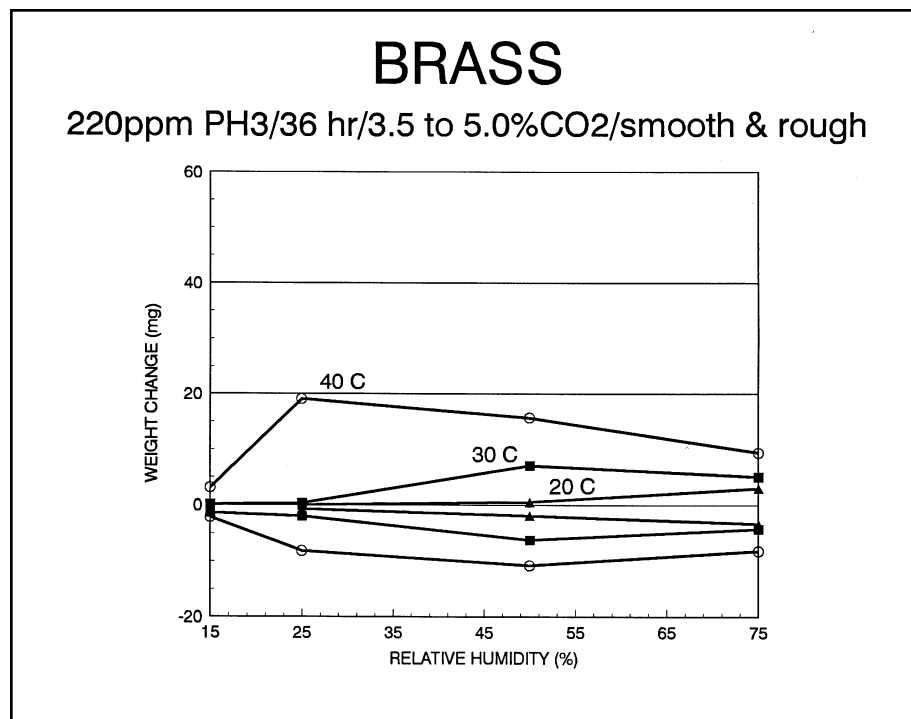


Figure 13. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

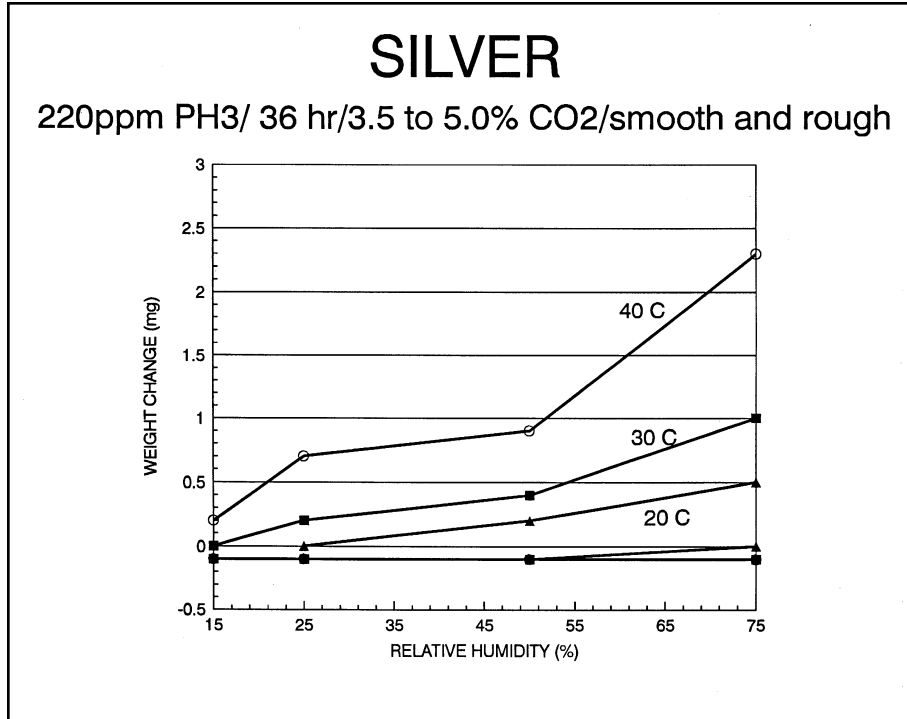


Figure 14. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

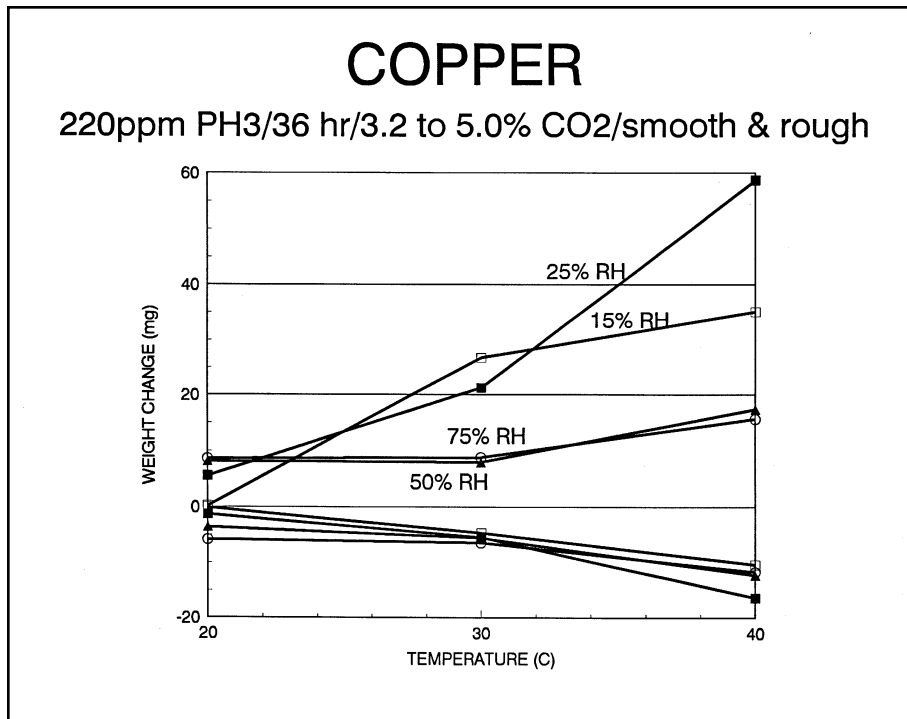


Figure 15. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

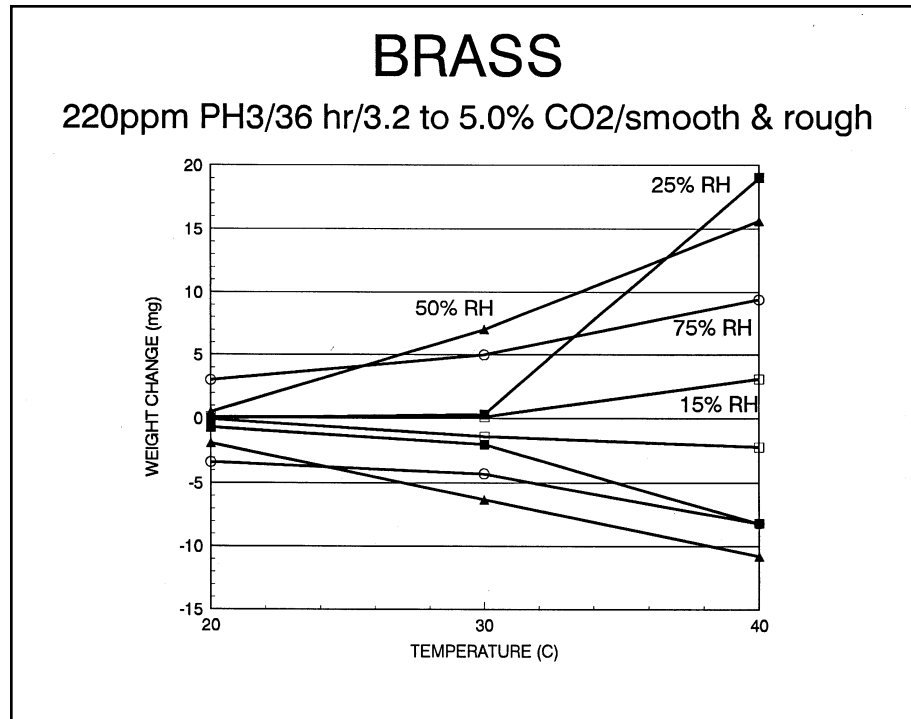


Figure 16. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

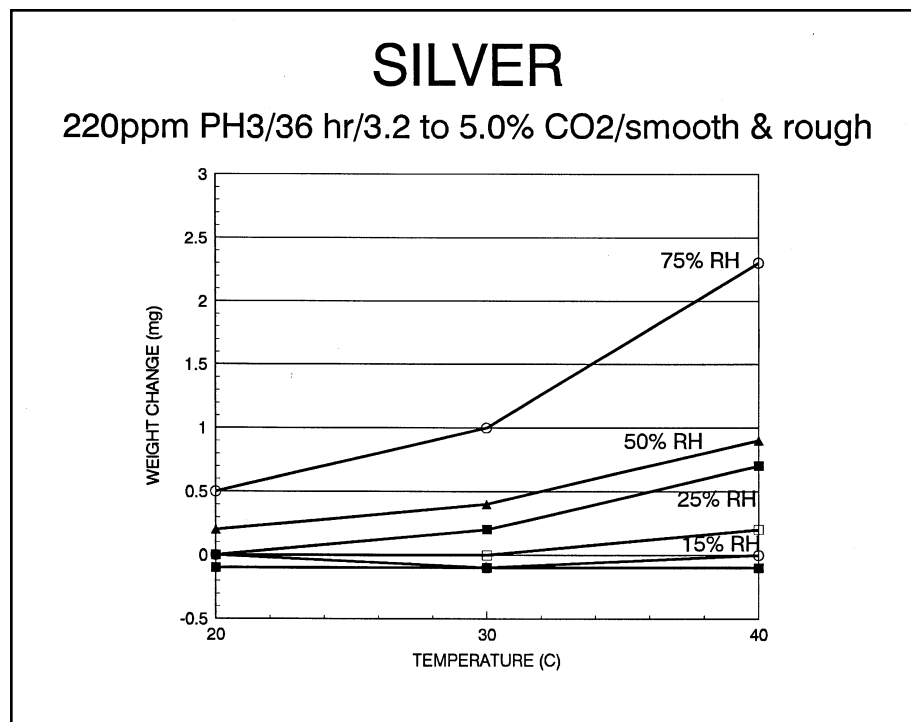


Figure 17. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

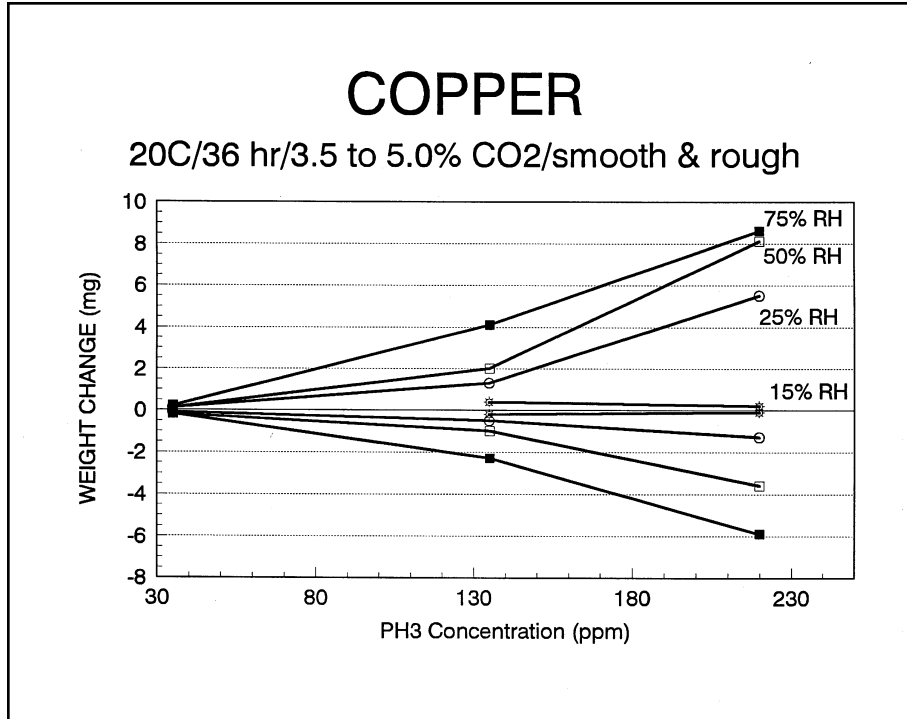


Figure 18. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

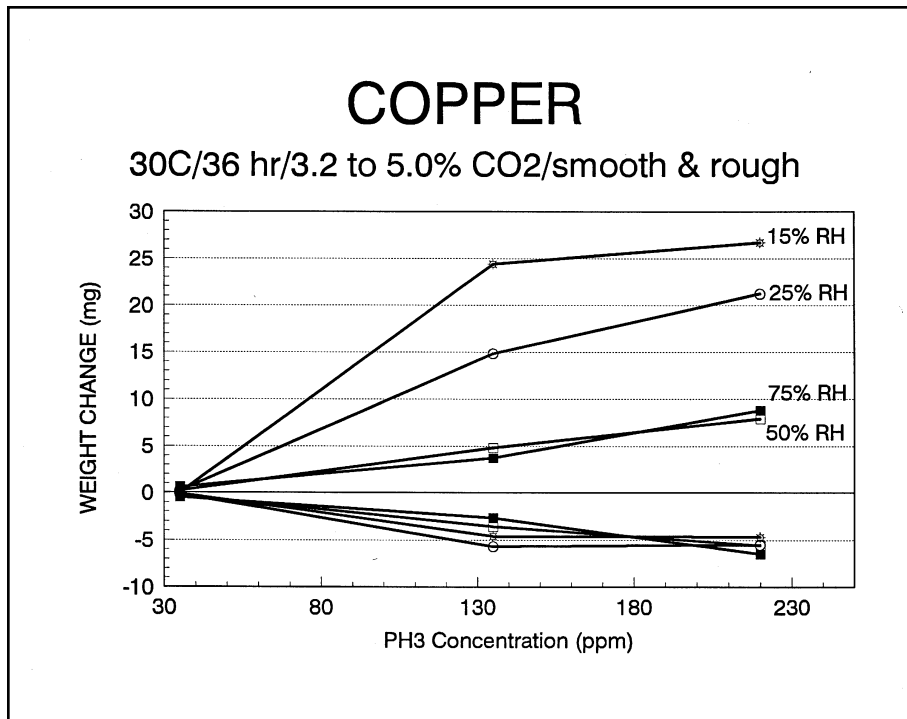


Figure 19. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

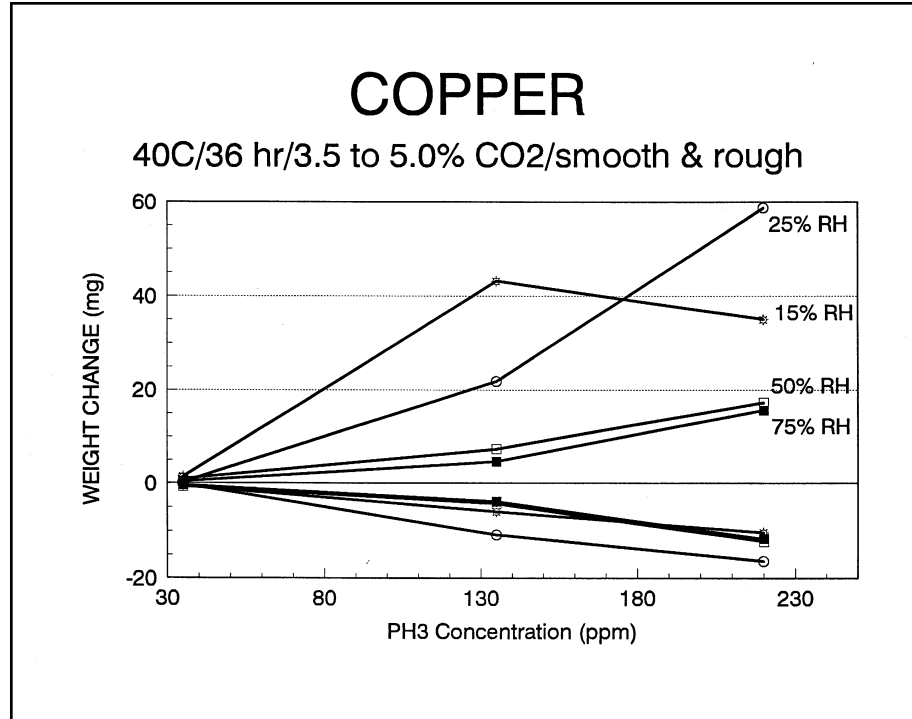


Figure 20. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

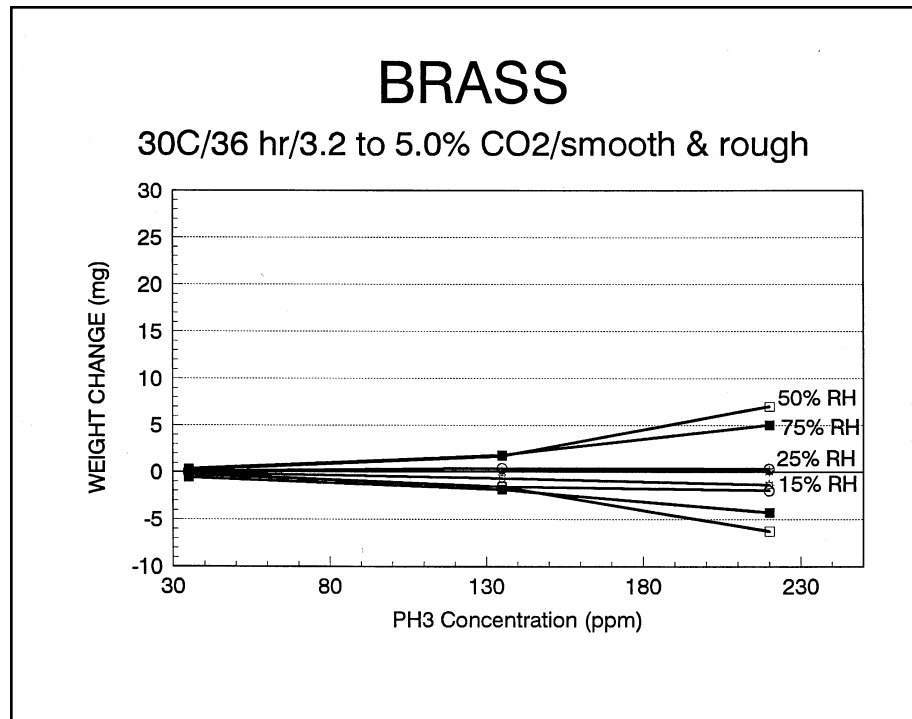


Figure 21. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

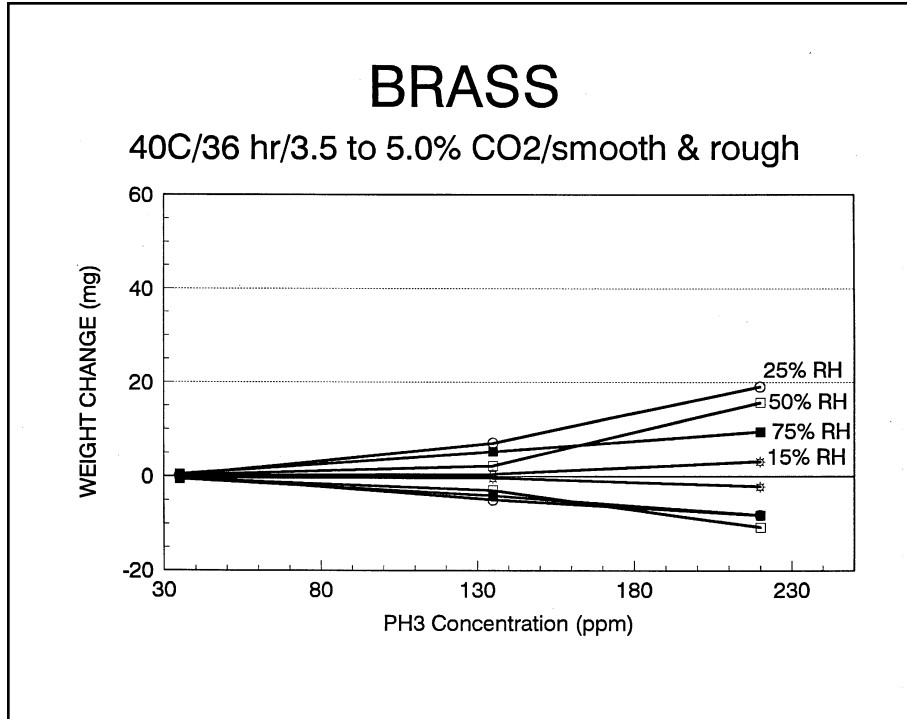


Figure 22. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

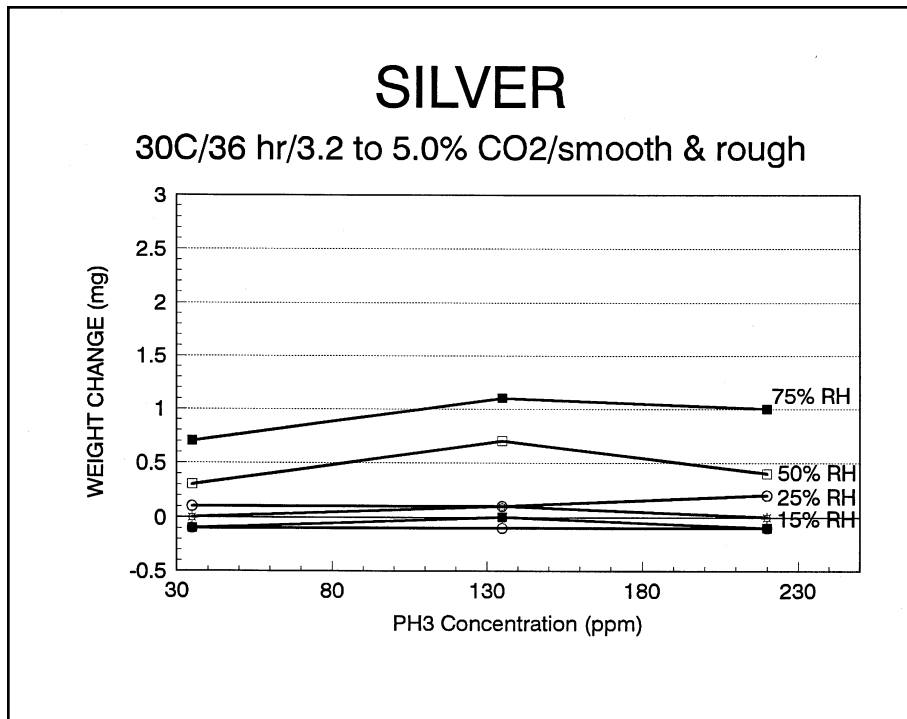


Figure 23. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

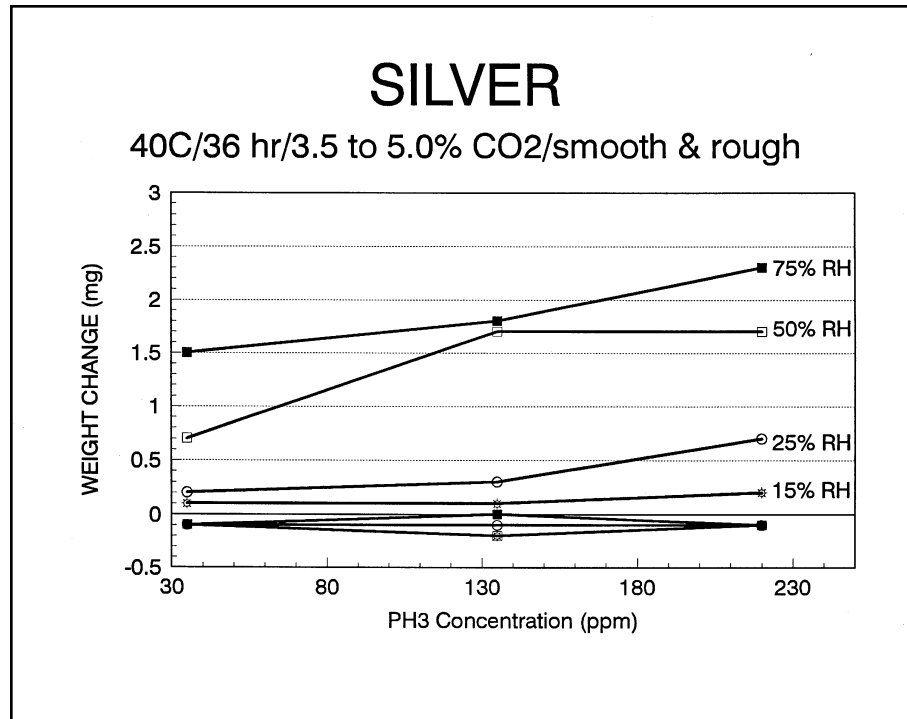


Figure 24. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

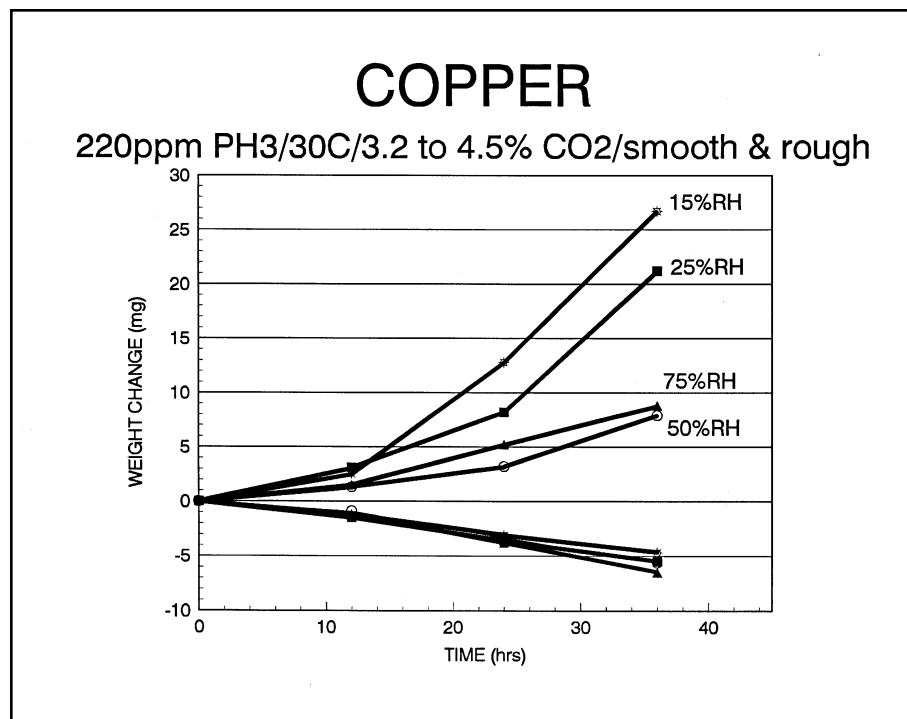


Figure 25. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

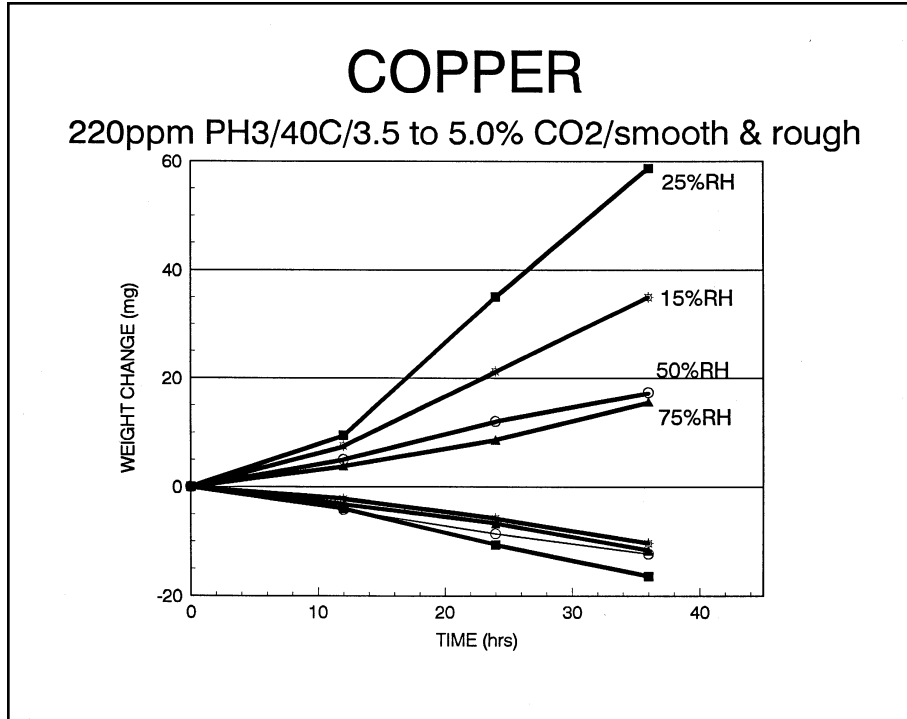


Figure 26. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

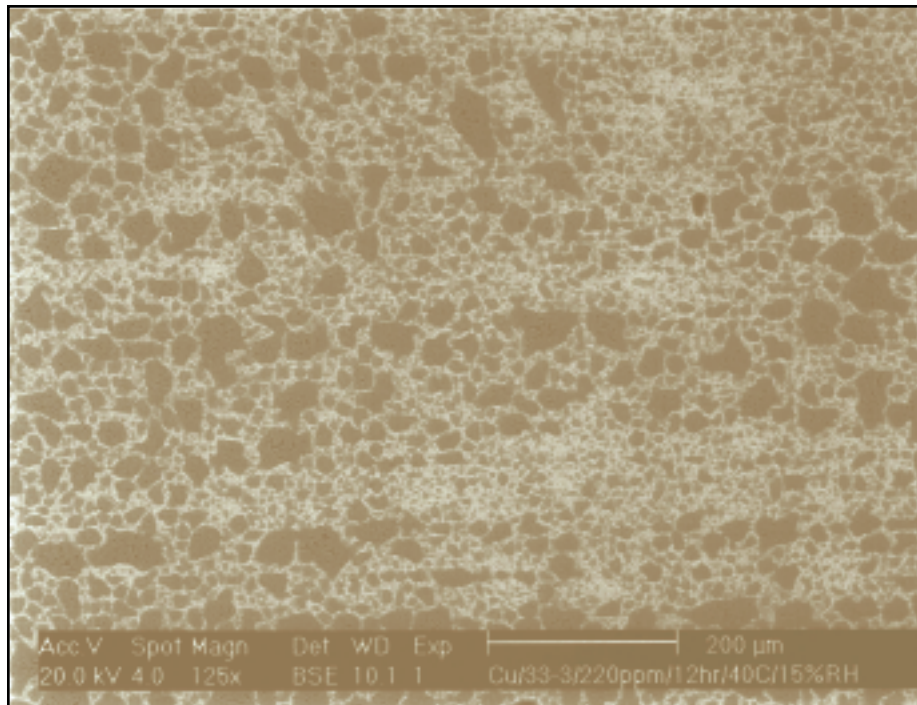


Figure 27. Scanning electron micrograph (BSE mode) showing the extent of surface coverage of copper sample in Figure 6a (SE mode)

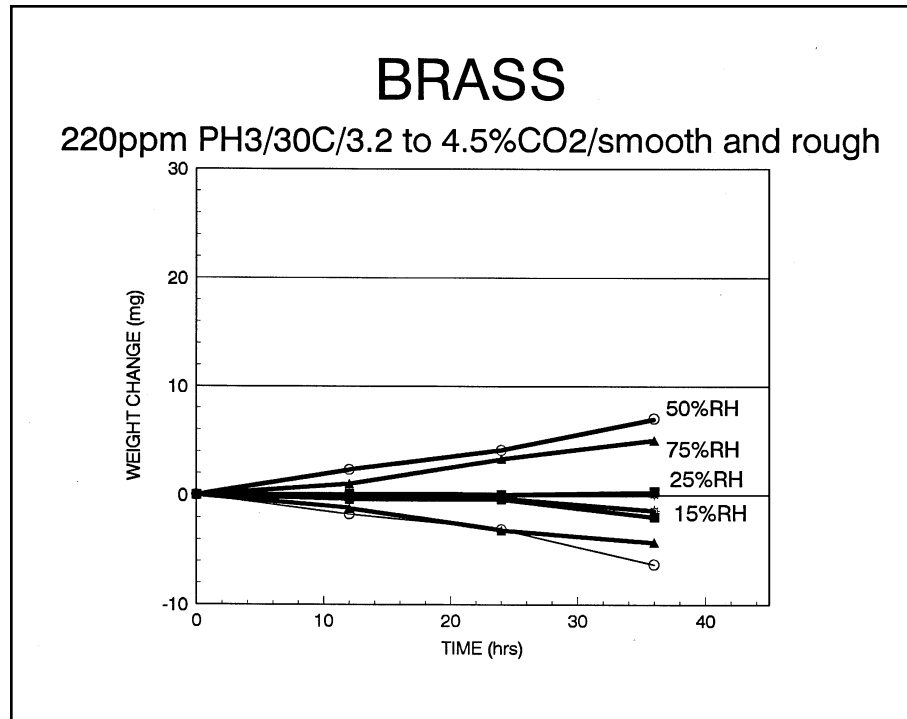


Figure 28. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

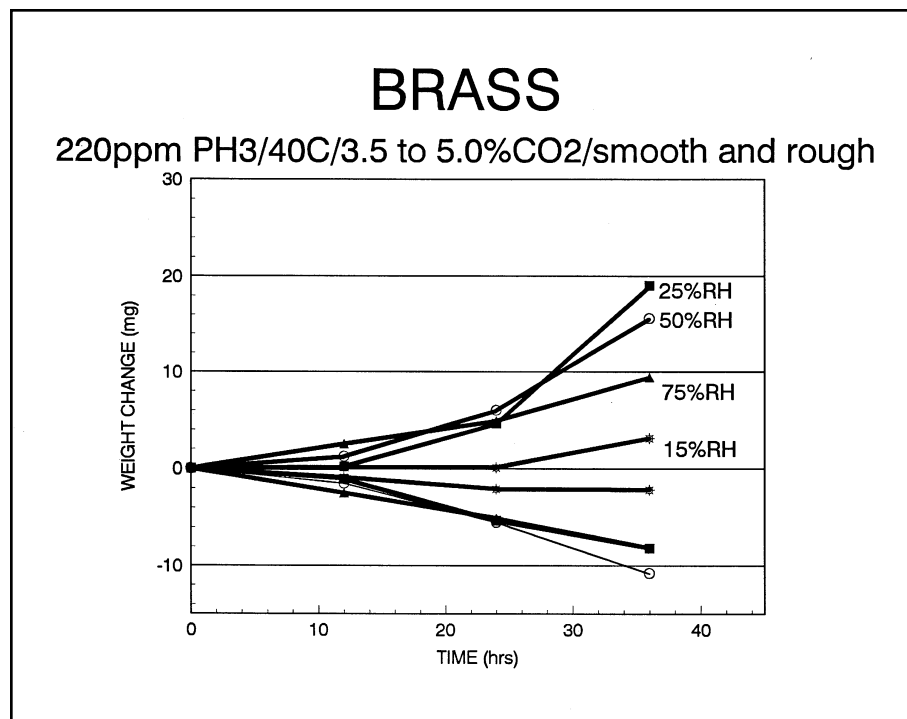


Figure 29. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

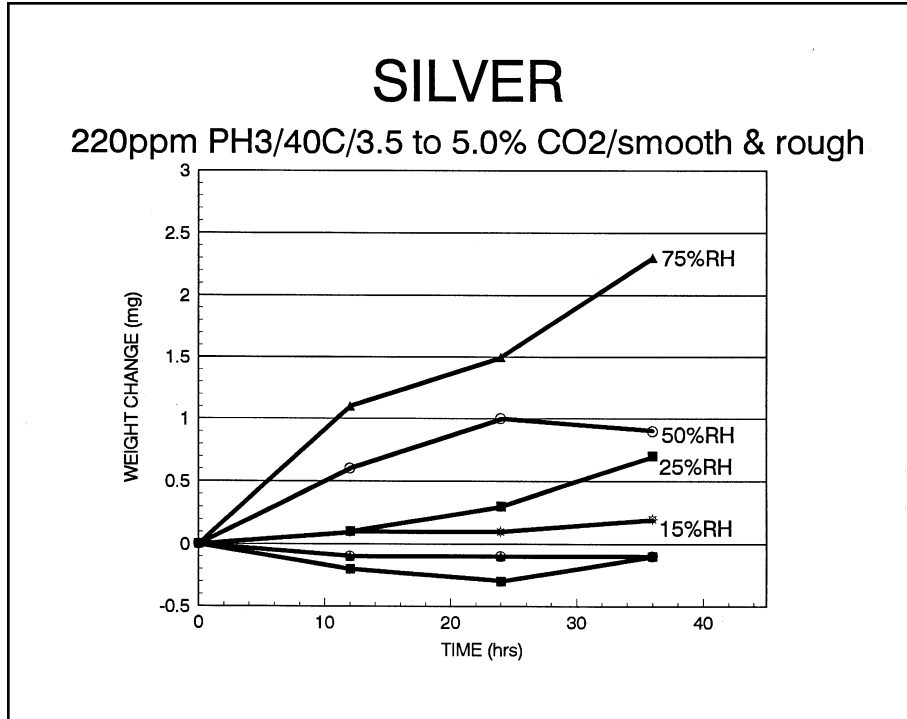


Figure 30. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

APPENDIX A

Tables of weight gain and weight loss are compiled in Appendix A for the following experimental parameters:

20°C, 5.0% CO₂, 35 ppm PH₃

20°C, 5.0% CO₂, 135 ppm PH₃

20°C, 3.5% CO₂, 220 ppm PH₃

20°C, 5.0% CO₂, 220 ppm PH₃

30°C, 5.0% CO₂, 35 ppm PH₃

30°C, 3.2% CO₂, 135 ppm PH₃

30°C, 5.0% CO₂, 135 ppm PH₃

30°C, 3.2% CO₂, 220 ppm PH₃

30°C, 4.5% CO₂, 220 ppm PH₃

40°C, 5.0% CO₂, 35 ppm PH₃

40°C, 5.0% CO₂, 135 ppm PH₃

40°C, 3.5% CO₂, 220 ppm PH₃

40°C, 5.0% CO₂, 220 ppm PH₃

20C/35 ppm PH₃/5.0% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	XX	-	-	-	XX	0.1	-	0.1
		24 hr	XX	-	-	-	XX	-	0.1	0.2
		36 hr	XX	0.1	-	0.2	XX	-	0.1	0.1
	Rough	12 hr	XX	-	-	-	XX	0.1	0.1	0.2
		24 hr	XX	-	-	0.1	XX	0.2	0.2	0.2
		36 hr	XX	0.1	0.1	0.2	XX	0.2	0.2	0.2
Brass	Smooth	12 hr	XX	0.1	-	-	XX	-	0.1	0.1
		24 hr	XX	0.1	-	-	XX	-	0.1	0.2
		36 hr	XX	0.1	0.1	0.2	XX	0.1	0.1	0.2
	Rough	12 hr	XX	-	-	-	XX	-	0.2	0.2
		24 hr	XX	-	-	0.1	XX	-	0.2	0.2
		36 hr	XX	0.1	0.1	0.2	XX	-	0.2	0.3
Silver	Smooth	12 hr	XX	-	-	-	XX	-	-	-
		24 hr	XX	-	-	-	XX	-	-	-
		36 hr	XX	-	-	0.1	XX	-	-	-
	Rough	12 hr	XX	-	-	-	XX	0.2	0.3	0.2
		24 hr	XX	-	-	-	XX	0.2	0.2	0.2
		36 hr	XX	-	0.1	-	XX	0.2	0.2	0.2

The solder samples gained no weight under these test conditions

All samples mounted parallel

20C/135 ppm PH₃/5.0% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	-	0.3	0.8	-	-	0.2	0.5
		24 hr	-	0.1	0.6	2.1	-	0.1	0.3	1.4
		36 hr	0.2	0.7*	1.5	4.2	0.1	0.3	0.8	2.2
	Rough	12 hr	-	-	0.3	0.9	0.1	0.2	0.3	0.6
		24 hr	0.1	0.3	0.9	2.3	0.1	0.3	0.5	1.4
		36 hr	0.6	1.8	2.5	3.9	0.2	0.6	1.2	2.4
Brass	Smooth	12 hr	-	0.1	0.1	0.4	-	-	0.1	0.5
		24 hr	-	-	0.1	0.7	0.1	0.1	0.3	1.0
		36 hr	-	0.1	0.4	1.2	0.1	0.3	0.8	1.9
	Rough	12 hr	-	-	-	0.2	0.2	0.2	0.3	0.5
		24 hr	-	-	-	0.3	0.2	0.3	0.3	1.0
		36 hr	-	-	0.1	0.6	0.2	0.3	0.6	1.5
Silver	Smooth	12 hr	-	-	-	-	-	-	-	-
		24 hr	-	-	-	-	-	-	-	0.1
		36 hr	-	-	0.1	0.3*	-	-	-	-
	Rough	12 hr	-	-	-	0.1	0.2	0.2	0.2	0.1
		24 hr	-	-	0.1	0.1	0.1	0.3	0.2	0.2
		36 hr	-	-	0.1	0.4	0.2	0.2	0.2	0.2

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

20C/220 ppm PH₃/3.5% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	XX	-	1.2	1.8	XX	-	0.7	1.3
		24 hr	XX	0.4	3.2	4.6	XX	0.1	1.7	3.3
		36 hr	XX	4.4*	6.5	6.4	XX	1.2	2.8	4.7
	Rough	12 hr	XX	0.2	2.1	2.2	XX	0.2	1.6	1.4
		24 hr	XX	0.9	4.6	5.9	XX	0.3	2.2	3.2
		36 hr	XX	7.2*	10.9	10.7	XX	1.6	4.6	6.6
Brass	Smooth	12 hr	XX	-	0.3	1.1	XX	0.1	0.3	1.0
		24 hr	XX	-	0.4	1.3	XX	0.2	0.3	2.0
		36 hr	XX	-	0.9	4.5	XX	0.8	2.0	3.9
	Rough	12 hr	XX	-	-	0.2	XX	0.2	0.4	0.7
		24 hr	XX	-	-	0.2	XX	0.3	1.3	1.3
		36 hr	XX	0.1	-	1.7	XX	0.6	2.0	2.4
Silver	Smooth	12 hr	XX	-	0.1	0.1	XX	-	-	-
		24 hr	XX	-	0.1	0.2	XX	-	-	-
		36 hr	XX	-	0.2	0.4	XX	-	-	-
	Rough	12 hr	XX	-	-	0.1	XX	0.3	0.2	0.1
		24 hr	XX	-	0.1	0.2	XX	0.2	0.2	0.1
		36 hr	XX	0.1	-	0.3	XX	0.1	0.2	0.1

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

20C/220 ppm PH₃/5.0% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	-	0.1	0.5	1.2	-	-	0.3	0.9
		24 hr	0.1	0.3	2.4	4.1	-	0.2	1.1	2.6
		36 hr	0.2	4.4*	6.1	5.1	-	1.1	3.1	5.1
	Rough	12 hr	0.1	0.1	0.6	1.7	0.1	0.1	0.4	1.0
		24 hr	0.1	0.6	4.1	6.7	0.1	0.2	1.6	3.9
		36 hr	0.2	6.1*	8.9	12.0	0.1	1.2	4.0	7.0
Brass	Smooth	12 hr	-	0.1	-	0.7	-	-	0.2	0.8
		24 hr	-	-	0.1	1.7	-	0.1	0.8	2.2
		36 hr	0.1	-	1.1	4.5	-	0.8	2.0	4.3
	Rough	12 hr	-	-	-	0.4	0.2	0.2	0.4	0.8
		24 hr	-	-	-	0.2	0.2	0.2	0.9	1.3
		36 hr	-	-	0.1	1.4	0.2	0.7	1.6	2.8
Silver	Smooth	12 hr	-	-	-	0.1	-	-	0.1	0.1
		24 hr	-	-	0.3*	0.2	-	-	-	-
		36 hr	-	-	0.4*	0.6	-	-	-	-
	Rough	12 hr	-	-	0.3	0.3	0.2	0.3	0.1	0.2
		24 hr	-	-	0.1	-	0.2	0.2	0.2	0.3
		36 hr	-	-	0.2	0.7	0.2	0.3	-	-

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

30C/35 ppm PH₃/5.0% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	-	-	-	0.2	0.1	0.1	0.1	0.1
		24 hr	-	-	0.2	0.2	-	0.1	0.2	0.2
		36 hr	-	0.1	0.3	0.6	-	0.1	0.3	0.5
	Rough	12 hr	-	-	-	0.2	0.1	0.1	0.2	0.3
		24 hr	-	0.2	0.2	0.2	0.2	0.1	0.1	0.2
		36 hr	0.1	0.2	0.1	0.5	0.1	0.2	0.3	0.5
Brass	Smooth	12 hr	-	-	-	0.1	-	0.1	0.2	0.3
		24 hr	-	0.1	0.1	0.3	0.1	-	0.2	0.3
		36 hr	-	0.1	0.2	0.3	0.1	0.1	0.2	0.5
	Rough	12 hr	-	-	-	0.1	0.1	0.1	0.2	0.3
		24 hr	-	-	-	0.2	0.1	0.2	0.2	0.3
		36 hr	-	-	0.2	0.3	0.1	0.2	0.3	0.6
Silver	Smooth	12 hr	-	-	-	0.1	-	0.1	0.1	-
		24 hr	-	-	0.3	0.5	-	-	-	-
		36 hr	-	0.1	0.4	0.7	-	-	-	-
	Rough	12 hr	-	-	0.1	0.1	0.1	0.1	0.2	0.1
		24 hr	-	-	0.2	0.6	0.1	0.2	0.2	-
		36 hr	-	0.1	0.2	0.6	0.1	0.2	0.2	0.1

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

30C/135 ppm PH₃/3.2% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	-	0.1	0.4	1.0	-	0.1	0.4	0.9
		24 hr	2.4*	3.3*	1.2	1.1	0.8	1.0	1.0	1.0
		36 hr	21.2*	16.0*	2.9	2.8	4.2	6.4	1.8	1.8
	Rough	12 hr	0.3*	0.4*	0.6	0.9	0.3	0.4	0.5	0.7
		24 hr	3.9*	3.5*	2.4	2.1	1.2	1.7	1.6	0.5
		36 hr	27.3*	16.2*	4.9	3.4	4.0	7.7	3.6	2.8
Brass	Smooth	12 hr	0.1	-	0.7	0.5	-	0.2	0.6	0.6
		24 hr	-	-	1.6	0.9	0.4	0.6	1.2	0.7
		36 hr	0.1	0.3	3.0	2.0	1.0	0.5	2.0	1.8
	Rough	12 hr	-	-	0.5	0.4	-	0.3	0.5	0.4
		24 hr	0.1	0.1	0.5	0.5	0.3	0.7	0.9	0.8
		36 hr	0.1	-	1.6	1.7	1.4	1.1	1.6	1.8
Silver	Smooth	12 hr	-	0.1	0.1	0.3	-	-	-	-
		24 hr	-	-	0.1	0.2	-	-	-	0.1
		36 hr	0.1	-	0.9	0.7	-	-	-	-
	Rough	12 hr	-	-	0.1	0.3	0.1	0.2	0.1	0.1
		24 hr	-	0.1	0.2	0.6	0.1	0.1	0.1	0.1
		36 hr	0.1	0.1	0.7	1.0	-	0.1	-	-

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

30C/135 ppm PH₃/5.0% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	0.3	0.8	1.2	-	0.2	0.4	0.7
		24 hr	2.9*	3.4*	2.3	3.3	1.3	1.0	0.9	1.8
		36 hr	23.3*	13.8*	5.1	4.5	4.8	4.2	4.6	3.6
	Rough	12 hr	0.1*	0.7*	1.1	1.1	0.2	0.4	0.8	0.9
		24 hr	5.6*	4.5*	3.3	2.4	1.9	1.6	2.1	1.6
		36 hr	26.0*	13.3*	6.1	3.9	5.2	4.5	4.2	2.6
Brass	Smooth	12 hr	-	0.1	0.9	1.1	0.1	0.2	0.6	0.9
		24 hr	-	0.1	0.8	1.2	0.1	0.7	0.8	1.6
		36 hr	-	0.9	1.5	1.6	0.1	3.1	1.6	1.6
	Rough	12 hr	-	0.1	0.4	0.9	0.2	0.2	0.6	0.9
		24 hr	-	-	0.4	0.9	0.1	0.7	1.4	1.5
		36 hr	-	0.3	0.8	1.9	0.2	1.6	1.2	2.2
Silver	Smooth	12 hr	-	-	0.1	0.4	-	-	-	-
		24 hr	-	-	0.5	0.6	-	-	-	-
		36 hr	0.1	0.1	0.4	1.4	-	-	-	-
	Rough	12 hr	-	0.1	0.1	0.4	-	-	0.1	0.1
		24 hr	-	0.1	0.1	0.7	0.1	-	0.1	-
		36 hr	0.1	0.1	0.7	1.2	0.1	-	0.1	0.1

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

30C/220 ppm PH₃/3.2%CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	1.2*	1.2	0.9	0.1	0.5	1.0	0.7
		24 hr	2.9*	8.2*	2.8	1.9	0.7	3.6	2.8	1.6
		36 hr	31.6*	23.4*	7.8	5.3	4.2	5.6	6.0	4.3
	Rough	12 hr	1.2*	1.8*	1.8	1.3	0.3	0.8	1.1	1.0
		24 hr	2.0*	8.6*	7.8	3.7	0.6	2.4	5.0	2.7
		36 hr	21.9*	13.8*	8.9	6.3	3.7	4.4	6.7	4.8
Brass	Smooth	12 hr	0.1	-	3.1	0.9	0.1	0.4	3.1	0.9
		24 hr	0.1	-	6.5	2.7	0.2	0.6	6.5	2.3
		36 hr	0.2	0.9	20.4	9.3	1.8	2.1	10.7	5.9
	Rough	12 hr	0.1	-	1.5	1.0	0.2	0.5	1.4	1.2
		24 hr	-	-	0.9	2.3	0.5	0.7	1.5	2.4
		36 hr	-	0.1	7.4	4.4	1.7	1.7	5.1	3.9
Silver	Smooth	12 hr	0.1	-	0.1	0.1	-	0.1	-	-
		24 hr	0.1	0.1	0.1	0.7	0.1	-	-	-
		36 hr	-	0.1	0.6	1.3	0.1	-	-	-
	Rough	12 hr	-	0.1	0.1	0.4	0.2	0.1	0.2	0.1
		24 hr	-	-	0.2	0.9	0.1	0.2	-	0.1
		36 hr	-	0.3	0.4	1.3	0.2	0.2	0.1	-

The solder samples gained no weight under these test conditions

*Samples were wet

25 & 50% RH - samples mounted parallel

15 & 75% RH - samples mounted radially

30C/220 ppm PH₃/4.5% CO₂

Sample Area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	1.6	1.3	0.9	1.9	0.8	1.1	0.5	1.4
		24 hr	27.9*	9.0*	2.3	6.0	6.8	4.2	2.2	4.9
		36 hr	21.2*	13.5*	5.0	11.1	4.8	4.7	3.6	8.9
	Rough	12 hr	6.9*	8.2*	1.4	2.0	3.4	3.7	1.0	1.6
		24 hr	18.3*	6.8*	5.0	9.3	4.1	4.1	3.1	5.9
		36 hr	31.9*	34.0*	9.9	12.6	6.1	7.4	5.9	8.1
Brass	Smooth	12 hr	-	0.2	3.8	1.0	-	0.6	1.4	1.2
		24 hr	-	-	7.4	6.9	-	-	2.9	4.8
		36 hr	-	0.3	14.7	5.5	1.0	3.8	6.6	4.3
	Rough	12 hr	-	-	0.8	1.1	0.4	0.2	0.7	1.6
		24 hr	-	-	1.5	1.4	0.5	0.2	1.3	3.4
		36 hr	-	-	1.9	0.9	1.2	0.2	2.8	3.2
Silver	Smooth	12 hr	-	-	0.4	0.1	-	0.2	-	-
		24 hr	-	-	0.3	0.2	-	-	-	0.1
		36 hr	-	0.1	0.4	0.8	-	-	0.1	0.1
	Rough	12 hr	-	-	0.2	0.3	-	0.5	0.3	0.1
		24 hr	-	-	0.3	0.3	-	-	-	0.1
		36 hr	-	0.1	0.3	0.6	-	0.1	0.1	0.2

The solder samples gained no weight under these test conditions

* Samples were wet

All samples mounted radially

40C/35 ppm PH₃/5.0% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	-	0.1	0.2	-	0.1	0.1	0.1
		24 hr	0.2	-	0.5	0.3	0.1	-	0.4	0.1
		36 hr	0.3	0.1	0.7	0.4	0.2	-	0.5	0.3
	Rough	12 hr	0.1	0.1	0.1	0.2	0.2	0.1	0.2	0.2
		24 hr	0.4*?	0.1	0.4	0.3	0.2	0.1	0.5	0.2
		36 hr	2.4*	0.3	1.1	0.4	1.0	0.3	0.8	0.4
Brass	Smooth	12 hr	-	-	0.1	0.2	0.1	-	0.1	0.3
		24 hr	-	-	0.3	0.4	0.1	-	0.3	0.2
		36 hr	0.1	0.2	0.3	0.5	0.2	-	0.4	0.5
	Rough	12 hr	-	-	-	0.1	0.1	0.1	0.3	0.2
		24 hr	-	-	0.1	0.2	0.2	-	0.5	0.4
		36 hr	-	-	0.1	0.3	0.3	0.1	0.5	0.6
Silver	Smooth	12 hr	-	-	0.2	0.2	-	-	-	-
		24 hr	-	-	0.6	0.6*	-	-	-	-
		36 hr	-	-	0.2	1.3*	-	-	-	-
	Rough	12 hr	0.1	-	0.4	0.6	-	0.1	0.2	0.1
		24 hr	-	0.2	0.7	1.3	0.2	0.1	0.2	0.1
		36 hr	0.2	0.3	1.1	1.6	0.1	0.1	0.2	0.1

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

40C/135 ppm PH₃/5.0% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25%+ RH	50% RH	75% RH	15% RH	25%+ RH	50% RH	75% RH
Copper	Smooth	12 hr	-	1.0	1.6	1.2	0.1	0.7	1.2	1.0
		24 hr	8.4*	4.5	3.8	2.4	2.1	1.7	2.7	2.3
		36 hr	40.9*	19.1	5.9	5.0	5.9	7.9	3.2	4.1
	Rough	12 hr	1.7*	3.7	2.3	1.2	0.6	1.7	1.9	1.0
		24 hr	22.6*	13.8	5.3	2.2	3.7	9.0	3.6	1.9
		36 hr	45.2*	24.5	8.6	4.1	6.0	13.8	5.5	3.6
Brass	Smooth	12 hr	-	0.3	0.6	0.7	0.2	0.6	0.7	0.9
		24 hr	0.1	1.7	1.5	2.2	0.4	1.6	2.3	2.3
		36 hr	0.7	11.9*	3.2	4.7	0.4	6.1	3.7	3.8
	Rough	12 hr	-	-	0.2	0.8	0.4	0.9	0.8	0.9
		24 hr	-	-	0.4	1.6	0.2	1.5	1.1	1.7
		36 hr	-	2.1	1.2	5.6	0.4	3.9	2.3	4.4
Silver	Smooth	12 hr	-	-	0.3	0.7*	-	-	-	-
		24 hr	0.4	0.1	0.4	1.3*	-	-	-	0.1
		36 hr	-	0.3	1.3	2.0*	-	-	-	-
	Rough	12 hr	-	0.1	0.6	1.0	0.4	0.3	0.2	0.2
		24 hr	0.1	0.1	1.1	1.3	0.3	0.4	0.2	0.2
		36 hr	0.1	0.3	2.0	1.5	0.2	0.2	0.2	0.1

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

+A power failure near the end of the experiment turned off the PH₃ and caused the humidity to rise. The copper samples had obviously been wet during the experiment but were dry when removed.

40C/220 ppm PH₃/3.5% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	6.2*	7.4*	4.5	3.5	2.0	2.9	3.6	2.4
		24 hr	19.8*	29.3*	10.5	7.4	6.2	10.2	7.6	5.4
		36 hr	37.7*	64.0*	17.6	11.9	10.6	18.7	12.3	11.1
	Rough	12 hr	9.0*	12.9*	5.7	4.0	2.2	5.3	4.4	3.2
		24 hr	22.8*	36.6*	15.7	9.9	4.7	11.0	9.3	6.0
		36 hr	34.6*	62.4*	19.8	18.8	11.9	16.4	12.0	12.2
Brass	Smooth	12 hr	0.1	0.2	1.5	3.2	1.1	0.9	1.1	2.4
		24 hr	0.2	2.2	4.2	2.8	2.9	5.7	5.0	4.4
		36 hr	1.2*?	25.6*	9.9	6.7	0.3	12.1	9.8	7.3
	Rough	12 hr	0.1	0.1	0.2	1.3	0.9	1.7	1.2	2.2
		24 hr	-	-	2.3	2.0	1.8	3.8	3.5	3.5
		36 hr	-	2.1	5.4	7.7	0.2	1.6	6.0	6.0
Silver	Smooth	12 hr	0.1	-	0.4*	0.8*	-	-	-	-
		24 hr	0.1	-	0.8*	1.2*	-	0.1	-	-
		36 hr	0.2	0.3	1.1*	1.6*	-	-	-	-
	Rough	12 hr	0.1	0.1	0.3	0.8	0.2	0.4	0.2	0.3
		24 hr	0.1	-	0.5	1.3	0.2	0.3	0.2	0.2
		36 hr	0.1	0.2	1.0	2.4	0.2	0.2	0.2	0.2

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

40C/220 ppm PH₃/5.0% CO₂

Sample area = 0.13 dm ²			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	6.5*	6.0*	4.0	4.2	2.1	2.6	3.6	4.4
		24 hr	20.1*	33.7*	8.9	8.5	6.1	8.6	8.0	7.3
		36 hr	34.6*	55.7*	13.4	16.9	9.4	15.1	11.8	11.6
	Rough	12 hr	8.2*	11.2*	5.9	3.5	2.6	5.1	5.1	2.9
		24 hr	21.9*	40.3*	12.7	8.7	6.1	13.1	9.3	8.1
		36 hr	33.4*	52.6*	18.3	14.6	9.5	15.4	13.1	11.8
Brass	Smooth	12 hr	0.1	0.4	2.4	3.5	1.3	0.6	2.1	3.0
		24 hr	-	14.3*	14.8	10.1	1.7	7.4	10.2	8.2
		36 hr	11.1*	31.2*	32.4	16.7	6.4	11.5	16.9	11.5
	Rough	12 hr	-	0.1	0.5	2.0	0.3	1.2	1.4	2.5
		24 hr	-	1.8	2.8	4.6	1.9	4.4	3.3	4.3
		36 hr	0.1	16.9*	14.8	6.5	1.9	7.4	10.5	7.8
Silver	Smooth	12 hr	-	0.2	0.7*	1.4	-	0.1	-	-
		24 hr	0.2	1.1*	1.1*	1.5*	-	0.1	-	-
		36 hr	-	1.4*	2.2*	2.7*	-	-	-	-
	Rough	12 hr	-	0.2	0.9	1.3	0.5	0.4	0.2	0.3
		24 hr	0.1	0.2	1.4	1.8	0.5	0.5	0.2	0.1
		36 hr	0.3	0.9	2.3	2.5	0.3	0.2	0.3	-

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel



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