CORROSION OF METALS IN PHOSPHINE

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A preliminary series of steady-state exposure experiments of metals in phosphine 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 220ppm)
- 4 levels of relative humidity (15, 25, 50 and 75%)
- 2 CO_2 levels (3.5 and 5%)
- 3 exposure times (12, 24 and 36 hours).

This work quantified the extent of surface deposit formation and metallic dissolution of different metals in phosphine and identified at wet/dry morphology change as a function of relative humidity 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..

Based on the results and recommendations of this study, a second phase (sponsored by the USDA, Government of Canada, Canadian National Millers Association, Degesch America Inc. and Pestcon Systems Inc.) was completed in 1999 and was focused on the following four tasks:

Task 1 Expand the database for copper and nickel at intermediate relative humidities 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. 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 400ppm PH_3. No wet regime was observed at 85ppm PH_3.

Task2 Expand the database for copper and nickel to 400 and 600ppm PH_3 and 0% CO_2 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 PH_3 concentrations up to only 220ppm had been studied.

Task 3 Cyclical/repeat exposures were performed to determine the cumulative effect in terms of weight changes. Exposures at 220ppm PH_3 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
- 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 to the work outlined above, copper samples were included in a ship-hold fumigation trial carried out in Toronto on June 5-8, 1999 where various phosphine fumigants were used. The results of this field trial 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. An investigation showed that failure resulted from the thinning and over-heating of the lead to an integrated circuit chip.