

**THE DEVELOPMENT OF A REPRODUCIBLE SCREENING METHOD
TO DETERMINE THE MECHANISMS AND EFFECTS OF ORGANIC ACIDS
AND OTHER CONTAMINANTS ON THE CORROSION OF
ALUMINUM-FINNED COPPER-TUBE HEAT EXCHANGER COILS**

Richard A. Corbett
Corrosion Testing Laboratories, Inc.
Newark, Delaware 19713

ABSTRACT

Indoor corrosion failures of aluminum-finned copper-tube evaporator coils, and also in some systems without aluminum fins, is a menacing issue in the heating, ventilation, and air conditioning (HVAC) industry. Extensive laboratory testing has verified the development of a reproducible screening method to assess suspected contaminants of producing premature failures of copper tube resulting from a very localized form of corrosion known as “formicary corrosion” [a/k/a “ant nest corrosion”]. This paper provides a historical perspective on formicary corrosion and various mechanisms.

BACKGROUND

Indoor corrosion failures of aluminum-finned copper-tube evaporator coils, sometimes without aluminum fins, is a menacing issue in the heating, ventilation, and air conditioning (HVAC) industry. Of note, significantly from Japanese research, is the conclusion that approximately 10% of all premature failures of copper tube result from a very localized form of corrosion known as formicary or “ant nest” corrosion. Based on this fact alone, the HVAC industry worldwide has recognized that formicary corrosion, albeit not identified as such in most instances, accounts for many premature failures in copper products. Some geographic areas within the United States have experienced higher incidences of formicary corrosion than others, and likewise, some homes experience multiple failures while those around them appear immune. Failures typically manifest as leaks that form under the aluminum fin pack area of the evaporator coil within a few years of installation. A comprehensive study by Carrier⁽¹⁾ has identified this form of corrosion in most coil brands from all the major suppliers.

There are two main forms of pitting corrosion found on aluminum-finned copper coils: general pitting and formicary corrosion. General pitting is caused by an aggressive chemical species, such as chlorides, that contribute to large pits observable with the unaided eye. Formicary corrosion, sometimes referred

to as “ant-nest” corrosion, appears as isolated or multiple pinhole pits so fine that they are not visible to the unaided eye. The copper surface will typically be discolored adjacent to the corrosion pit(s).

Surface films can vary from dull gray-black to red-brown or purple, depending upon the specific environment. The morphology of the corrosion damage within the metal comprises a series of minute interconnecting tunnels of random direction resulting from branching of the pits. The corrosion initiates from the tube surface and progresses rapidly into the tube wall. Perforation usually occurs in weeks or months, and not years. The term *ant nest corrosion* is attributed to Yamauchi.⁽²⁾ The unique morphology so closely parallels an ant’s nest (remember as children playing with the “Ant Farm”), hence the terminology adopted to describe the phenomenon.

Previous work^(3,4) reported on potential sources of chemical species causing formicary corrosion as coming from tube manufacturer and chiller fabrication fluids.

Literature Review

An exhaustive search of the literature, within the public domain, was undertaken resulting in some 58 technical articles germane to the subject.⁽¹⁻⁵⁸⁾ Many of the earlier works [1980’s and 1990’s] were published in Japanese, and were based on failure analysis and testing in the Japanese HVAC industry. Recently, American authors submitted publications based on their investigations of this form of corrosion.^(1, 3-7)

The Canadians first described this form of attack in the literature. In 1977 Edwards, *et al.*⁽⁸⁾ investigated the failure of copper tubing with aluminum fins in an air conditioning unit of a large public building. The leaks were evident during installation when the unit was pressurized. The tubes were pressure tested with an antifreeze solution, wrapped in plastic with the ends capped, and stored for a year before installation. A label left on the tubes said there could be residual antifreeze solution inside. The pitting started on the inside diameter. Edwards, *et al* proposed that there was a breakdown of the residual fluid in the tube, although they consider other options such as chloride induced pitting.

The literature may be broken into discrete areas such as failure analysis,^(2-5,8-13) laboratory testing procedures to replicate formicary corrosion,^(2-3, 10-13, 15-30) and preventative measures.^(2,6-10, 12, 14, 22, 24, 31-38)

EXPERIMENTAL METHODS

In the development of a reproducible screening method to determine the mechanisms and effects of organic acids and other contaminants on the corrosion of aluminum-finned copper-tube heat exchanger coils, the formicary tests were undertaken with alloy C122 [UNS C12200] copper tubing obtained from a single manufacturer. The tubes had been welded and annealed. They were approximately 3/8” in diameter with a minimum wall thickness of 0.012-inches.

Test specimens were cut to a length of 2.5-inches, engraved with an identification number, cleaned with methanol and acetone, and warm air dried. The tubes were handled with gloves during and subsequent to cleaning.

The test vessels were one-liter glass jars with a wire bale and a Buna rubber gasket. A film of polyethylene [known to be non-reactive and not contaminate the test] was used to isolate the gasket from the test vapor.

The copper tubes were suspended at a 45° angle near the top of the test vessels using a length of Gore-Tex™ thread, above 100mL of the test solution. Temperatures were maintained by placing the jars in heated ovens or refrigerators.

Initial Test Matrix

Prior studies had shown that formic and acetic acid would cause formicary corrosion, and would serve as controls for the refinement of a test method. The analysis of condensate on drip pans under condenser units that failed by formicary corrosion revealed a ratio of 20% formic to 80% acetic acid. This mixture would represent field conditions. Uninhibited ethylene glycol was used in some HVAC processing fluids. Ethylene glycol would form glycolic acid. This acid was known to cause corrosion of copper, but it was not in the same “family” as formic and acetic. Therefore, this chemical could validate the laboratory bench test method.

Prior studies showed that concentrations of 1000 and 10,000 ppm [parts per million] of acid cause formicary corrosion. In an effort to determine a lower critical concentration, 100 ppm of acid was additionally selected.

Temperature cycling proved to be more aggressive than isothermal testing; cycling over an 8-hour warm (40°C), 16-hour ambient (20°C) schedule had been successful. Two other cycles were evaluated to represent extreme conditions for evaporator and condenser tubes: 40°C / 4°C and 55°C / 20°C, with the same time periods.

Thus, the initial test matrix consisted of:

| | | | | |
|----------------|-----------|----------|-----------------------|-----------------|
| Acid: | Formic | Acetic | 20% Formic/80% Acetic | Ethylene Glycol |
| Concentration: | 100 ppm | 1000 ppm | 10,000 ppm | |
| Temperature: | 40C / 20C | 40C / 4C | 55C / 20C | |

Exposure periods were 70 and 180 days, with the exception of the 10,000 ppm concentration where the tests were terminated after 15-days.

Revised Test Program

Due to the success of reproducing formicary corrosion with various acids, concentrations, and temperature cycles, a more refined study was undertaken to determine if there was a critical concentration required to initiate and propagate formicary corrosion. Three formic acid (100 ppm, 50 ppm and 20 ppm) concentrations with five (5) ten-day exposure periods with duplicate test vessels were evaluated. From the results of the 180 day test, above, the optimum temperature cycle of 40°C / 20°C was chosen. Every ten days 6 test vessels were opened and the tubes removed. A section was cut from the top of each tube, mounted, polished, and evaluated. The mounts were ground and polished three times so that every mount had data from 3 locations.

Other Contaminants

During tubing fabrication and evaporator/condenser manufacture, a number of drawing, forming, and stamping lubricants are used. Some of these fluids can decompose to form carboxylic acids in moist air, particularly in the presence of aluminum oxide and warm temperatures.

Twelve fluids, representing a plethora of these lubricants, were selected to evaluate their stability and decomposition products. Two types of degradation techniques were employed: thermal and water hydrolysis.

Thermal degradation was accomplished by combining aluminum oxide [alundum boiling chips] with the test fluid into a culture tube. The culture tube was then placed into an oven at 200°C for one hour. After cooling to room temperature the sample was analyzed by FTIR [Fourier Transformation Infrared Spectroscopy] to determine if the fluid sample had broken down to form carboxylic compounds. The remaining fluid was then added to de-ionized water, vigorously shaken, and centrifuged. The water phase was analyzed by IC [ion chromatography] for the presence of specific carboxylates [such as formate (formic acid) and acetate (acetic acid)].

Hydrolysis was accomplished by combining aluminum oxide, the test fluid, and de-ionized water into a pressure vessel, which was sealed and placed into an oven at 100°C for 48 hours. After cooling to room temperature the water phase was analyzed by IC for the presence and concentration of carboxylates.

EXPERIMENTAL RESULTS

Initial Test Matrix

Surface observations and qualitative analysis of surface corrosion products

The entire outer diameter (OD) surface of the copper tube after the exposure periods was discolored brown, with a mottled pattern of dark green corrosion products adhered to it. Upon removal from the test container, the surface of the copper tube was wet. Microscopic examination of the tube surface revealed that the dark green corrosion products comprised of fine crystals. And, it was observed that there were pinholes within the crystals.

Figure 1 shows an SEM image of the dark green corrosion products adhering to the surface of the copper tube. It can be seen that the crystals are vertical, with regularity, and the sizes are approximately the same. Qualitative analysis by IC of these crystalline corrosion products confirmed formate ions, if exposed to formic acid, acetate ions if exposed to acetic acid, and formate and acetate ions if exposed to the acid mixture. Consequently, it is believed that corrosion products on the surface of the copper tube are comprised of cupric carboxylates.

Observations on cross-section

The copper tubes were cross-sectioned after the exposure periods, and examined using a metallograph. Figure 2 shows one example. It can be seen from this photograph that corrosion products, clearly different from the material adhering to the surface, pack the interior of the pinholes. The proportion of the pinhole taken up by corrosion products increases toward the interior of the pinhole, near the leading edge of the advancing corrosion, compared with the region near or on the surface of the copper tube. The findings confirm other characteristics, such as branching and the fact that corrosion tunnels do not advance in a set direction.

Using microscopic FTIR and cross polarized light, the corrosion product within the pinhole comprised of ruby red, cuprous oxide phase mixed with another gray phase. The individual grains of the gray phase were smaller than the minimum area of analysis (15 μm x 28 μm) of the instrument. However, five spectra of the gray corrosion product were compared to a spectrum of bluish-green crystals found on the surface of the tube, identified by IC as being copper formate. These five spectra all exhibited a broad absorption band around 1505 to 1535 cm^{-1} and 1325 to 1360 cm^{-1} , similar to those prominent in the bluish-green crystals. The results show that the gray material in the pinholes contained copper formate,

Quantitative Depth of Attack

Summarized in Tables 1 and 2 are the results of the 70-day and 180-day exposure periods, respectively, to different acid concentrations and temperature cycling.

Revised Test Program

Summarized in Table 3 are the results of the 50-day exposure to various low concentrations of formic acid. All exposure periods produced formicary corrosion, even at 20 ppm after 10 days. This implies that if there is a critical concentration for initiation of formicary corrosion, it must be substantially below 20 ppm, and probably at the ppb [parts per billion] level.

An occasional morphology that included thin blue lines was observed on the cross-sections at the 20 and 50 ppm concentrations. An etch revealed the presence of intergranular attack where the thin blue lines had been seen and indicated preferential grain boundary attack, Figure 3.

Other Contaminants

Summarized in Table 4 are the results of the degradation of various lubrication fluids. There is no clear-cut method for degradation of the tested fluids. Some fluids are more susceptible to thermal degradation, while others are more influenced by water hydrolysis. Agreeably, some of the fluids exhibit minimal degradation, while others are significantly degraded into low molecular weight carboxylic acids. Studies are continuing to evaluate the effects of these degradation products on producing formicary corrosion utilizing the test method developed in this program.

DISCUSSION

The results of this testing program have confirmed that a laboratory test method can reproduce formicary corrosion. Go/no go results are attainable in as little as 10 days exposure. Quantitative results as to the depth of attack are limited to the nature of the branched tunnels. Figure 6 provides a schematic illustration of a typical formicary corroded tube. Although it is true that through-wall failure penetrates the wall from one side to the other, formicary corrosion does not take a direct path (Figure 6a). This places a burden on the investigator in trying to locate through-wall penetrations and the extent of attack that has occurred, which is dependent on where the tube is cross-sectioned for examination (Figures 6b and 6c).

Given the characteristics of the formicary corrosion process, the technique of quantifying the extent of formicary corrosion becomes one of heuristic methodology [solving a problem by trial and error]. What is important is the presence or absence of formicary initiation sites that again utilizes the heuristic methodology [self-education] for knowing what characteristics to recognize when examining a tube suspect of a through-wall penetration. After examining several hundred tubes, tell tale signs of attack are recognized, such as discoloration of the tube and corrosion product accumulation. Small red or purple sites amid the brown patina of the copper tube are indications of pinholes. Likewise, bluish-green crystals that appear at 200 to 500X magnification are signs that oxidation is taking place other than the formation of surface cuprous or cupric oxide.

The presence of intergranular attack and small quantities of copper formate within the labyrinth of the formicary are significant findings that assist in explaining the mechanism of attack. Up until now, most of the mechanism theories have been based on speculation or limited evidence, as reviewed below.

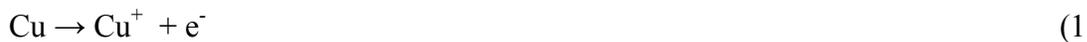
Notoya's Theory

The 1977 SEM analysis by Edwards *et al.*⁽⁸⁾ found Cu, Fe, P, S, Ca, and Cl in the corrosion deposits of their formicary failure. They speculated that the breakdown of the inhibited antifreeze, possible high concentrations of O₂ and CO₂ in the condensate inside the tubes, or the presence of chlorides, might have caused the pitting. However, they were puzzled how any of these could have led to such aggressive corrosion.

In 1983, Yamauchi *et al.*⁽²⁾, reported to have produced formicary corrosion in the laboratory with a solution that contained 1,1,1-trichloroethane. They believed the solvent was breaking down to hydrochloric acid and phosgene that were acting as the corrodants.

In 1988 Notoya *et al.*⁽⁹⁾ reported producing laboratory formicary corrosion with four different carboxylic acids, the most aggressive being formic acid. Their formulas and explanation were widely adopted, and a slightly modified version is duplicated here:

Discontinuities in the oxide film are attacked by the organic carboxylic acid present and copper is oxidized:



Carboxylic acid anions and copper cations continue to form a copper complex:



(Where X is the selected carboxylic acid)

The copper complex is oxidized to form cuprous oxide (Cu₂O) and copper carboxylate:



Micro-cracks are formed in the pit wall due to the volume expansion of the Cu₂O.

The copper carboxylate complex attacks the pristine crack surfaces and the cuprous complex reforms:



These reactions then recur and are autocatalytic.

The standard cathodic reaction in an acidic solution is:



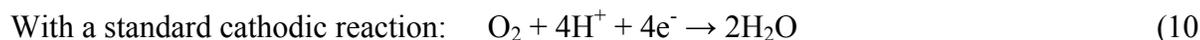
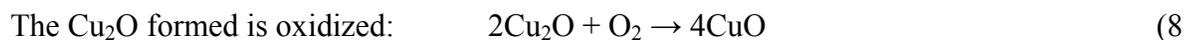
Alternate Theory

In 1993 Miya *et al.*⁽¹⁹⁾ describe a theory that is based on capillary action drawing water into the pit with surface tension at the mouth of the pit. Notoya accepts capillary force as an explanation for water transport and how pits can proceed in the direction opposite to gravity, but argues that condensation inside the pits may be equally valid.

Miya felt that capillary action did not account for observations that corrosion products were more prevalent deeper inside the pit. Miya believed that the absence of copper formate and even carbon inside

the pit, as evidenced by SEM and EPMA work, caused problems for Notoya's equations 3 and 4. While admitting that copper formate was soluble in the water used for polishing, Miya did not feel that all traces of it should have disappeared. He proposes alternate formulas, involving the presence of formic acid in the spongy Cu₂O, but without a copper formate complex.

Two alternate methods for producing Cu₂O were advanced by Miya:



Miya thought that traces of formic acid, which were not removed during polishing, were evaporated in the SEM when the vacuum was drawn. He proposes that the tunnel morphology is related to the amount of water present at the mouth of the pit: a low amount of water forms a narrow tunnel and a larger amount of water forms a broadening tunnel. He also points out that in failure analyses traces of sulfur and chlorine are commonly found and thinks their role in formicary corrosion needs to be understood.

In 1994 Nagata and Kawano⁽²⁰⁾ give a formula for the hydrolysis of 1,1,1-trichloroethane to acetic acid as:

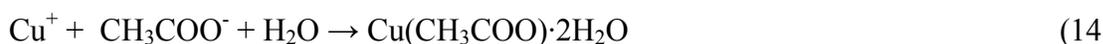


Baba and Kodama⁽²¹⁾, writing in 1995, produced potential pH (*E*-pH) diagrams for copper with acetate and formate solutions. Using XRD and FTIR they were unable to find copper carboxylate [Cu(I)X] complexes in their work, but said this might be an issue of concentration. They noted that their mechanism was similar to Notoya's.



Tunneling was accounted for by activation at the pit front and passivation on the pit walls. Notoya⁽²⁸⁾ saw their thermodynamic work as a validation.

Cano et al,⁽²⁹⁾ in 1999, adopted the basis of Notoya's formulas with acetic acid, but added hydrates.

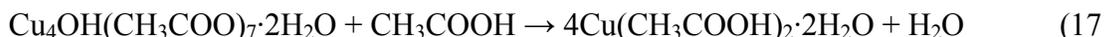


Equations 14 and 15 are autocatalytic and recur.

Other Investigations

In 1998 Lopez et al⁽³⁹⁾ published a study on copper corrosion due to small concentrations of acetic acid vapor. The focus was on the development of patinas in the atmosphere, but their research is interesting and applies to formicary corrosion. Phosphorous deoxidized copper plates were exposed to the vapor of 5 concentrations of acetic acid vapor for a period of 21 days at 30°C. The solutions were changed once a week. The concentrations used were 10, 50, 100, 200, and 300 ppm in the vapor phase. These would roughly correspond to levels of 600, 3,000, 6,000, 12,000, and 18,000 ppm in the test solution (for comparison to the studies done by other researchers mentioned here, who did not calculate the vapor phase concentrations). The maximum corrosion rate was 23 mdd (milligrams per square decimeter per day). The corrosion products were thoroughly analyzed using an SEM, XRD, FTIR, and thermogravimetric and thermodifferential analyses. Electrochemical tests were also run. Although aware of Notoya's work, they apparently did not make cross-sections or look for formicary corrosion. At the concentrations they used they would definitely have found formicary corrosion.

Their descriptions and photographs of the plates they exposed are quite applicable to the corrosion products on the OD (outside diameter) of tubes exposed to acetic acid vapors. They propose formulas for the formation of the copper hydroxide acetate and the copper acetate, which they found.



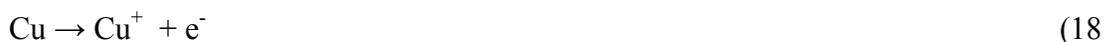
They believe that at lower concentrations the acetic vapor reacts with the wet copper surface but at higher concentrations droplets of acetic acid are deposited on the surface.

In 2000, the same researchers⁽⁴⁰⁾ replaced the acetic acid with formic acid but used the same experimental conditions and analysis techniques. They used triplicates and reported a reproducibility of over 95%. The vapor concentrations of 10, 50, 100, 200, and 300 ppm roughly correspond to test solution concentrations of 140, 700, 1,400, 2,800, and 4,200 ppm. These are different from the acetic solution concentrations above because formic acid and acetic acid have different vapor pressures. As with the acetic acid tests, apparently no cross sections were made, and so formicary corrosion was not reported.

Proposed New Mechanism

It is this author's proposal that the true branching tunnels associated with formicary corrosion in copper alloys are purely the result of formic acid, and that other carboxylic acids create more classical shaped pits. As such the mechanism for formicary corrosion is as follows:

Grain boundaries provide the weaknesses in the oxide film, and the copper is locally oxidized:



formic acid anions and copper cations form as cuprous formate:



The cuprous formate is oxidized to form cuprous oxide (Cu₂O) and cupric formate:



The cupric formate complex attacks the pristine grain boundary surfaces [intergranular corrosion] and the cuprous complex reforms:



These reactions, (20 and (21, then recur, and are autocatalytic.

The standard cathodic reaction in this acidic solution is:



The intergranular boundaries are enlarged, consuming the whole grain, and thus affect adjacent grains that are equally consumed. This continues until a void filled with cuprous oxide exists. The gray phase seen at high optical magnification, in association with the red cuprous oxide, is hydrated cupric formate [$\text{Cu}(\text{COOH})_2 \cdot 4\text{H}_2\text{O}$].

CONCLUSIONS

Formicary corrosion continues to baffle investigators who have yet to agree upon a mechanism, much less be able to predict behavior, except acknowledge that it requires four elements to simultaneously occur, namely air (oxygen), moisture (water), a low molecular weight organic acid (possibly a decomposed lubricant), and a copper alloy. From the results of this study, a reproducible screening method has been developed to evaluate the effects of organic fluids susceptible of promoting formicary corrosion.

Suspending a test sample above a reservoir of a hydrolyzed fluid in a sealed vessel and cycling the temperature from 40°C to 25°C during a 16 to 8 hour period will create conditions favorable to initiate and propagate formicary corrosion. Test results have demonstrated that the critical concentration of formic acid required to initiate attack is less than 20 ppm, and that significant attack can occur within ten days of exposure.

Formicary corrosion initiates along grain boundaries [intergranular corrosion] and then propagates into the grains [dissolution]. This can account for the “micro anodes and voids” described by others, and the apparent random tunneling observed in cross-sections.

ACKNOWLEDGEMENTS

This work was supported by the Air Conditioning And Refrigeration Technology Institute [ARTI], under ARTI 21-CR Research Project 611-50055. The author kindly acknowledges the contributions of Dr. Peter Elliott and Dr. Takenori Notoya for their generous assistance in sharing their experiences on the subject of formicary corrosion. A special thanks is due to Mr. David Severance for his contributions in the laboratory testing.

REFERENCES

1. Carrier Corporation, *Indoor Coil Corrosion*, 6 pages (2000).
2. Yamauchi, S.; Nagata, K.; Sato, S.; Shimono, M. *Journal of the Japan Copper and Brass Research Association*, 22, 132-140 (1983).
3. Elliott, P., Corbett, R. A. *Corrosion 99*, NACE: Houston, paper 342 (1999).

4. Corbett, R. A., Elliott, P. *Corrosion 2000*, NACE: Houston, paper 00646 (2000).
5. Hoffman, R. A., *Corrosion 98*, NACE: Houston, paper 709 (1998).
6. Lenox, R. S., Hough, P.A. *ASHRAE Journal*, November, 50-56 (1995).
7. Tetley, G., Heidenreich, M., Smith, K. *Air Conditioning, Heating, & Refrigeration News*, 203, 5-6 (1998).
8. Edwards, J.O., Hamilton, R.I., Gilmour, J.B. *Materials Performance*, 16(9), 18-20 (1977).
9. Notoya, T., Hammamoto, T. *Corrosion Engineering*, 37, 97-99 (1988).
10. Notoya, T., Hammamoto, T., Kawano, K. *Sumitomo Light Metal Technical Reports* 30 (3), 9-14 (1989).
11. Notoya, T. *Corrosion Engineering*, 39, 353-362 (1990).
12. Isobe, G., Inoue, T., Nagata, K., Notoya, T., Baba, H., Hidaka, F., Watanabe, M., Atsumi, T., Minamoto, K., Kodairo, M., Takagi, F. *Corrosion Asia*: Singapore, paper 106 (1992).
13. Takahashi, T., Shiraishi, Y., Saito, Y., Ogawa, H., Watanabe, M. *Journal of the Japan Copper and Brass Research Association*, 31, 143-150 (1992).
14. Kelly, G. J., Lepelaar, P., Notoya, T. *Process Corrosion and Prevention 2000*, Australian Corrosion Association: Australia, paper: *Under Insulation Corrosion of Chilled Water Copper Piping* (2000).
15. Hamamoto, T., Imai, M. *Sumitomo Light Metal Technical Reports*, 33 (4), 23-29 (1991).
16. Nagata, K. *Journal of the Japan Copper and Brass Research Association*, 31, 135-142 (1992).
17. Isobe, G. *Furukawa Review*, 10, 119-126 (1992).
18. Notoya, T. *Metals Technology*, 62, 23-28 (1992).
19. Miya, K., Kawarai, H., Matsuoka, H. *Zairyo (Journal of the Society of Material Science Japan)*, 42, 917-922 (1993).
20. Nagata, K., Kawano, K. *Journal of the Japan Copper and Brass Research Association*, 33, 7-16 (1994).
21. Baba, H., Kodama, T. *Corrosion Engineering*, 44, 279-287 (1995).
22. Miyafuji, M., Ozaki, R., Tsuchiya, A., Kuroda, T., Minamoto, K. *Journal of the Japan Copper and Brass Research Association*, 34, 159-167 (1995)
23. Notoya, T. *Zairyo-to-Kankyo (Corrosion Engineering)*, 46, 731-735 (1997).
24. Notoya, T. *Corrosion and Prevention 1997*, Australian Corrosion Association: Australia, paper 002 (1997).
25. Notoya, T., *Localized "Ant's Nest" Corrosion in Copper Tubes*, unpublished oral presentation (2000).
26. Notoya, T. *Journal of Material Science Letters*, 16, 1406-1409 (1997).
27. Ueda, K., Isobe, G. *Journal of the Japan Copper and Brass Research Association*, 38, 220-225 (1999).
28. Notoya, T. *Journal of the Japan Copper and Brass Research Association*, 38, 30-37 (1999).
29. Cano, E., Simancas, J., Polo, J. L., Torres, C. L., Bastidas, J. M., Alcolea, J. *Materials and Corrosion*, 50, 103-110 (1999).
30. Notoya, T. *draft paper, Localized "Ants Nest" Corrosion in copper Tubes Caused by Ginko fruit Juice* (2001).
31. Notoya, T., *Journal of the Japan Copper and Brass Research Association*, 30, 37-42 (1991).
32. Notoya, T., Corrosion Control; *Proceedings of the 7th Asian Pacific Corrosion Control Conference*, International Academic Publishers (Pergamon): New York, pp194-197 (1991).
33. Notoya, T. *Journal of Materials Science Letters*, 10, 389-39 (1991).
34. Notoya, T. *Memoirs of the Faculty of Engineering, Hokkaido University*, 8 (79), 15-21 (1991).
35. Notoya, T. *extended abstract for the Electrochemical Society Symposium* (1991).

36. Notoya, T., Inoue, T., Nagata, K., Takagi, F., Minamoto, K., Baba, H., Isobe, G., Atsumi, T., Hidaka, F., Watanabe, M., Kodaira, M. *Proceedings of the International Symposium for the Control of Copper and Copper Alloys Oxidation*, University of Rouen: Rouen, pp 77-81 (1992).
37. Notoya, T., Yamamoto, H., Katsuyama, K., Miyo, M. *Proceedings, 8th European Symposium on Corrosion Inhibitors (8SEIC) Ann. Univ. Ferrara, N.S., Sez. V, Suppl. N. 10*, pp 1021-1030 (1995).
38. Notoya, T. *Proceedings, Eurocorr 2001*, paper: Localized “Ants Nest” Corrosion on Coated Copper Tubes (2001).
39. Lopez-Delgado, A., Cano, E., Bastidas, J. M., Lopez, F. A. *Journal of the Electrochemical Society*, 145, 4140-4147 (1998).
40. Bastidas, J. M., Lopez-Delgado, A., Cano, E., Polo, J. L., Lopez, F. A. *Journal of the Electrochemical Society*, 147, 999-1005 (2000).
41. Brasunas, A. deS., Ed., *Corrosion Basics*, NACE: Houston, p39 (1984).
42. Notoya, T. *Bulletin of the Faculty of Engineering, Hokkaido University*, 162, 45-54 (1992).
43. Nagata, K., Kawano, K. *Sumitomo Light Metal Technical Reports*, 35, 28-35 (1993).
44. Notoya, T. *Boshoku Gijutsu*, 35, 742. (Entirely in Japanese) (1986).
45. Notoya, T. *Abstracts of the International Conference on Advances in Corrosion and Protection*, University of Manchester: Manchester, paper 152 (1992).
46. Notoya, T. *Haikan Gijutsu (Plumbing Technology)*, 53, 51-56. (Entirely in Japanese) (1993).
47. Notoya, T. *Journal of the Japan Copper and Brass Research Association*, 37, 27-33 (1998).
48. Notoya, T. *Materials: Journal of the University of Science and Technology Beijing*, 6, 129-132. (1999).
49. Notoya, T., Atsumi, T., Kawano, K., Ando, T. *Report of a Joint Study, Hokkaido University and Sumitomo Light Metal Industries*, 15 pages (1999).
50. Notoya, T. *Rust Prevention*, #6, 1-3. (2000).
51. Short, G. D. *ASHRAE Journal*, 1995, December, 88.
52. Trane Corporation, *Copper Tube Corrosion and Indoor Coil Leaks*, 4 pages (undated).
53. Notoya, T., Hammamoto, T. *Journal of the Japan Copper and Brass Research Association*, 29, 109-116 (1990).
54. Sato, S., *Journal of the Japan Copper and Brass Research Association*, No. 2 (2001).
55. Notoya, T. *Materials Performance*, 32 (5), 53-57 (1993).
56. Notoya, T. *Corrosion Engineering*, 46, 319-321 (1997).
57. Evans, U.R. *The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications*; St. Martins: New York, pp492-493 (1960).
58. Atrens, A., Pennisi, M. S., Schweinsberg, D. P., Eds., *Step Into the 90's, Transactions of the First Joint Conference on Corrosion, Finishing, and Materials*, Australian Corrosion Association: Australia, pp 565-573 (1989).

Table 1
70 Day Exposure Period

| Solution | ppm | Cycle °C/°C | General pitting (mils) | | Formicary pitting (mils) | |
|-------------------------------------|-----|----------------|------------------------|-------------------|--------------------------|-------------------|
| | | | Max | Avg. ⁿ | Max | Avg. ⁿ |
| Formic* | 10k | 55/20 | 2.2 | 2.2 | 1.6 | 0.9 |
| | | 40/20 | 5.9 | 2.9 | 6.1 | 5.3 |
| | | 40/4 | 3.0 | 2.6 | 5.9 | 4.5 |
| Acetic | | 55/20 | 2.0 | 1.7 | 2.0 | 1.4 |
| | | 40/20 | 4.1 | 4.0 | 4.5 | 2.8 |
| | | 40/4 | 3.3 | 2.5 | 3.2 | 2.6 |
| 0.20Formic 0.80Acetic | | 55/20 | 3.5 | 2.6 | 2.6 | 1.4 |
| | | 40/20 | 6.9 | 3.7 | 3.3 | 2.5 |
| | | 40/4 | 3.0 | 2.8 | 3.9 | 2.4 |
| Formic | 1k | 55/20 | 1.0 | 0.8 | 1.0 | 0.8 |
| | | 40/20 | 6.5 | 6.1 | 11.8 | 10.6 |
| | | 40/4 | 5.3 | 4.1 | 6.7 | 5.4 |
| Acetic | | 55/20 | 1.6 | 1.1 | 1.6 | 1.1 |
| | | 40/20 | 3.5 | 1.8 | 2.2 | 1.6 |
| | | 40/4 | 0.8 | 0.7 | 2.0 | 1.2 |
| 0.20Formic 0.80Acetic | | 55/20 | 1.4 | 0.9 | 1.2 | 1.0 |
| | | 40/20 | 1.4 | 1.0 | 1.2 | 0.9 |
| | | 40/4 | 1.8 | 1.5 | 2.6 | 2.0 |
| Formic | 100 | 55/20 | 0.8 | 0.7 | 0.7 | 0.6 |
| | | 40/20 | 1.6 | 1.0 | 2.0 | 1.2 |
| | | 40/4 | 5.1 | 3.5 | 3.5 | 2.3 |
| Acetic | | 55/20 | 0.5 | 0.4 | 0.5 | 0.3 |
| | | 40/20 | 0.7 | 0.6 | 0.8 | 0.6 |
| | | 40/4 | 0.2 | 0.2 | 0.3 | 0.2 |
| 0.20Formic 0.80Acetic | | 55/20 | 1.4 | 0.5 | 0.2 | 0.1 |
| | | 40/20 | 0.4 | 0.3 | 0.5 | 0.3 |
| | | 40/4 | 0.4 | 0.2 | 0.2 | 0.1 |
| Ethylene glycol Thermal Degraded | | 55/20 | 0.1 | 0.1 | 0.4 | 0.4 |
| | | 40/20 | 0.2 | 0.2 | 0.3 | 0.2 |
| | | 40/4 | 0.2 | 0.1 | 0.2 | 0.1 |

* 15-day exposure at 10,000ppm formic acid
n =The average of up to 5 of the deepest pits.

Table 2
180 Day Exposure Period

| Solution | ppm | °C/°C | Max | Avg. ⁿ | |
|--|-------|-------|-------|-------------------|-----|
| Acetic | 10k | 55/20 | 5.8 | 5.0 | |
| | | 40/20 | 12.3 | 11.8 | |
| | | 40/4 | 4.8 | 4.3 | |
| 0.20Formic 0.80Acetic | | 55/20 | 3.2 | 2.7 | |
| | | 40/20 | 9.9 | 9.2 | |
| | | 40/4 | 4.8 | 4.0 | |
| Formic | | 1k | 55/20 | 1.6 | 1.3 |
| | | | 40/20 | 10.6 | 7.1 |
| | | | 40/4 | 7.1 | 6.5 |
| Acetic | 55/20 | | 0.9 | 0.8 | |
| | 40/20 | | 2.7 | 2.3 | |
| | 40/4 | | 3.2 | 1.7 | |
| 0.20Formic 0.80Acetic | 55/20 | | 2.5 | 1.6 | |
| | 40/20 | | 1.6 | 1.3 | |
| | 40/4 | | 3.5 | 2.6 | |
| Formic | 100 | 55/20 | 1.3 | 0.9 | |
| | | 40/20 | 1.3 | 0.9 | |
| | | 40/4 | 6.6 | 4.8 | |
| Acetic | | 55/20 | 0.4 | 0.4 | |
| | | 40/20 | 1.7 | 1.2 | |
| | | 40/4 | 0.4 | 0.3 | |
| 0.20Formic 0.80Acetic | | 55/20 | 0.6 | 0.4 | |
| | | 40/20 | 1.2 | 0.8 | |
| | | 40/4 | 0.4 | 0.3 | |
| DI Water | 55/20 | Nil | Nil | | |
| | 40/20 | Nil | Nil | | |
| | 40/4 | Nil | Nil | | |
| Ethylene glycol Thermal degraded | 55/20 | 0.2 | 0.2 | | |
| | 40/20 | 0.2 | 0.2 | | |
| | 40/4 | 0.7 | 0.5 | | |

n=The average of up to 5 of the deepest pits.

Table 3
50 Day Test Summary
Maximum pit depths (mils) of 3 separate polishes on a 40/20°C cycle

| Concentration (ppm) | 10 Days | 20 Days | 30 Days | 40 Days | 50 Days |
|---------------------|---------|---------|---------|---------|---------|
| 100 | 6.1 | 1.4 | 3.4 | 6.4 | 7.1 |
| 50 | 2.1 | 3.6 | 5.8 | 5.1 | 6.0 |
| 20 | 2.1 | 0.5 | 2.9 | 1.8 | 2.7 |

Table 4
Ion Chromatograph Testing of Submitted Lubricating Fluids

| CTL ID# | Thermal Degradation | | Boiling Water Hydrolysis | |
|---------|---------------------|---------------|--------------------------|---------------|
| | Acetate (ppm) | Formate (ppm) | Acetate (ppm) | Formate (ppm) |
| 1 | <1 | 1 | 3 | 7 |
| 2 | 5 | 2 | 43 | 18 |
| 3 | 4 | 3 | 10 | 39 |
| 4 | 21 | 5 | 0 | 0 |
| 5 | 16 | 9 | 61 | 18 |
| 6 | 2 | 0 | <1 | 1 |
| 7 | 729 | 406 | 580 | 160 |
| 8 | 54 | 34 | 6 | 63 |
| 9 | 2 | 0 | 0 | 0 |
| 10 | 26 | 2 | 26 | 24 |
| 11 | 3 | 3 | 7 | 9 |
| 12 | 2 | 5 | 23 | 24 |

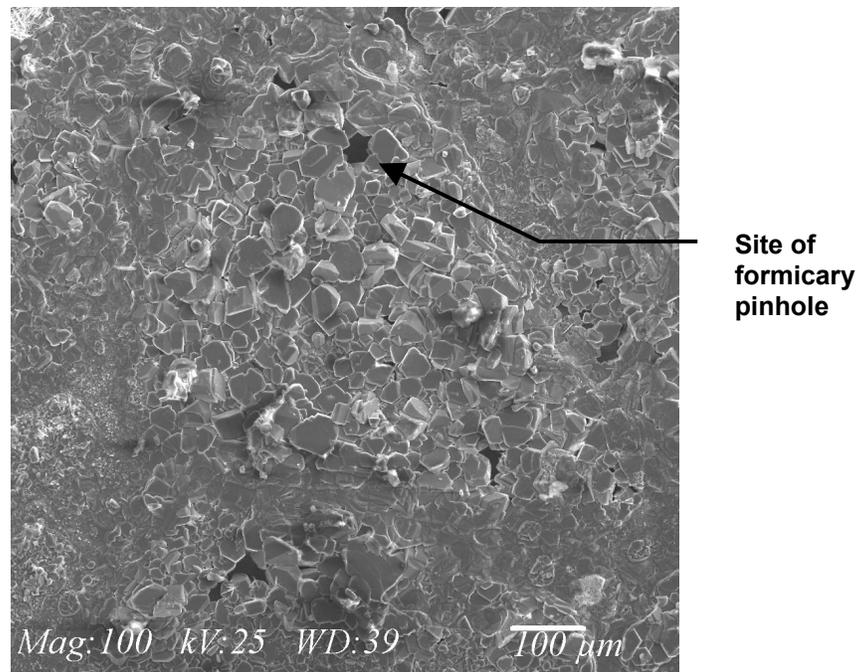


Figure 1
SEM image of dark green crystals adhering to the surface of copper tube.
(100X original magnification)



Figure 2
Typical cross-section of formicary corrosion, noting the penetration advancing parallel and perpendicular to the cut surface. (250X original magnification)

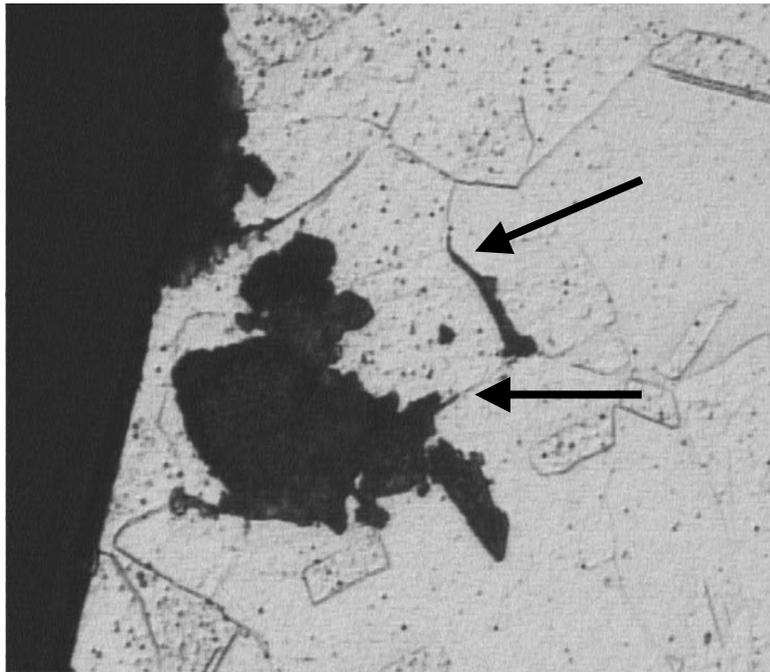


Figure 3
Intergranular nature of formicary corrosion, at arrows. (1250X original magnification)